INSTITUTE OF CHEMISTRY CEYLON

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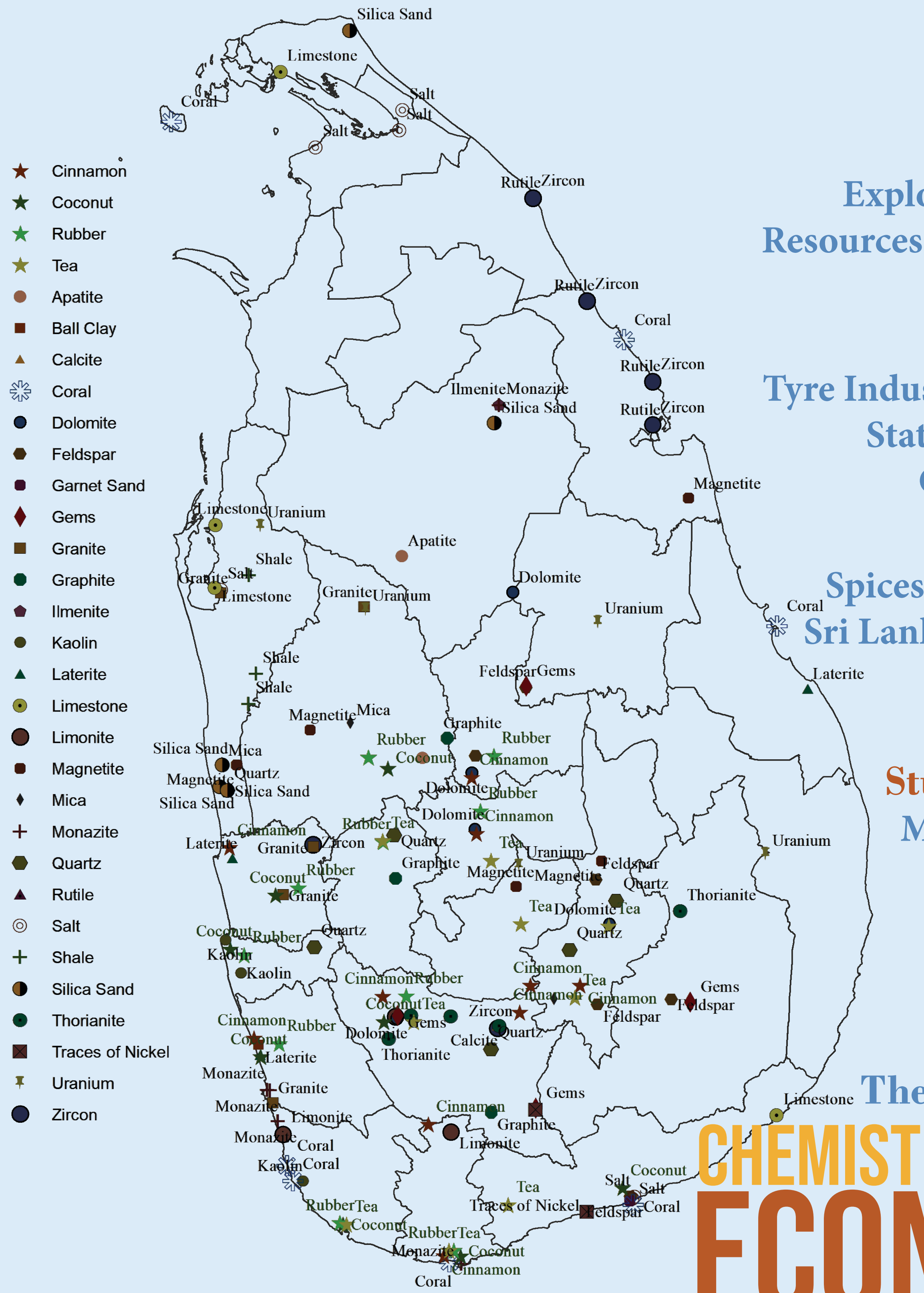

Exploiting Mineral Resources for Economic Prosperity

Tyre Industry – Current Status and Future Opportunities

Spices, Chemistry & Sri Lankan Economic development

Student Corner
Metal Hydrides

Themed Collection
CHEMISTRY DRIVEN ECONOMY

The Tri Annual Publication of the Institute of Chemistry Ceylon

Chemistry in Sri Lanka

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The Tri-Annual Publication of the Institute of Chemistry Ceylon

Founded in 1971, Incorporated by Act of Parliament No. 15 of 1972

Successor to the Chemical Society of Ceylon, founded on 25th January 1941

Vol. 38 No. 1 **April 2021**

Theme for the year -

Sustainable Development through Chemical Sciences

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Outline of our Institute

The Institute of Chemistry Ceylon is a professional body and a learned society founded in 1971 and incorporated by act of Parliament No. 15 of 1972. It is the successor to the Chemical Society of Ceylon which was founded in 1941. Over 50 years of existence in Sri Lanka makes it the oldest scientific body in the country.

The Institute has been established for the general advancement of the science and practice of Chemistry and for the enhancement of the status of the profession of Chemistry in Sri Lanka. The Institute represents all branches of the profession and its membership is accepted by the government of Sri Lanka (by establishment circular 234 of 9-3-77) for purposes of recruitment and promotion of chemists.

Corporate Membership
Full membership is referred to as corporate membership and consists of two grades: **Fellow (F.I.Chem.C.)** and **Member (M.I.Chem.C.)**

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(i) directly become Licentiate
(ii) obtain corporate membership in a lesser number of years.

Tech.I.Chem.C.
Those who have passed the DLTC examination or LTCC examination or have obtained equivalent qualification and are engaged in the practice of Chemistry (or chemical sciences) acceptable to the Council are entitled to the designation Tech.I.Chem.C.
Members/Fellows with Membership for Life are entitled to the designation of **Chartered Chemist (C.Chem.)** on establishment of a high level of competence and professionalism in the practice of chemistry and showing their commitment to maintain their expertise.

All corporate members (Members / Fellows) are entitled to vote and become Council/ Committee members whether Chartered Chemists or not.

Membership Applications
Any application for admission to the appropriate class of membership or for transfer should be made on the prescribed form available from the Institute Office.

Current Subscription Rates
Fees should be payed on 1st of July every year and will be in respect of the year commencing from 1st July to 30th June

Fellow	Rs. 2000
Member	Rs. 2000
Associate	Rs. 1500
Licenciate	Rs. 1200
Technician	Rs. 750
Affiliate	Rs. 1200
Membership for Life	Rs. 15000

Entrance Fee

All the grades	Rs. 1000
Processing Fees*	Rs. 500
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*per application for admission/transfer to any grade

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Council 2020/2021

Editorial and Publicity Committee

CHEMISTRY IN SRI LANKA

Chemistry in Sri Lanka is a tri-annual publication of the Institute of Chemistry Ceylon and is published in January, May and September of each year. It is circulated among the members of the Institute of Chemistry and students of the Graduateship/DLTC course and libraries. The publication has a wide circulation and more than 750 copies are published. Award winning lectures, abstracts of communications to be presented at the annual sessions, review papers, activities of the institute, membership news are some of the items included in the magazine.

The editor invites from the membership the following items for publication in the next issue of the Chemistry in Sri Lanka which is due to be released in May 2021.

- *Personal news of the members*
- *Brief articles of topical interests*
- *Forthcoming conferences, seminars and workshops*
- *Latest text books and monographs of interest to chemists*

All publications will be subjected to approval of the 'Editorial and Publicity Committee' and the Council of the Institute of Chemistry Ceylon.

Further, prospective career opportunities for chemists, could be advertised in Chemistry in Sri Lanka at a nominal payment. The editor welcomes suggestions from the members for improvement of the publication.

6th Emeritus Professor J.N.O. Fernando Memorial Oration

Education – Then and Now, Classical vs Modern

M.R.M Haniffa

Senior Lecturer, Department of Chemistry, Open University of Sri Lanka

I am grateful for the opportunity of having to deliver the oration on the occasion of the commemoration ceremony to mark the 6th Death anniversary of our beloved Emeritus Professor JNO Fernando, JNO for all us. It is indeed a great honour and perhaps, a form of recognition of my close association with Prof JNO.

Let me begin on a philosophical note and a quote from my most respected international personality, Prof Abdul Kalam, former President of India.

"*Dream is not that which you see while sleeping, it is something that does not let you sleep*".

In quoting Prof. Abdul Kalam, may I mention that I tried to follow this quotation in preparing for this oration. I did dream about it, talking to myself and rehearsing in my own way.

At the outset, may I state that I am not trying in any way to compare the old with the new. Comparisons indeed may not be valid as the process of globalization and exponential growth in communication and information technology has brought in its wake an entirely new generation; many of them may not be able to comprehend how the old generation led their life; no electricity, no water supply, no cell phones (land phones were a rarity). Rather, my objective is to take you through the period 1960's – mid 1970's, over 50 years period and to give an insight into the education system then based on my own personal experience. Hence, I chose a very simple title for my oration in order to meet that objective and to drive home a message this afternoon.

I may seem boastful since I am sharing my experience then with all of you here today; please bear with me because it is not my intention. Rather, I hope I can give a simple message to the current generation who are blessed with many facilities that we did not have then. This period - mid 1960's and early 1970's was one that we will not forget easily. I feel that this oration would give all of you from the kuppi lamp era to reflect, reminisce and ponder. A cup of tea with the papers in one hand was a common feature, a form of informal learning / exchange of ideas under stress free conditions. In this context, I must say that I am happy to note that we did not have all the latest technology then; no TV, no cable network, photocopying facilities, smartphones etc. Many do not use the pen and paper when it comes to taking down missed notes; instead they get screenshots / photos. Use of modern technology is growing by the day and no doubt, members of the older generation, now find it difficult to keep pace with the rest. Obviously, we cannot live in the past; rather we need to adjust to suit the needs of the times.

Let me provoke some thoughts in this regard with the following slides (as presented in my PowerPoint presentation) referring to the past (then) and present (now). The humour is there and so is the message for you and me. Let me cite one example from the above slides with the following quotes: "Land phones united the family – then; mobile phones divided the family- now" is the message on one of the slides. I am sure many will agree with this message.

Primary Education at Beminiwatte Vidyalaya

I had my early schooling at Beminiwatte Vidyalaya off Mawanella in the early sixties up to grade 5. Apart from English, all other subjects were taught well, including Buddhism. I had no problems. In fact, if I remember correctly, I did well in Buddhism. We start the day by reciting Gatha. I remember what I recited then and in fact, it had a very soothing effect in commencing studies.

The standard of living may have been very low compared to that of today; the students came in very simple attire – sarong and shirt etc, barefooted in most cases; we wore a blue pair of shorts and rubber slippers, seemingly representing the "elite" or upper class. However, as far as I can recollect, discipline and education were of high standard. There was no question; pindrop silence prevailed when the Principal, in a coat and tweed sarong with a thick belt, stood in the middle school and observed what was happening in the lower and upper class rooms; of course, he carried the almighty cane inside the coat sleeves. I must also mention that I have hardly seen him using the cane, such was his command and authority and more importantly, management skills (I am sure he had no formal qualifications in this respect).

One of the problems now is the high cost of living; our earnings do not match up to the demands and contentment is very rare in this so-called "rat race". I do not think I need to elaborate on this. Life was very simple then; we had ample time to join with our little friends to play, swim in the river by the side (Maha Oya), pluck mangoes, hunt for firewood etc. All this and more has had a profound effect on oneself; no formal education can give you that which is very much needed in real life. Looking back on the motto of this school – "කරතොත් හොඳට", and the depth of the embedded meaning in those two words, is striking; it is very much relevant now as it was then. Whoever coined those two words of wisdom more than half a century ago were visionaries of the past that we hardly come across today. I continue to remember these two words even after 50 odd years and do quote these words whenever I get an opportunity to do so. The meaning is profound. I do not think the outcome would be the same by a direct translation into English or Tamil. "හොඳට" is literally related to the word "good". However, on analysis, one could relate it to "පිරිසිදු චේතනාව" (purity of intention), ethics, honesty, integrity etc. I remember the statement "Integrity is to do the right thing when nobody is watching you" was prominently displayed in one of our newsletters several years ago.

Secondary Education at TCK

I was virtually put into the deep end then when I was placed in the English medium classes at Trinity College Kandy (TCK); I was totally at sea when the rest of the class were conversing in English. It is a long and tough story but I somehow I managed to grasp the language (understand at least) within one year of classical teaching and learning. In fact, some of us were given Special English Prizes at the end of the first year at TCK.

Classical Teaching

Classical Teaching of a language involved reading, writing and spelling, where strict procedures were followed by a set of dedicated staff members, then.

It is my experience over the past 4-5 years, that the habit of reading books/papers (an important aspect to develop one's language skills) has gradually come down to a point so much so that hardly anyone does any reading now, that which those in the '60s and '70s did. When the question "who *read* the newspaper this morning?" is posed to the students in a class, virtually no hands are raised. On the contrary, in the same breath, when the question "who *does not* have a cell phone" is asked, once again, virtually no hands are raised, a good example of the status of the old (then) and present era (Now).

Thomas Edison (1847-1931)

The story of Thomas Edison is very well known and hence, I will not go into the details. I am citing only one example from the past to illustrate a point regarding education then.

He was a self-made inventor. In fact, he still remains one of the greatest inventors, very well-known because of his invention of the light bulb. However, there is an important message in terms of education then (almost two centuries ago). Let me quote from about Thomas Edison:

"*A hyperactive child, prone to distraction, he was deemed "difficult" by his teacher. His mother quickly pulled him from school and taught him at home. At age 11, he showed a voracious appetite for knowledge, reading books on a wide range of subjects. In this wide-open curriculum Edison developed a process for self-education and learning independently that would serve him throughout his life.*" That was then.

Much emphasis is placed on formal education now and hence, there is no time for independent learning and thinking, two important traits for one's natural, in-born talents to blossom and mature. Let me also refer to one of his farsighted thoughts on the future:

"*I'd put my money on the sun and solar energy. What a source of power! I hope we don't have to wait until oil and coal run out before we tackle that.*- Thomas Edison

We are exploring solar power only now, something that was forecast then, 200 years ago.

Modern day

The advent of the latest technology has changed our lifestyle including education to a great extent. Look at some of the terminology in this era - upload, download, Twitter, Whatsapp, chat, Facebook, SMS, Zoom, Google and many more; it is mind boggling. I must admit that the younger generation would be more competent to talk about them than myself.

Before ending my oration, may I refer to the following quotes involving time.

- "*The bad news is TIME FLIES; the good news is you are the PILOT*"

  Micheal Altshuler

- Some are old at 18; some are young at 90. Time is a concept that humans created.

The meaning and message in the above quotes are very clear; they are applicable at all times, THEN and NOW. Finally, in conclusion, may I refer to the two words "කරතොත් හොඳට" once again as my take home message to all of you.

__Mr. M. R. M. Haniffa__ graduated from the University of Colombo, obtaining a BSc Special Degree in Chemistry with Second Class (Upper Division) Honors, and completed his Masters degree in Chemistry at the University of Hawaii at Manoa (USA). He has served as the Dean of the College of Chemical Sciences in 2015 and as a Past President of the Institute of Chemistry Ceylon (2016-2017). He is currently serving as a Senior Lecturer at the Department of Chemistry, Open University of Sri Lanka.

Cover Page

The cover image provides a glimpse of the distribution of resources which have the potential of powering chemical industries that are strategically important for the sustainable development of the Sri Lankan economy. Local industries centered on plantations and mineral resources can contribute immensely to the growth of a "Chemistry-Driven Economy". This issue brings to light the impact these resources can have on the advancement of the national economy. This map was drawn by Dr. Inoka Peiris and Ms. Sonali Herath using ArcGIS software.

Appreciation

Ajith Perera: Chemist, Cricketer, Disability Rights Activist

In Memoriam

Ranil D. Guneratne

SLINTEC Academy, Sri Lanka Institute of Nanotechnology

On October 29, 2020, Ajith C.S. Perera, a well known activist for the rights of disabled people in Sri Lanka, passed away at the age of 64. He eventually lost a brave but uphill battle against kidney failure, diabetes, and various infections, with the added complication of being a paraplegic.

Ajith was educated at Royal College and the University of Colombo, graduating with a B.Sc. (General) degree, with a Second Class (Lower Division) from the latter institution in 1975. Despite only having a general degree, he was appointed as a Tutor by the Department of Mathematics, and as an Assistant Lecturer by the Department of Chemistry. He later obtained an M.Sc. in Analytical Chemistry, being one of the first students to register for what was then a brand new master's degree programme at Colombo. With these qualifications he joined the pharmaceutical industry, working successively for Glaxo Ceylon, Mackwoods Winthrop, and Hemas Pharmaceuticals. He also played cricket for the University of Colombo, and went on to qualify as a scorer and a cricket umpire.

In 1992, Ajith was at the peak of his career. He had recently joined Hemas, where he was in charge of quality assurance, and was the Hony. Secretary of the Royal Society of Chemistry's Sri Lanka section. He had also been appointed to the international panel of cricket umpires, and was within days of officiating at a Test Match between Sri Lanka and New Zealand. He was returning home one night from a meeting of the RSC, during a violent storm, when a tree fell on his car on Bauddhaloka Mawatha. His driver was killed instantly. Soldiers from a nearby army post rescued Ajith and took him to hospital, where he was found to be paralysed from the waist down. Months of treatment and therapy from physicians both in Sri Lanka and in the UK failed to restore movement to his legs, and he remained wheelchair bound for the remaining 28 years of his life.

Ajith was a man who was active in both body and mind, and the loss of physical activity, which would have caused many people to retreat into severe depression, only served to raise his mental energy levels. Deprived of the ability to work in a normal job—Sri Lanka even now has very little provision for the wheelchair bound to work in offices and similar workplaces—he took to writing. Over the years, he would write many articles to the press, but his major works were two books on cricket, written during the late 1990's. The first, *The Golden Age of Sri Lanka Cricket*, was the story of Sri Lanka's victory in the 1996 World Cup. The second, *Thinking Cricket*, was essentially a manual for players, full of advice and wisdom, in which he drew heavily on his experience as an umpire. Ajith had a unique style of writing, but in order to ensure linguistic correctness, he asked me for editorial assistance with the latter book. I was still living in the U.S. at the time, and he would send me a chapter at a time for me to edit and return to him.

During this time, Ajith had come to realise how little effort the establishment in Sri Lanka made to provide even basic amenities for the disabled, such as wheelchair access to buildings, special toilets for the disabled, etc., all of them normal and available in many other countries. This was true despite nearly two decades of civil war, which had resulted in hundreds of disabled military veterans. With characteristic energy, Ajith became a lobbyist for the disabled. Realising that he would be a more powerful voice if he represented an organisation, but not wishing to be trapped in the agenda of others, he set about creating his own lobby. Thus, in 2005, *Idiriya* was born. Its members were his close friends and family, including my wife (his sister) and myself. Ajith became its General Secretary, and in that capacity did all the work – fund-raising, lobbying government ministries, banks, and private hotels, filing cases before the Supreme Court, and organising press conferences. He became a public figure. Even foreign embassies took note, and he was a regular invitee to many embassy functions. Largely because of his efforts, Sri Lanka has made considerable progress in recognising the needs of the disabled, and wheelchair access is now a requirement for public buildings.

Time took its toll on Ajith, as it does with everyone, and during the last few years he found it increasingly difficult to maintain the pace and intensity of his commitment. His kidneys began to fail about a year before his demise. Although his twin careers as a chemist and as a cricket scorer/umpire were prematurely cut short, both those communities remember him with respect. The disabled are a community which, as Ajith himself was fond of pointing out, eventually includes most of us, at some time or another, for one reason or another – injury, loss of limb, paralysis, certain diseases, or simply age. For his single-handed efforts on their behalf, the society will remember him with gratitude.

Requiescat in pace.

Dr. R. D. Guneratne *graduated from the University of Colombo with a B.Sc. in Chemistry and completed his Ph.D. at Cornell University, U.S.A. He has served as a post-doctoral research associate at the University of Iowa and Bennington College, Bennington, Vermont, and as an Associate Professor at Spring Hill College, Alabama. He returned to Sri Lanka to join the Department of Chemistry at the Open University of Sri Lanka and later moved to the University of Colombo, where he served until his retirement in 2017. He is currently serving at the SLINTEC Academy, Sri Lanka Institute of Nanotechnology.*

Guest Editorial

Chemistry Towards the Enhancement of Economic Growth & Development

Deepal L. Bataduwa Arachchi

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Economic growth, one of the major macro-economic goals, is determined by many factors and among them; the importance of technological advancement is too well known and well documented. Importantly, science and technology go hand in hand and it is believed that technology without science is unsustainable. Varying levels of growth and development achieved by countries around the world to a greater degree, have been determined by the extent of industrial, technological and physical science advancements made by the given country. Lower levels of industrial, technological and scientific advancement make economic progress of a country inadequate, thus making the standard of living of its citizens lower. Progress achieved by the developed countries in the said spheres over the years is too obvious and this has contributed in no small measure to elevate these nations to the higher income bracket with very high standard of living.

Careful and closer analysis of the growth patterns and development statuses of countries around the world would reflect the fact that the higher the relative productivity in basic science, for example Chemistry and Physics, the higher is the economic growth momentum and the level of development achieved. An adequate investment in basic science is necessary in achieving speedy and faster economic growth, thus improving quality of life of people. It is vital, especially for middle-income countries like Sri Lanka to achieve higher scientific productivity as it significantly correlates with current as well as future wealth creation. Strong and closer link exists between scientific development and the wealth of nations. The contribution of scientific productivity in creating economic wealth, thus human development neither can be underestimated nor be overlooked.

The advances in sciences has brought enormous benefits to nations all over the world and advancements in Chemistry in particular have contributed in creating wealth, thus immensely enhancing the human well-being over many centuries. Wealth of constructive ideas could be derived by closely analyzing the role of Chemistry in the process of development, especially in the developed countries over the years, starting from 18th century. Advances made in physical sciences, including Chemistry lead to the growth of world Gross Domestic Product by many folds, notably in advanced industrialized countries.

Chemistry's contribution to the advancement of a diverse and wide array of fields is noteworthy. Not only in the material and product development, quality control, but also in producing electrical energy, chemistry has made a striking contribution. Dramatic advancements have been witnessed in many important fields like agriculture, pharmaceuticals, medicine, biotechnology, information technology & telecommunications etc., over many decades and chemistry has made a vital contribution towards this, especially from the latter part of the 20^{th} century. These advancements have improved the human wellbeing beyond imagination, through the enhancement of health and quality of life. In the global context, the benefits from the developments in chemistry and other physical sciences have not been equally distributed. Nevertheless, it is important for a middle-income country like Sri Lanka to deeply explore the possibilities of utilizing the advances made in science, chemistry in particular to develop many economically vital areas with a view to enhancing the wellbeing and the quality of life of its citizens.

Sri Lanka is well endowed with mineral deposits and the economic significance of the mineral-based industrial sector is widely acknowledged. Mineral-based industries produce a wide array of items and contribute significantly to the national production. Although the policy of successive governments has been to discourage exports in mineral form and to encourage domestic end product manufacturing, still reasonable number of minerals are exported in mineral form, without any value addition, for example, Graphite, Mica, Quartz and mineral sand like Zircon. Pulmuddai mineral reserve, Apatite rock Phosphate and Copper – Magnetite deposits of this country are of high economic significance and possibilities should be explored and effective actions must be taken to set up related industries, for example, production of fertilizer and rechargeable batteries etc. Achieving a rapid expansion of the economy is vital in improving the living standards, thus lifting people out of poverty and the development of mineral resources and related industries is an important pre- requisite towards this end. Throughout, Sri Lanka has emphasized on export led economic growth, yet this country has a narrow range of products to be exported to narrow range of markets. This could be overcome to some degree by developing mineral resources and related industries, but the main obstacle in achieving this objective has been the lack of research and development in product manufacturing utilizing minerals available in the country. This is an area where the policy makers could effectively and productively utilize the advances made in chemistry. Many important lessons could be drawn from other nations towards this.

Mineral related industrial sector is not the only sector in which the advancement of chemistry could be productively utilized but there are other vital sectors like pharmaceutical, agriculture, energy and many more. For example, advances in chemistry are useful in achieving the vital objective of the present health authority of this country, i.e. to reduce the reliance on imported medicinal drugs by producing some locally to save valuable foreign exchange. Be it increasing the food production, improving the sanitary and health conditions advancements in sustainable and green chemistry could be widely employed.

Voluminous amounts of information are available in relation to the contribution of chemical sciences towards the enhancement of wellbeing of the humankind, yet it is impossible to touch all the relevant areas in the limited space available. If this piece of writing has thrown some light into, otherwise this neglected area, encouraging the relevant parties to constructively act, then the objective of this write up is achieved.

Mr. Deepal L. Bataduwa Arachchi *received his MA in Economics and Postgraduate Diploma in Economic Development from the University of Colombo. He currently serves as a Senior Consultant at the Faculty of Management Studies, the Open University of Sri Lanka.*

Themed collection - Chemistry Driven Economy

Themed Collection

Uplifting "Ceylon Tea" with Chemistry

Damayanthi Dahanayake

Principal Research Scientist, Petroleum and Lubricant Testing Laboratory, Industrial Technology Institute

Introduction

"Ceylon tea" is a globally reputed unique brand that has stayed true to its value and promise on pure quality, throughout decades. It is known for its high levels of catechins, and unmatched taste with specific aroma. In 2019, tea exports accounted for US$ 1.35 billion of income[1] to the national economy. as the fourth largest tea exporter in the world. Tea export will continue to be the key economic value adder to Sri Lankan economy not just from the revenue of exporting tea, but also from the large population that is directly and indirectly involved in the industry.

Even though some competitors like Kenya entered the export market later than us, they have still managed to build a strong footing in the global trade, by challenging Sri Lanka's ability to maintain its past success, Sri Lanka is no longer a cheaper tea producer in the global arena due to its cost of labor and production compared to other low cost global competition. Thereby Sri Lanka has strategically drifted (or in the midst of drifting) to high-quality value-added producer from its positioning as a low cost producer. In the recent past, similar economic evaluation was also evidenced in Sri Lanka's apparel industry with the rise of multiple apparel factories engaging niche and value added production with selected large scale producers in global value chains.

Gaining such repositioning as a unique brand of "Ceylon Tea", with a set of values added to it, is one of the key advantages of Sri Lankan tea industry. However, it is also evidenced that Sri Lanka has still a long way to go in terms of repositioning to claim a value added differentiated end product from a 'bulk tea' export as a commodity product. Countries such as UAE are identified as large exporters of tea simply due to their ability of importing, value addition and re-exporting such products.

With increasing health consciousness, tea is currently gaining an increasing demand on its medicinal value.[2] Ceylon Tea can re-position itself as a revived brand that focus on health, value addition and as a differentiated product on customer demand and convenience, while maintaining its pure quality with the brand promise. Such market repositioning is only possible with the industrial players, those who are capable of changing the game by bundling up with scientific research. This article is aimed to provide a conscious synopsis on the chemical components of tea with the potential new avenues towards the value addition of tea products.

Chemistry of tea leaf

The most important and characteristic components of tea leaf are the polyphenols in the cell sap, which undergo a series of chemical changes when the leaf is macerated during manufacture. These compounds are mainly the derivatives of gallic acid and catechin. From the polyphenolic category, flavonoids are the most abundant in tea flush. Structurally, flavonoids are 2-phenyl benzopyran based scaffolds. These compounds can be classified into six groups: flavones, flavanones, isoflavones, flavanols, flavonols and anthocyanidins.[3] Catechins are the major flavanols in tea. During the black tea manufacturing process, these compounds can be subjected to oxidative dimerisation or polymerisation. The two key enzymes in tea leaves are, polyphenol oxidase and peroxidase involved in oxidation of polyphenols. It contains minerals, biochemical intermediates, carbohydrates, proteins and lipids in small quantities.[4]

During the oxidative polymerization process in black tea processing, the least catechin content and highest theaflavins and thearubigin content was observed as compared to oolong and green tea. Flavonols (such as quercetin, kaemferol, myricetin and their glycosides) and anthocyanidins are also found in the flush in appreciable amounts, but they do not usually undergo a significant chemical change during black tea manufacturing process.

The free sugars found in tea shoots are glucose, fructose, sucrose, raffinose and stachyose. Free sugars are responsible for the synthesis of catechins in tea shoots, which form heterocyclic flavour compounds during processing of black tea and contributing towards water-soluble solids in tea liquor. Cellulose, hemicellulose, pectins and lignins are responsible for the formation of crude fiber content in black tea. Theanine alone contributed around 60 per cent of total amino acid content. Amino acids are playing a major role in development of tea aroma and the taste during the processing of black tea.[5]

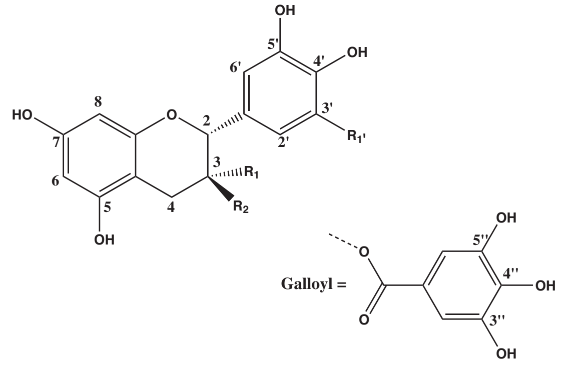
Chemical Composition of tea brew

The tea brew contains the hot water soluble components of made tea, which are extracted into boiling water used for infusion. Those chemical constituents are responsible for the taste and flavour as well as the nutritional value of the tea brew.

The main nutrients in tea brew are carbohydrates, fat and proteins. But their composition with respect to their contents in the food, are significantly less. Tea is also a rich source of dietary minerals, where potassium is prominent.

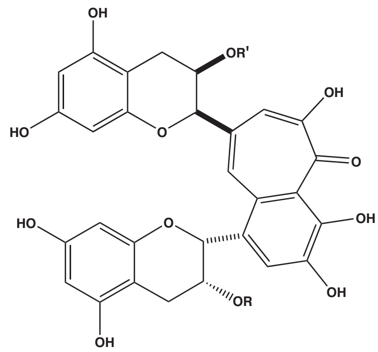
The tea brew also contains a significant amount of non-nutrient components, which have important biological functions other than energy production. The major non-nutrients are the polyphenols and the methylxanthine caffeine. Tea is unique in having huge amounts of polyphenols, which is up to 40 per cent of the solids extracted into the tea brew[4]. Catechins such as epicatechin (EC), epicatechin gallate (ECG) and epigallocatechin gallate (EGCG), are also responsible for the quality of the tea brew.[6]

The level of biotransformation of catechins into oxidized form during processing of tea leaves results in three main types of tea called black tea (fully oxidized), oolong tea (partially oxidized), and green tea (non-oxidized). As a major part of the catechins rearrange to theaflavins and thearubigins in black tea, individual catechins are less compared to green tea.



R_1	R_2	$R_{1'}$	
H	OH	H	(+)-Catechin (C)
OH	H	H	(-)-Epicatechin (EC)
OH	H	OH	(-)-Epigallocatechin (EGC)
Galloyl	H	H	(-)-Epicatechingallat (ECG)
Galloyl	H	OH	(-)-Epigallocatechingallat (EGCG)

Figure 1: Structure of catechins



Compound	R	R'
Theaflavin (TF1)	H	H
Theaflavin-3-monogallate (TF2a)	Galloyl	H
Theaflavin-3'-monogallate (TF2b)	H	Galloyl
Theaflavin-3,3'-digallate (TF3)	Galloyl	Galloyl

Figure 2: Structure of Theaflavins

Tea health benefits

Black tea has many important biological effects in favor to our health. In general, it is reported that drinking black tea is almost equal to drinking green tea in terms of the antioxidant properties.[7] Polyphenols and caffeine have beneficial pharmacological effects and give tea its unique dietary significance. Caffeine is a well-known stimulant acting on the central nervous system. It increases alertness and reduces feeling of drowsiness and fatigue. Polyphenols are strong antioxidants, which are mainly responsible for the beneficial effects of tea.

It is active against inflammation, and some types of cancer.[8,9] DNA damage and mutagenesis can be reduced by black tea. Preventing cardiovascular diseases, effecting gastrointestinal tract, lowering cholesterol level and influencing the hormonal balance, and antioxidant activity, improving bone mineral density are also reported as beneficial outcomes of tea.[10-12] With the inherent enzyme inhibiting and receptor blocking properties, tea is also being well documented for its antiviral activity[6]. Theaflavin activity against Herpes simplex virus type 1 and Sindbis virus, has been proven.[13]

Tea market products with value addition

Tea is mainly marketed as black tea, green tea and oolong tea. In Sri Lanka, we are mainly exporting black tea and a small quantity of green tea. There are other value added products such as tea bags, organic tea, flavoured tea, tea extracts, and instant tea. The beneficial polyphenolic compounds have a higher potential to value addition. Catechins, theaflavins, thearubigins can be used in value added products.

<u>Tea bags with value addition:</u>

Sri Lanka is popular in tea bag market today. This can be improved with our natural flavours like cinnamon, cardamom etc. Avoiding artificial flavours by moving towards natural components currently has a higher market trend. This will positively impact on the country's spice industry as well.

Value addition to the tea cup with other beneficial ingredients like *Garcinia*, can be a good marketing strategy for an international market.

<u>Organic tea:</u>

Heavy usage of pesticides and weedicides have become a serious problem in the tea industry today. The global concern to minimize the chemical residues in tea has been implemented by many countries with imposing minimum residue level (MRL) less than 0.1 ppm for most of the pesticides.[14] Organic tea is a good opportunity to obtain a high market share as some European countries and Japan are well concerned of the fertilizer and pesticide usage for tea. In order to achieve this, the tea gardens should be maintained as free from synthetic pesticides, weedicides or fertilizers. The resulting low yield could compensate for the high quality of organic tea in terms of market value. Presently some companies move towards manufacturing organic tea. Awareness programs highlighting the benefits of pure Ceylon tea would popularize our brands in the competitive global market.

<u>Instant tea:</u>

As the fast moving world ask for convenient food, tea also should be presented in different types other than the traditional black tea. Instant tea plays a major role in competing with other soft drinks globally. We can popularize these products with improved health properties. Addition of water soluble polyphenolic parts in high concentration and reduced sugar content would improve the quality of the tea. Instant tea can be produced with black tea, green tea, or oolong tea. The tea waste coming as a byproduct of the black tea process can be used for instant tea as well. Cold water insoluble part of instant tea which is also known as tea cream, can be used in many other applications explained below.

<u>Tea in confectionary products:</u>

The cold water insoluble tea has a higher amount of catechins which has numerous health benefits. This can be introduced in biscuits, and bakery products as a value added product. Cream added biscuits, cookies can be incorporated with tea polyphenols.

<u>Tea in cosmetics:</u>

The tea cream with catechins come as a waste product of the instant tea can be used in cosmetics such as soaps, facial wash, bath gel, body lotions etc. The saponins extracted by the tea waste can be used in soap production.

The catechins can be incorporated with liposomes and increase the efficiency of skin penetration. Anti-aging and anti-wrinkling cream formulations can also be prepared as value added products using the novel tool such as nanotechnology.

Nutraceutical applications with theaflavins:

Cellular damage caused by the reactive oxygen species (ROS) can be scavenged by tea polyphenols. These ROS accounts for aging, age related diseases and cancer.[15] The usage of antioxidant molecules to reduce oxidative stress appears to be an ideal approach for cancer prevention.[16] The antioxidant activity of theaflavins and other catechins can be used in nutraceutical drugs. The inherent weaknesses of polyphenols such as low solubility and unfavourable pharmacokinetics can be overcome with suitable carriers like liposomes.[17] Thus, there is a high potential area in nutraceutical industry for tea polyphenols as antioxidants.

Tea as a natural colorant

The unique colour of tea can be applied as a colouring agent in fabric and food industry. The natural dyes are accepted by environmentally concerned market segment over the world. Tea tannins can be extracted by waste tea and use as a colorant. It is reported that cellulose and jute fabric can be used to make a value addition with tea unique colours[18].

Summary

The brand value of Ceylon Tea can be carefully utilized to take Sri Lankan Tea to the next level in the global market. Exporting bulk tea as a commodity is not the way forward for Sri Lanka to compete with ever increasing low cost competition. Identifying the new avenues for value addition with proper understanding and usage of chemistry is important. The health benefits with tea compounds can be used in value added products such as instant tea, organic tea, confectionary and bakery products, nutraceutical products, cosmetics, and coloring agents. While in the past 150 years we managed to dominate this globally, speedy action from policy level to an end-to-end industry corroborated execution plan is essential to make sure its success in future years to come.

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Themed Collection

Tyre Industry – Current Status and Future Opportunities

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The global rubber products industry includes over 50,000 products that serve different consumer needs in diverse applications. The automotive sector, which comprises of tyres, tubes, and automotive rubber components, is the major contributor to over 60% of the total global rubber products. Besides the automotive sector, mining, medical & sports, aerospace, agriculture, construction, machinery, engineering and electrical appliance manufacturing industries are the major drivers of the rubber products industry. The global statistics for 2015 reveal that the rubber products industry has yielded total revenue estimated at US$ 400 billion by transforming nearly 27 million tons of natural and synthetic rubber into value added products and this value is expected to reach US$ 600 billion by 2025. However, the market value of raw rubber worldwide amounts to US$ 40.71 billion, and comparative products turn over shows a noteworthy value addition in the conversion process of rubber into products. The global scenario with respect to production and consumption of natural and synthetic rubber is given in Table 1. The data indicates that within a couple of decades the rubber consumption has increased by almost 76% and that shows a significant growth in the rubber products industry.

Rubber product manufacturing is a labour-intensive industry involving many "state-of-the-art" machinery. Technologies are continuously changing with the improvements that shift the production possibilities further. It is important to note that advances in technology are a result of innovations and innovative practices leading to product diversification and process improvements bringing in enhanced productivity. This is well established in the global rubber products industry through deep rooted research and development segments.

Impact of COVID – 19 Pandemic on the Rubber Industry

The coronavirus pandemic has had an adverse economic and social impact on all businesses around the world including the rubber industries as well. The

Table 1: Global Situation of Rubber Supply & Consumption in '000 MT

Description	Year of Production				
	1995	2000	2005	2010	2015
Natural Rubber Production	6,070	6,811	8,921	10,403	12,277
Synthetic rubber Production	9,380	10,870	12,025	13,277	14,460
Total Rubber Consumption	**15,450**	**17,681**	**20,946**	**23,680**	**26,737**
Natural Rubber Consumption	5,950	7,108	9,049	10,759	12,146
Synthetic rubber Consumption	9,210	10,830	11,731	13,225	14,563
Total Rubber Consumption	**15,160**	**17,938**	**20,780**	**23,984**	**26,709**

(IRSG-Rubber Statistic, 2017)

Association of Natural Rubber Producing Countries (ANRPC) stated that the global plastics and rubber products market was expected to decline from US$ 1378.6 billion in 2019 to US$ 1345.4 billion in 2020 at a negative compound annual growth rate (CAGR) of 2.5%. In view of disruption of global economic activities and restrictions on imports, material inputs such as carbon black, silica, rubber chemicals, and many other rubber compounding ingredients were experiencing interrupted supply. Even under difficult conditions, the rubber industry has a leading role to play, since rubber as a versatile material that facilitates numerous needs of humans. The supplying of rubber products to medical, agriculture and transport sectors is vital during the pandemic to save the lives, to retain a secure food supply and to ensure safe movement of people. Under the circumstances, companies shifted rapidly to online channels, automated production tasks, increased operational efficiency by innovative operating models, and sped up decision making and implementation of advances in communication technologies.

STATUS OF SRI LANKAN RUBBER INDUSTRY

Plantation Sector

Sri Lanka embarked on the rubber industry with the planting of few germinated rubber seedlings by Sir Henry Wickham in 1876 and this historic event was the stepping stone in venturing into commercial rubber plantation in the wet zone. Sri Lankan rubber industry has been a long standing contributor to the island's economic and social well-being. It is understood that rubber is a trust industry that rest on a sustainable resource base, capable of contributing immensely for the growth of economic development in the country.

In 1976, plantation sector produced 156 million kg of raw rubber and 5% of this was utilized for producing finished products while majority of this was consumed by the Ceylon Tyre Corporation. The remaining bulk quantity was exported as raw rubber without any value addition. In early 1970's over 200,000 hectares of land were covered by rubber plantation. Unfortunately, within five decades this has dropped to around 150,000 ha. The local annual demand for rubber is about 140 million kg, and the current production stands at around 80 million kg creating a major deficit in production. Hence in 2018, over 76 million kg of natural rubber in both dry rubber and latex forms have been imported to meet the shortfall. Table 2, represents the position of natural rubber produced in the country in the past decade starting from the year 2008.

Table 2: Natural rubber status in Sri Lanka

Year	Production in million kg	Exports in million kg	Domestic Consumption in million kg
2008	129.2	48.6	80.1
2009	136.9	56.0	84.9
2010	153.0	51.5	107.2
2011	158.2	42.6	111.7
2012	152.1	37.4	110.0
2013	130.4	23.6	107.3
2014	98.6	16.3	85.6
2015	88.6	10.4	127.4
2016	79.1	16.2	142.0
2017	83.1	17.2	128.14
2018	82.6	13.98	135.24

(Rubber Development board – Statistics)

At present, the local rubber industry provides over 300,000 direct and indirect job opportunities to Sri Lankans across various professions as knowledge workers. Furthermore, the local rubber industry extends its employment opportunities to all categories of trained skilled workers in various disciplines in both product manufacturing and plantation sectors. Thereby, this industry makes an enormous contribution to the socio-economic wellbeing of both rural and urban populations in Sri Lanka.

Products Manufacturing Sector

The Sri Lankan rubber industry can be broadly classified into two sectors namely latex based products and dry rubber products. Latex products include medical, industrial, and household gloves; hygienic or pharmaceutical articles, latex thread, and articles of apparel and clothing products. Dry rubber products sector encapsulates tyres and tyre related products, and non-tyre products. When considering rubber exportation, dry rubber-based products have an export value share of 78 percent whereas the latex based rubber products have a comparatively limited share of 22%.

Rubber industry is positioned as the fourth largest source of foreign income for the country accounting for approximately 8% of export income. In 2013, value of rubber-based products made locally exceeded US$ 1,084 million, whereas export value of finished product is US$ 864.4 million and the revenue gained by export of raw rubber was only US$ 71 million. Although Sri Lanka is not a producer of synthetic rubber (SR), the consumption of SR was over 12% of total rubber consumption. The synthetic rubber imports which stood at 14.4 million kg in 2013 increased to 23 million kg in 2019 and was expected to double in 2024, since there is a greater potential for the industry to move forward in the direction of specialty products with higher value addition. To achieve this goal, the industry should focus on synthetic rubber-based product diversification to cater to a more sophisticated quality conscious market. However, under the current situation due to the COVID-19 pandemic, set targets and future forecast may have to be reviewed.

The country's rubber products industry is based on about 4,530 manufacturing units of small, medium and large-scale enterprises dispersed mostly in western and southern provinces. All large and medium-scale rubber industries can provide employment for knowledge workers in disciplines of Management, Technology, Engineering and Science, and to a great extent to technically skilled work force. Nearly 95% of industry turnover is generated by around 7% of the manufacturing units and the contribution by small and medium sized enterprises (SMEs) is estimated to be less than 5%.

Within a relatively short period of less than four decades, the Sri Lankan rubber industry has become a reputable major world supplier of quality rubber products and this appears to be the result of collective inputs of all stakeholders who are part of the industry.

Rubber Tyre Industry

From the early days of the automobile upto now, tyre manufacturing has gone through many technological advancements. The tyre manufacturing process technology will continue to develop to accommodate issues related to safety, health and environment and to exploit the advantages of new materials such as nano-composites, plasma surface modified carbon blacks, and the development of computer simulation techniques in product design, process improvements and in product performance analysis. The tyre industry maintains its position as the largest in the rubber product sector that transforms around 60% of natural and synthetic rubber globally available in producing products.

Within the rubber industry, the tyre sector enjoys the highest value addition and turnover, and retains its position as the largest player in the global market for rubber products. It was valued at $ 112.16 billion in 2019, and is projected to reach $ 154.40 billion by 2027, at an estimated growth over 5% based on global economic status. Sri Lankan tyre industry earned a revenue of US$ 549 million in 2018, which is 63% of the total value of rubber goods exported in the same year.

Functional Features of Rubber Tyre

The major function of the rubber tyre is to protect the wheel rim and offer tractive force between the road surface and the vehicle. Since it is manufactured from rubber, it also provides a flexible cushion, thereby reducing the impact of the vibrations while absorbing the shock of the vehicle. Rubber also offers many other technological properties such as resistance to wear and tear, good tensile, resilience and excellent elasticity. Combination of these rubber properties plays a vital role in maintaining high performance of tyres in use.

The tyres are manufacture as solid or pneumatic (filled with air) and made with natural rubber or using blends of natural and synthetic rubber. Tyres are distinguished by their end use, type of construction, and performance characteristics.

- Passenger car tyres maintain top performances in terms of safety, driving stability, fuel efficiency and mileage.
- Tyres for medium-duty and heavy trucks and buses manufactured by processes that are supported by the latest technologies in achieving high mileages, reliable power transmission and low consumption of fuel.
- Segment of low cost tyres that are used for three wheelers, motorcycle as well as bicycles. Rubber tyres also find number of applications in castors that are used in small movable objects such as material transport trolleys, shopping carts, wheel chair or a hospital bed.

There is an increase in the market for tyres due to the rise in the vehicle production and the market is further supported by the availability of sizable replacement volumes. The tyre sector dominates over the non-tyre sector with a value share of 85 percent of dry rubber product exports in Sri Lanka.

Solid Tyres

Solid tyres are non-pneumatic, slow moving and mainly used for off – road industrial applications. The solid tyres are manufactured by constructing layers of rubber comprising of base, cushion and the tread around a metal frame or a wheel structure followed by a moulding and vulcanizing process. Product shows different features depending on the type of equipment or the vehicle where the tyre is fitted. Solid industrial tyres are primarily used in material handling vehicles in areas such as airports, seaports and transporting goods for storage and they still play an important role in agriculture, industrial and construction sectors. (Figure 1)

Sri Lanka enjoys the position as the world's leading solid rubber tyre manufacturer and over 13 industrial enterprises are currently engaged in manufacturing or retreading solid tyres for export. As the global hub for solid tyre manufacturing, Sri Lanka caters to nearly 25% of the global demand that exist for solid and industrial tyres.

Resilient Black Solid Tyres

Resilient Solid Tyre– Non-Marking

Resilient Solid Tyre Sectional View

Figure 1: Resilient Solid Tyre

The solid tyre sector earned US $ 352 million in year 2011 and US $ 331 million in year 2012 while exporting tyres mainly to Belgium, Germany, Italy and USA. USA is the largest importer of solid tyre from Sri Lanka. The tyre and tyre-related products sector contributed to 2.8% of total cumulative merchandise exports from Sri Lanka, which amounted to US$ 11.7 billion in 2017. Although the pneumatic tyres find uses in many applications, the solid tyre still plays an important role in agriculture, industrial and logistic sectors and is used in variety of unique industrial applications owing to their special features including the extreme product stability, economical, puncture-resistant, and maintenance-free nature. Solid tyres have a high load-bearing capacity in extreme service conditions and are best suited for forklift trucks, airport vehicles, heavy-duty transport vehicles, platform trucks, and other industrial vehicles.

Pneumatic Tyres

In pneumatic tyres the air is held under pressure inside the tire. Until recent times, pneumatic tyres had an inner tube to hold the air pressure, but now the automotive tyres are designed to form a pressure seal with the rim of the wheel. Pneumatic tires are used on many types of vehicles, including cars, motorcycles, buses, trucks, heavy equipment, aircraft and bicycles (Figure 2). At present, the global pneumatic tyre market is dominated by radial and cross ply tires. The top automotive tyre manufacturers in the world include Japan, China, Korea and India.

One of the biggest benefits of using pneumatic tyres is their ability to absorb the unevenness of terrain. This allows for a smoother ride, and less bumping and shaking; and provided with a thicker tread, which provides traction to drive over loose and uneven surface.

Figure 2 : Pneumatic Tyres in range of applications

Sri Lanka (then Ceylon) initiated the first facility to retread used pneumatic tyres in 1936 under the "Ceylon Defense Force" and its primary objective was to retread tyres of defense vehicles needed in World War II. In 1959 as a joint venture, a plant was setup to manufacture bicycle tyres and inner tubes using Japanese technology. The pneumatic tyre manufacturing factory was setup in mid-1970 with Russian technical assistance at Kelaniya and was named "Ceylon Tyre Corporation" and this served as the nucleus of the rubber products industry in Sri Lanka. This plant was also considered as the largest bulk consumer of natural rubber and its annual consumption was 5 million kg. In 1983, Samson Rubber Industries (Pvt) Ltd with its flagship brand DSI Tyres started its operations on pneumatic tyres and currently positioned as the market leader for bicycle, motorcycle, three-wheeler tyres and tubes in Sri Lanka.

Sri Lankan pneumatic tyre sector accounts for approximately 38 percent of total tyre sector earnings in 2012. This sector earned US$ 19.9 million by exporting 9,632,000 units in 2011 and in 2012 turnover was increased to US $ 27.7 million and export volume increased to 10,066,243 units.

FUTURE PROSPECTS

1. Focus on Domestic Market

During the period 2015-2019, automobile population in Sri Lanka has witnessed a sizable growth and stood at over 8 million motor vehicles in 2019. There had been an overall increase of vehicle population by about 28% in the year 2019 whereas motorcycles and three-wheelers contributing to over 80% of the total vehicle population. The country's tyre market is dominated by this market segment in terms of tyre volumes. All these vehicles would contribute to a huge replacement market for tyres.

The country has imported US$ 2.8 million worth of tyres and tyre-related products. This potential domestic market needs to be exploited well, especially in sectors of passenger car, three wheeler and motor cycle.

2. Expansion of Existing Plants & Embarking on New Ventures

At present, CEAT Kelani Holdings is considered to be the largest domestic manufacturer of cross ply and radial tyres in Sri Lanka. CEAT recently embarked on a three-billion-rupee project to expand the manufacturing capabilities and improve efficiency. Furthermore, Sri Lanka's largest tyre manufacturing enterprise Ferentino Tyre Corporation (Pvt) Ltd, with US$ 250 million investment was setup in Horana, and initiated its production early 2021. The factory will engage in manufacturing passenger car radials, and tyres for motor cycles, bicycles, three-wheelers, trucks, buses and industrial solid tyres. It is also expected to generate 3,000 new jobs opportunities and envisage in using local talent with European technology. However, it is understood that further investment is needed in the area of pneumatic tyres in order to make a significant impact in the global arena of tyre market.

3. **Advancement in Tyre Technology**

- The demand for high performance, reliable, and technologically advanced specialty tyres are greatly needed when facing increasing demand. The global market of specialty tyres, valued at US$ 20 billion, includes industries that have significant stakeholder influence in the global economic climate. These comprise the agricultural, mining, forestry, industrial and off-road tires and aviation industries. In pneumatic tyres, introduction of advanced technology in the manufacturing process is expected to move the industry forward and create greater impact on specialty tyre market.
- A number of improvements have been made to winter tyres or snow tyres that have improved traction and control in heavy precipitation and freezing temperatures. Winter tyres combine extremely low rolling resistance, exceptional driving comfort, and first-class grip on snowy or icy roads. The improvement of these special features is the result of new technological developments and they represent the future of winter tyre technology.
- Constant improvements in rubber chemistry and tyre design create exciting and innovative designs for tyres that offer greater mileage and improved performance in extreme weather conditions. Innovations in tread patterns, sidewall design and overall tire construction have made today's higher-performing tyres more reliable than ever before.

4. **Human Resource Needs**

There are many challenges in producing knowledge workers needed by the polymer-based products manufacturing industry. In this context, universities and professional institutions need to design study courses that would minimize the knowledge and skills gap between universities and the polymer industry. The future job market in the polymer field depends on the versatility and innovative thinking of graduates. It is therefore a priority for institutions engaged in tertiary education to mould our youth in preparation for future growth of this industry.

5. **Addressing the Gender gap**

Today in Sri Lanka, women make up over 51% of the total population and their literacy rate stands at 90.8% which means that the industries can be benefited greatly by engaging female workers. Currently, over 50% of the female students follow industry-recognized study courses in the polymer field. Many women still struggle to get into top positions in the industry due to the existence of the "glass ceiling". As a primary contributor to the economic growth of the country, the rubber industry should pave the way for gender equality and create opportunities for career developments and addressing of the gender pay gap.

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Exploiting Mineral Resources for Economic Prosperity

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Sri Lanka has an abundance of high-quality mineral deposits which have not been efficiently utilized for economic development of the country. While some have not been exploited to their full potential, others are sold at a pittance to overseas buyers. Our industrial policies have never entailed using mineral resources for economic development.

Exploitation of mineral resources without the concomitant development of a chemical industry is meaningless; neither is possible without the other. At present, we do not have a single chemical industry in Sri Lanka going by its true definition of chemicals reacting to give a product. The only exception is petroleum refining at Sapugaskanda Refinery where chemical reactions take place during the cracking process. Actually, we have gone on the reverse gear on chemical industry. During the time when the Paranthan chemical factory was functioning, it had manufactured caustic soda for the soap industry and even manufactured hydrochloric acid and chlorine for a brief period of time. The fundamental requirements for chemical industry are the manufacture of an acid and a base. One of the common indicators of industrial development of a country is the number of sulphuric acid plants which it has in operation.

Phosphate minerals

Eppawela rock phosphate deposit discovered in 1971 is considered as one of the best phosphate deposits in the world because of its high phosphorus content (38-42% as P_2O_5). Since its discovery, the ore is only utilized in the supply of powdered rock phosphate for plantation crops. However, it is not suitable for short term crops such as rice and vegetables because of its low solubility. Around 100,000 tons of soluble phosphate fertilizer in the form of triple super phosphate is imported annually to Sri Lanka at a price of about Rs. 60,000 per ton.

We have an abundance of high-quality minerals which can be exploited if there is a chemical industry in Sri Lanka which will supply the basic chemicals required for such exploitation. A case in point is the utilisation of our Eppawela phosphate deposit to produce superphosphate fertiliser. If we manufacture sulphuric acid locally, then it is possible to produce single superphosphate from apatite which can then be used to fulfill our demand for phosphate fertiliser. This process involves simple mixing of powdered rock phosphate with sulphuric acid. The acid diluted to about 90% is added to finely powdered apatite rock and mixed using paddles. The mixture is allowed to stand for a period of 2-6 weeks, a process called curing. It involves no liquid effluent and hence has a minimal adverse impact to the environment. This method does not require a complex technology and can be carried out even in a clay pot on a small scale.

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(aq) \rightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4(s)$$

The mixture obtained here is generally sold as single superphosphate (SSP) and it has the additional advantage of providing sulphur to the soil in the form of $CaSO_4$. This is a definite advantage over triple superphosphate, which has no sulphur component, given that many soils of Sri Lanka are sulphur deficient. Sulphuric acid is the cheapest mineral acid and the production process of sulphuric acid is economically viable. However, this industry has not yet commenced in Sri Lanka and as a result we continue to import superphosphate fertilisers from other countries. Moreover, utilizing Eppawela phosphate in fertilizer, has more favorable environmental impacts, since it contains very low levels of heavy metals compared to the levels in imported TSP which contains unacceptable amounts of cadmium and arsenic. High analysis fertilisers such as triple superphosphate and diammonium hydrogen phosphate are not suitable for Sri Lanka considering the high cost of equipment and environmental damage caused by phosphogypsum.

What is attractive is that the entire cost of commissioning an SSP plant can be recovered in about 3 years while providing the phosphate fertiliser at half the current price. Meanwhile, Sri Lanka imports around one hundred thousand tonnes of triple superphosphate yearly, spending a massive amount of money. The fertiliser subsidy the Government has to incur per year is around Rs. 5 billion while a complete SSP factory along with a sulphuric acid plant can be commissioned for about Rs. 5 billion.

Mineral sands

Beach deposit of mineral sands at Pulmoddai is considered as one of the best sand deposits in the world with about 60-70% mineral content. The main constituents are ilmenite (75-80%), rutile (8-12%), zircon (8-10%), magnetite (2-3%) and smaller amounts of monazite, garnet, sillimanite and quartz. These are separated and sold in raw form ever since the mineral sands corporation came into existence in the 1960s.

Sri Lanka is currently exporting ilmenite in the raw form at a price of about $ 150 a ton while importing about 100,000 tons of titanium dioxide (purified form of ilmenite) at a price of $ 2250 a ton. TiO_2 is widely used as a white pigment in paints, plastics, and other industries. It is widely used as an optical brightener and making photocopy paper involves the use of titanium dioxide.

The process of making pigment grade titanium dioxide involves digestion of ilmenite with concentrated sulphuric acid to obtain titanyl sulphate.

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O$$

The titanyl sulphate is next hydrolysed to give titanium dioxide.

$$TiOSO_4 + H_2O \rightarrow TiO_2 + H_2SO_4$$

A research carried out at the Sabaragamuwa university describes a patented low temperature process to synthesise nano TiO_2 involving diluted hydrochloric acid.

Even titanium metal can be extracted from ilmenite or rutile. Here, rutile is heated with coke and chlorine at about 1000 ^{0}C.

$$TiO_2 + C + Cl_2 \rightarrow TiCl_4 + 2CO$$

Rutile contains iron impurities, which results in a ferric chloride impurity being formed during this reaction. TiCl4 can be separated by fractional distillation and then reduced to titanium metal by using Mg.

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

Titanium metal has many industrial and medical uses. It is used to produce Ti alloys which are commonly used for the wings and engine parts in airplanes. Titanium is one of the most biocompatible metals and its density is similar to that of the human bone and hence it is extensively used in orthopaedic implants such as hip balls, sockets and rods. It is also used in heart stents and dental implants.

Another valuable mineral sand deposit containing monazite is found in the coastline at Beruwela. A large offshore deposit was also discovered off the coast of Beruwela through an ocean survey. Monazite is an anhydrous phosphate of rare earths with a variable percentage of thoria (ThO_2). In the past, we had a small processing plant at Katukurunda for processing monazite to separate the rare earth phosphates found in this type of sand. This operation was abandoned after 1977. However, with the increasing demand for the rare earths today we are losing a valuable opportunity by shutting down this plant. Typically, the lanthanides in monazite consists of about 45–48% cerium, ~24% lanthanum, ~17% neodymium, ~5% praseodymium, and minor quantities of samarium, gadolinium, and yttrium. There is a high demand for rare earths because they are used in television screens, mobile phones, sensors, camera lenses, light emitting diodes, scanners, X-ray tubes, MRI contrast agents, etc. In addition, they are necessary for the permanent magnets industry and in many defence related industries. China has the monopoly in supplying rare earths to the entire world and any embargo on them will have serious repercussions to the entire electronics industry. It's high time to react for this demand and try to use our resources to get maximum economic benefits. The processes for the separation of the rare earths involves either sulphuric acid or sodium hydroxide. Digestion with concentrated sulphuric acid separates thorium as an insoluble phosphate while the rare earths go into the solution as a mixture of their sulphates. Further separation of rare earths is complicated with several solvent extraction steps and ion-exchange chromatography. However, value addition to monazite through acid digestion and selling the rare earth mixture has economic advantages compared to selling raw monazite.

Thorianite

Few scientists are aware that thorianite, an extremely pure form of thorium oxide was exported from Sri Lanka during the early 1900's from shallow dug pits at Nelluwa in the Galle district. Marie Curie's fundamental work on radioactivity was based on thorianite from Sri Lanka (Ceylon). Some other discoveries using our thorianite are; the Radioactive Decay Law, discovery of polonium and radon. The Sri Lankan origin of thorianite is clearly mentioned in her published research papers.

Quartz

High quality quartz is found at various locations around the country, including Galaha, Embilipitiya and Naula. The mined rock has been exported without any value addition for a long time. This rock can be processed as powders, and selling classified powders is more profitable than selling the raw form. Quartz from Sri Lanka has very high purity often exceeding 99.5%. It is one of the main raw materials used to produce silicon wafers used in the semiconductor industry. Silicon production involves the reduction of quartz (silica) at a temperature of around 1700 ^{0}C in an electric arc furnace. Silicon production from quartz is not practical in Sri Lanka owing to technological complexity and high electricity requirement. However, there are many other smaller industries which can be started with quartz as the raw material, such as manufacturing water glass (sodium silicate), quartz lenses and other quartz glass items which involves simple melting and reforming of quartz.

Graphite

There are several other minerals for which value addition can be carried out in Sri Lanka. The best quality graphite with a purity of about 99% have always come from Sri Lanka and only about 5% of the total graphite mined in Sri Lanka is used for local industries. In the past, Sri Lanka produced pencils using local graphite but now even the pencils are imported. Also, the Ceylon Ceramics corporation at one time had a small crucible factory at Hal-oya near Peradeniya where graphite was used to make crucibles for the foundry industry. We export almost all the graphite mined from the pits but import the finished products containing graphite, such as carbon brushes for motors, graphite greases and electrodes for dry batteries. The anodes of most batteries are made of graphite, and in lithium-ion batteries, approximately twice as graphite is used as lithium carbonate. The battery of a Nissan leaf car contains as much as 40 kg of graphite. There is increasing use of graphite in lithium batteries due to increased demand for laptops, CD players, mobile phones and power tools.

Advanced materials such as graphene and carbon nanotubes represent the high-end products of graphite. These have numerous applications such as in medicine for drug delivery, microchips, solar cells and batteries. In recent years, several researchers in Sri Lanka have discovered novel ways to make graphene using graphite employing more economically beneficial commercialization approaches. Graphene is considered as the thinnest, strongest and most conductive material, of both electricity and heat. Graphene batteries are light, charge easily and hold the charge longer and this can increase the travel range for electric cars. Since graphene is considered as the world's strongest material, it can be used to enhance the strength of other materials. Addition of even a trace of graphene to plastics, metals or other materials can make these materials stronger.

Iron and steel

There was a well-developed iron industry in Sri Lanka long before the British Colonial times. Archaeological evidence points out to a well organised steel industry dating back to 1200 A.D., long before Europe's first bellow driven iron manufacturing came into operation. It is believed that the famous swords of Damocles were made from steel manufactured in Sri Lanka. There is evidence for a large steel manufacturing facility in the southern slopes of the Samanalawewa area where wind tunnels were used to create the high temperatures required for the iron making process. A British archaeologist working in the Samanalawewa area in the early 1990's, actually produced iron by reconstructing such wind tunnels using iron ore available here. This work has been published in the prestigious journal Nature, and the molten slag flowing out of the furnace she built for this process appeared on the cover page of the journal. Unfortunately this steel industry died soon after the British came into power. Recently a good quality magnetite ore has been discovered off Buttala by geologists of the University of Peradeniya. This ore contains about 60 –70% iron in quite pure form and is found at the surface. Its quality is higher than that of iron ore deposits already recorded, which are found elsewhere in the country. Even by exporting this ore without value addition, considerable foreign exchange can be earned. We have ample deposits of iron ore and also limestone deposits in Sri Lanka and only coke has to be imported to manufacture iron and steel.

Limestones

There are three types of limestones in Sri Lanka: sedimentary limestones in the Jaffna and Puttalam districts, coral limestones along the south-western coast and crystalline limestones in the central highlands. Sedimentary limestones are used for the cement industry and dolomitic limestones used for glass and wall tile industries. There is a calcite deposit at Balangoda which is pure calcium carbonate. Yet, we import around 100,000 tons of precipitated calcium carbonate annually for various industries such as toothpaste, paints, plastics and drug industries. Precipitated calcium carbonate required for these industries can be made starting with this deposit of calcite. The process involves first calcining the calcite in a furnace and then slaking the lime produced to yield calcium hydroxide.

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Resulting milk of lime is then carbonated using carbon dioxide which is produced during the initial calcination stage.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3$$

This suspension is filtered to obtain a cake which is dried and ground to give precipitated calcium carbonate. Occasionally, the calcium carbonate particles are treated with fatty acids to give enhanced surface activity.

Other minerals of economic significance

The red soils and the serpentine rocks found at Ussangoda in the Hambantota district, contain about 2-3% nickel. An electrolytic method for extracting nickel from these rocks has been reported. However, a cheaper and a more practical method is to extract the rocks with sulphuric acid to obtain nickel sulphate which can be directly used for the electroplating industry. This can be done even as a household industry since no expensive machinery is required.

Another mineral deposit of potential importance is the iron pyrites ore at Seruvila which also contains about 1% copper. This is a unique deposit because it is the only sulphur and copper containing mineral in Sri Lanka. Like other similar deposits in the world, this ore also has around 3-5 ppm of gold. This ore can be roasted to obtain iron oxide and sulphur dioxide which can be used to manufacture sulphuric acid. Copper can be separated during the metallurgical operation and the matter containing copper can be treated to recover any gold.

There is also a smaller magnesite deposit at Wellawaya and this is a useful raw material to produce magnesium oxide, which is used as a refractory material. In addition, magnesium carbonate is used as an additive in the pharmaceutical industry.

Conclusion

This account illustrates the importance of using our mineral resources for the economic development of the country. Mineral development requires the concomitant development of a chemical industry. There should be at least a sulphuric acid plant and also a caustic acid plant. A salt based chemical industry to produce sodium hydroxide can produce chlorine, hydrogen and hydrochloric acid which has many industrial uses. Research done on mineral resources by universities and the opinions of local scientists should be considered in mineral exploitation. Novel and simple methods which can even be carried out in households should be seriously considered by policy makers.

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Spices, Chemistry & Sri Lankan Economic development

Ranjith Dayananda

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Historical anecdotes about Sri Lankan spices have always been highlighted in all printed and electronic media. However apart from Ceylon Cinnamon (*Cinnamomum zeylinicum*) and pepper (*Piper nigrum*), and other spices concerned, as a country I doubt we could talk about others with the same spirit. When considering cultivated areas with some degree of increase on two major spice crops most of the other spices (eg. Chilli (*Capsicum annuum*), Ginger (*Zingiber officianalle*), turmeric (*Curcuma longa*), cardamom (*Elevataria cardamomum*), cloves (Eugenea carryophyllus), citronella (*Cymbopogan nardus*), lemongrass (*Cymbopogan citrate*) show statistically a marginal decrease and production volumes are also lower than the 20^{th} century.

With other major spice producing countries and their progress with science and technological inputs, we are far behind. Even amidst the popularity of Cinnamon and to some extent pepper, Sri Lanka has still not moved into large scale organized cultivation of spices when compared to neighbouring India, one of the largest spice producers.

From the cultivation perspective, development and emergence of high yielding, disease-resistant climatically tolerable improved varieties are rare to see. The involvement of chemistry and a chemist's role in the development of fertilizers, pesticides and weedicides with minimum environmental and biological impacts need to be in place for the cultivation and crop protection.

Value Addition

Value addition is a very common term and many feel that rather than exporting raw material why can't we add value to those and earn more foreign exchange. If the crop or product produced could be sold for a better price, maybe minimum 25-50% higher price, I consider it as a value-added product otherwise when the end product market value is lesser than the raw material there can't be value addition. As an example, one could produce cinnamon bark oil as a value-added product from Cinnamon bark. With the current value of quality Cinnamon bark (quills), one has to spent at least 100kg of bark to get 1kg of cinnamon bark oil merely with highest quality characteristic special grade cinnamon bark oil may be a maximum value of Rs 65,000/- producer incurred cost of Rs. 240,000/- for 100 Kg of Cinnamon bark which is currently selling a minimum of Rs.2400/- (C5- Cinnamon quills).

Hence though the technology is available (for a nominal cost) one should not try to convert all available raw material to the so-called value-added product such as its oil, oleoresin or extract.

When considering the requirement of spices as a food ingredient, the highest quality has the maximum value when they are packed with customer's expected quality with the attractive hygienic package. Hence, value-added good quality spice is the best form with the most economically significant returns. As value addition is concerned with microbiological cleanliness, well preserved chemical characteristics with unique Sri Lankan spice flavour, attractively packed with international packaging and labelling requirements always give maximum returns. Ceylon cinnamon, Sri Lankan pepper and ginger will certainly fetch the highest market price provided that they possess;

- excellent cleanliness
- high and consistent quality
- steam sterilization
- grinding and blending ability, depending on the specific product.

Branding and marketing are key if you want to supply consumer-packaged spices and herbs. Moreover, packaging requires serious attention. You need to make sure that your logo and the packaging design fit the European market and match your buyer's preferences.

When considering the market segment for value-added spices China is the main supplier of crushed/ground spices and herbs, mainly paprika and ginger (87% and 11% respectively). India is the second-largest supplier of crushed/ground spices and herbs. In addition, it is the largest supplier of all types of mixtures to Europe. For spice and curry mixtures, Pakistan plays a relatively major role as the second-largest supplier. While Indonesia is a relatively large and a developing supplier of crushed and ground spices, Vietnam and Thailand are smaller but still, significant suppliers of value-added spices and herbs.

The European or American market for value-added spices and herbs in crushed or mixed form that are directly sourced from developing countries, is growing, but competition with European processors remains fierce. Especially for consumer-packaged spices and herbs, the first step in adding value to a spice would be crushing or grinding a spice or producing mixtures in consumer-packed form. An important first step to value addition is investing in the quality and food safety of your product.

Increasing demand for ethnic cuisines and exotic food products in European consumers could be an opportunity for those categories of value-added products. Most of the consumer-packaged products and brands from developing countries are available in the ethnic food shop market. These shops sell spices and herbs traditionally used in countries outside of Europe and used to primarily serve ethnic communities in Europe. As an example, if you go through some branded spice company websites they have a range of consumer-packaged products from developing countries. Buyers linked to these shops and webshops are experienced in trading consumer-packaged foods and are an interesting target for value-added spice products.

However, European and USA buyer requirements are very strict and the competition is strong. Sustainability is becoming more important in the spice and herb market and it is an important value-addition as consumers wants to know under which social and environmental conditions the product was produced. When packed spices and herbs are responsible for producing sustainability codes, it needs to ensure that packaging is sustainable; options include Rainforest Alliance, organic and fair trade. Stringent buyer requirements on sustainability and traceability throughout the chain of production is an important aspect, that is what the buyer relies upon (*e.g.* supplier codes or certification standard as proof to demonstrate traceability).

Furthermore, one has to comply with legal requirements for all spices, if not the product can be refused at the entry point. If it doesn't comply with the European legal requirements, your product can be refused at the border or withdrawn from the market. Moreover, it should comply with mycotoxins contamination risk for many spices. The EU sets maximum levels for mycotoxins for specific spices. For example, for pepper, ginger, turmeric or nutmeg, the maximum limit of aflatoxin B1 that can be present is 5.0 μg/kg (aflatoxin B1) and that of total aflatoxin content B1, B2, G1 and G2 is 10 μg/kg. The presence of banned pesticides or higher amounts of pesticides than allowed in the product is another issue faced in spice and herb exports. Salmonella is the most common type of microbiological contaminant found in spices and herbs, and is the major cause for the banning spices and herbs from the European market. Custom authorities reject spices and spice blends when containing undeclared, unauthorized or too high amounts of extraneous adulterants and additives. The contamination with PAHs is the result of bad drying practices.

Labelling

Consumer-packaged spices and herbs must adhere to strict food labelling requirements, presentation and advertising of foodstuffs as well as providing information on the nutrient content (such as protein, fat, fibre and carbohydrates content), making information easier to read and understand, with minimum font size for mandatory information;

- Indicate any allergens in the food product including information on the content of certain nutrients.
- Identical labels for products sold online (i.e. product labels in a shop and for distance-selling must meet the same requirements).

The focus of labelling requirements is to provide information to the consumer as much as possible; name of the food, ingredients/processing aids, net quantity, “Use by” date, storage conditions, name and address of the business, country of origin, lot No. In addition, any certification logo, or retailer logo in the case of private label products, should be displayed on the label.

The American Spice Trade Association (ASTA) has developed cleanliness specifications for spices to ensure that the spices meet federal regulatory requirements for safety and cleanliness. They were designed to meet or exceed the U.S. Food and Drug Administration's Defect Action Levels. (For more information Pl ref. ASTA website). The Quality Minima Document prepared by European Spice Association laid down requirements for the unprocessed spices and herbs, as well as additional buyer requirements which were not laid down in the legislation as the main reference for Europe and many key players in the market. Although this document does not cover consumer-packaged spices and herbs, you can use it to understand the chemical and physical parameters for unprocessed products.

In the case of each spice, there are specific grades, quality characteristics, and unique chemical and physical characteristics, to identify the best among the lot. However, in any raw material, there are off-grade immature crops that are broken or contaminated, those that do not meet minimum quality characteristics (eg. shape, size, low percentage of active ingredients, microbiologically not fit for human consumption).

Sustainability

Certain buyers require to prove sustainability as well as traceability from the supplier. Buyers will demand that you comply with their supplier codes or certification standard. The use of self-verification systems is expected to grow, and can use sustainability certification as proof to demonstrate traceability.

For consumer-packaged spices and herbs, one may find most opportunities in fair-trade certification. When you pack spices you will also be responsible for producing sustainability codes for your suppliers, you need to ensure that your packaging is sustainable. Options for sustainable packaging include alternatives to polluting materials (*e.g.* polyvinyl chloride (PVC), polyurethane (PU) or polystyrene (PS)).

Furthermore, to enhance the value of your product in the current scenario, some of the features one could incorporate into their spice product are;

1. **Food safety certification:** A guarantee that the product is safe. The most important food safety management systems in Europe are the BRC (British Retail Consortium) Global Standard, Food Safety System Certification (FSSC 22000), Quality Food Program (SQF). It's always better to find the buyer´s preference for a specific food safety management system, as some may prefer one system over the other.
2. **Quality management:** If your organization is with ISO 9000, you can show your buyers that you are taking quality seriously.
3. **Corporate social responsibility (CSR):** Almost all international companies have different requirements for CSR: signing their code of conduct or following common standards, such as Supplier Ethical Data Exchange (SEDEX), Ethical Trading Initiative (ETI) or the Business Social Compliance Initiative Code of Conduct (BSCI).

Quality spices that comply with the above, fetch a very high price. It is the real value addition if one expects to earn more profits from the spices.

So as far as value addition is concerned, those who could produce clean and sound spices are always in high demand. To maintain such standards, product manufacture with good agricultural practices (GAP) and also with good manufacturing practices (GMP) fetch a high value. Hence, maintaining all standard requirements, including sterilization, is the key for value addition. This also entails the product being produced as per Organic product certification guidelines set by internationally accredited certifying agencies such as Control Union, Royal Cert or the recently introduced Sri Lankan Organic Product Certification.

Ready-made spice powder and paste

Powdered spice in airtight packaging material is in enormous demand. Increased urbanization paired with a rise in the number of working women has reduced the time of cooking. Consequently, home-makers have started to demand readymade spice powder that includes chilli powder, black pepper powder, turmeric powder. Also popular are ready-made pastes of onion, garlic, ginger in packet form. An official report from Everest Spices Ltd. Reveals its exports about 10 per cent of its products to the US, West Asia, Singapore, Australia, New Zealand and East Africa. The total market size of branded spices is estimated to grow at 14 per cent annually.

Pepper (*Piper nigrum*)

It is a fact, that in the recent past pepper was imported from other major producing countries in very large quantities, claiming to be for value addition as pepper oil or pepper oleoresin. As one of the conditions of BOI, registered foreign and local companies are allowed to import raw material and turn them into value-added product and export (HS code of the end product should not be the same when value add) thereby helping the Government to earn foreign exchange and also establishment of companies to employ to cater to the local workforce. Based on this, several Indian processors such as Plant Lipid has established their massive extraction plants at our BOI zones (Mirigama). With the high reputation which we earned historically as one of the best quality pepper producers, India too exports a large amount of Sri Lankan pepper mainly as light berries for extraction process carrying out in India. However, as the largest pepper producer in the world, Vietnam annually produces more than 150,000 mt. Vietnam pepper, which is imported at a cheaper price, is used in the above plants; however, some lots which are believed to be released to the local market and claims to have Sri Lankan origin, was actually imported and re-exported again to India, resulting in heavy losses to Sri Lankan pepper producers.

Pepper is known as the king of spices; it is the most consumed spice in the world. Its pungency is due to a Nitrogen-containing alkaloid named piperine, Sri Lankan pepper contains more than 5% piperine whereas other major producers have only 3% piperine. At the same time, volatile pepper oil with terpene hydrocarbons which are responsible for its unique flavor, is much higher in local pepper. As Sri Lanka produced less than 2% of world production we should look into niche markets for value-added products such as high-quality black pepper, white pepper and green pepper products. As explained in the previous chapter high-quality pepper is not only about its physical and unique chemical characteristics but also about attractive clean black colour (could be achieved by blanching /steaming), consistent size of berries, microbiological cleanliness and so on., Though local pepper is rich with its flavour and supreme pungent taste, lack of microbiological quality found , the presence of unacceptable foreign and extraneous matter generally classified with the grade of Fair Average Quality (FAQ), indicates that value addition needs to start by avoiding the factors that lead to the deterioration of quality. Similarly, by appropriate sterilization, final clean product could be achieved which meets international standards. Still Sri Lankan pepper has a reputation as a pepper producer with minimum pesticide residue contaminants compared to other major producers.

A variety of products are being made from black pepper. Furthermore, a range of green pepper-based products are, canned green pepper, green pepper in brine, bulk-packaged green pepper in brine, cured green pepper, frozen green pepper, freeze-dried green pepper, pepper mayonnaise, pepper cookies, dehydrated green pepper, green pepper pickle, mixed green pepper pickle, green pepper sauce and green pepper-flavoured products. In this instance too, value addition as pepper oil or as pepper oleoresin also need to be properly evaluated before the establishment of the processing plant.

Furthermore, real value addition is in effect when the industry is manufacturing consumer end product such as flavours and fragrances from the essential oils or oleoresins. However, quantities required for such an industry need to be properly evaluated and also the need to assess the real value of such natural products when compared to synthetic counterpart arises.

Ginger (*Zingiber officianalle*)

The use of raw ginger as a culinary spice or as a herbal preparation is common in Sri Lanka. For Ayurveda, almost all dried ginger is exported from India. It is estimated at least 5-6 kg of raw ginger is needed for the production of 1kg of dry ginger. When browsing through supermarket shelves, among ginger-based products, ginger beer is the most famous and delicious bottled drink, its flavour is unique as it is produced from local ginger variety though fleshier Rangoon and Chinese varieties are also grown in Sri Lanka. As a value-added product, Elephant House Ginger Beer could be rated as the best among similar products in the market, which is made out of using only local ginger (ginger oleoresin). The final product is made from oleoresin obtained from the dried ginger, a complex process where solvent extraction followed by evaporation of residue solvent resulting in thick slow-flowing ginger oleoresin (5-6%).

Ginger has been reported to contain usually

1-3% of volatile oil, pungent principles *viz*., gingerols and shogaols and about 6-8 lipids and others. Ginger oil contains Zingiberene and bisabolene as major constituents along with other sesqui- and monoterpenes. Ginger oleoresin contains mainly the pungent principles of gingerols and shogaols as well as zingiberone. Shogaols have recently been found to be twice as pungent as gingerols1-4. Gingerol and shogol are two major compounds responsible for ginger flavor; comparatively the percentage of those and the collective presence of several minor compounds in local ginger is unique for its difference from the other two varieties. When value-added products are concerned, dried ginger is a raw material that one could store for years itself and one of the main herbs used in Ayurveda. Sri Lanka imports a large amount of dried ginger for Ayurveda herbal preparations. However, apart from a few organized, systematically maintaining plantations of ginger (out growers attached to Ceylon Cold Stores) no large scale ginger cultivations supply sufficient raw material for further processing. Apart from a few products (eg. ginger preserve in sugar solution, ginger cocktail prepared from fresh ginger), there are no sufficient value-added products processing in Sri Lanka targeting the export market.

Turmeric (*Curcuma longa*)

Turmeric happened to be the most talked-about spice in the recent past due to the ban of its importation. The Sri Lankan requirement was mainly satisfied from India, the largest producer of turmeric in the world. The use of turmeric not only as a nutraceutical but also as a cosmeceutical made its current importance more than its use as a culinary spice. However, the natural appealing colour it imparts on food and also its antibacterial activity makes it a popular culinary spice as well as a herbal medicine. Value addition is commonly done to introduce turmeric as clean sound fingers or as a powder. Apart from this, turmeric oleoresin is popular as a natural colouring agent (curcumin) in many foods such as butter and margarine. A product called Vegitone happened to be established as a safe yellow colour dye prepared from turmeric for industrial use. The cosmeceutical usage of turmeric is ever-increasing for facial and body lotions and creams due to not only its historically known benefits but published scientific literature in many reputed journals and also several patents already obtained by many countries (mainly India). As per several research papers published by Sri Lankan scientists from Universities, the Department of Export Agriculture (DEA) and by Industrial Technology Institute (ITI) curcumin content in local turmeric is much higher than the imported ones. However, as large-scale turmeric processors with improved technologies are not available in Sri Lanka, it will be hard to satisfy the turmeric requirement in the form of turmeric fingers, which was the common product imported to Sri Lanka, even though currently we have a large crop of turmeric. But it is good to see turmeric powder packets are now emerging into the market for a reasonable price. However, as it is common to find adulterated products one has to be vigilant when purchasing those powdered spices not only turmeric but other powdered spices as well.

Cinnamon (*Cinnamomum zeylinicum*)

Ceylon Cinnamon, also known as true cinnamon, is a commodity much expensive when compared to Cassia (*Cinnamomum aromaticum*). World market share for cassia variety is much more than that of Ceylon Cinnamon (85000mt:15000mt). Almost more than 95% of Ceylon cinnamon is produced in Sri Lanka while Madagascar and Seychelles are the other two major producers.

In both Cassia and Ceylon cinnamon, Cinnamaldehyde is the major compound where it is present 85-95% and 55-74% in the two volatile oils respectively. The flavour bouquet of Ceylon cinnamon is unique as in addition to cinnamic aldehyde and eugenol, several other oxygenated terpenic hydrocarbons are also found in Ceylon cinnamon. One of the major advantages of Ceylon cinnamon is that it does not contain the carcinogenic compound coumarin. Even in the instances when it is found to be present, it is very low compared to cassia (less than 0.004mg/kg).

Ceylon cinnamon bark is processed as a cigar like quill in several grades whereas Cassia is just a curled bark which is much harder when compared to Ceylon cinnamon. Presently, as a consumer item, cinnamon quills are cut in different sizes. 7.5, 10 or 12cm has a huge demand when packed in attractive packaging. In addition, cinnamon tea and cinnamon powder are the two other major consumer products that are exported. According to recent research carried out in Sri Lanka and all over the world, it is now well-proven that cinnamon has medical benefits in blood sugar control, hypertension etc., which in turn effectively increases its market share. South American region, Scandinavia and Europe are the major consuming countries.

Cinnamon leaf oil, bark oil and oleoresin are also manufactured in Sri Lanka. Cinnamon leaf oil is a real value-added product made from cinnamon leaves that remains after getting the stems for the production of cinnamon quills, quillings, featherings and chips. As its high value is concerned the use of quills for the distillation or extraction is never taking place; instead chips and other offcuts of bark are used for the extraction purposes. Several grades of Ceylon Cinnamon bark oil depending on the high aldehyde (55-70%) and also low eugenol (1-10%) content are in the trade. Cinnamon leaf oil has only one grade which needs to be more than 75% eugenol. In addition, the minimum presence of safrole and coumarin contents are also considered by most flavour houses.

Oleoresins, oils, extracts and seasonings

With the extensive usage of natural extracts, flavour and fragrance manufacturing company's all over the world are switching to process spice oleoresins. The demand for oleoresins and seasonings has led many players including Indian spice processing giants like Synthite, Plant Lipids and Kancor, to focus on research and technology to manufacture innovative value-added products such as oleoresins, extracts like essential oils, seasonings and organic spices. Flavours that can be used in the ready-to-cook and ready-to-eat food segments are some of the latest innovations. Some of them are isolating top aromas of spices through the carbon dioxide process for improving the fresh notes of spices in the final product. Absolutes from spices for various segments such as cosmetics, perfumes and even high-value food segments are also in demand such as new blended natural colours as per customer requirements.

Conclusion

Spices and value-added products of spices are in huge demand in the export market, particularly in Europe and the USA. The demand is ever-increasing with the growth of the population. By increasing the export of these products the nation's economy can be improved. GDP growth together with foreign exchange earnings could be much improved from the spice sector provided that the processors are knowledgeable with the current requirements of foreign buyers, in particular adherence to clean, unique Sri Lankan produce. Hence government must emphasize the promotion of high-tech equipment such as driers, sterilizers, grinders etc. for the spice processors with subsidiary prices. Though Sri Lanka is very much rich as a source of exceptional spices, unless we produce value-added spices and penetrate the modern consumers, we may remain as a bulk spice supplier allowing European, American or Indian giant companies to earn maximum profit through value addition at the destinations. Hence to get maximum economic benefits for the farmers and small scale spice suppliers, processors should switch to new technologies to produce value-added spice products.

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Themed Collection

Coconut Oil in A Nutshell: How BCC Lanka Limited preserves the Lankan touch in edible coconut oil products

Jayantha Wickramasinghe

BCC Lanka Limited

Can you tell us about the products your organization currently manufactures?

Our products are mainly centered on edible oil, soap, detergents and disinfectant. The types of edible oil products that we manufacture are white coconut oil and RBD coconut oil.

How do you obtain the raw material for those products? Are they 100% local raw material?

BCC currently does not have an oil mill; it used to own one, however its operation was halted following the lack of raw material (copra). Hence, we purchase coconut oil from a selected number of local oil mills, which are ideally located near coconut plantations and satisfy the standards followed by BCC. These standards include the storing conditions of copra, maintenance of oil storage tanks, cleaning of machinery, environmental factors and quality parameters. Different quantities are purchased each week as per the requirement.

100% local raw material is employed for the manufacture of our products, and mixing is prohibited to ensure unadulteration. We confirm this by testing for random samples at least twice or thrice a week. Earlier, we didn't check for aflatoxins, but ever since the issue regarding aflatoxins came to light, we test for them by sending samples batchwise to SGS. Oil which has a level well below the maximum limit of permissible aflatoxins, is then chosen for further operations. We, at BCC, always try to maintain our standards above those available in the market.

What are the challenges faced in the edible oil market today due to the low productivity caused by pests and diseases?

There is a drastic decline in the harvest and the size of the coconut fruit is smaller compared to those in the olden days, thus causing the price of a coconut to increase over the years. Earlier, oil mills used to purchase the coconut fruit for its size; now they purchase according to its number, since there aren't any significantly larger coconut fruits available. Crop diseases and infestations are the major causes for this phenomenon, which results in a low harvest.

Nowadays people try to avoid using too much cooking oil due to the fact that cardiovascular diseases have become quite common. What are your thoughts on this?

Coconut oil comprises 92% saturated fat out of which 62% are medium chain fatty acids and 30% are long chain fatty acids. 7% of unsaturated fat constitutes the rest. Cholesterol is absent in coconut oil, however repeated use of the same cooking oil might stimulate its formation, particularly when reusing it multiple times. Hotel kitchens use their cooking oil one time and discard it, without reusing the same oil over and over again. However, certain restaurants, eateries and street vendors purchase this discarded oil for a low price and use it for their food items, repeatedly. Upon the repeated use of this oil, particularly in deep frying, oxidized products are being formed. Consumption of food containing this oxidized fat may contribute in the risk of developing cardiovascular diseases.

Coconut oil helps maintain the LDL (Low Density Lipoprotein), which is considered as "bad cholesterol" and HDL (High density Lipoprotein) levels, which is considered as "good cholesterol", in the human body. It is a natural antioxidant and shows anti-bacterial, anti-viral and anti-fungal properties.

Can you explain briefly how you improve the shelf life of cooking oil and fats?

Normally, in BCC, we are focused on maintaining the shelf life for a longer period of time. Generally, shelf life decreases upon increasing rancidity of the oil. Hence, by preventing rancidification, we can improve shelf life. Exposure of the stored coconut oil to air and sunlight is kept at a bare minimum, and in addition, the absence of impurities is vital. One common practice to remove impurities is filtration of the oil whilst some manufacturers add preservatives. However, instead of adding preservatives, BCC employs the RBD (refined, bleached, and deodorized) process to increase the shelf life of edible coconut oil. The shelf life of RBD oil is found to be twice than that of normal coconut oil.

What would you expect from a fresh graduate or food chemist working in your organization?

We expect all our employees to follow the standard procedures involving product manufacture, from maintaining the necessary quality parameters. They should familiarize themselves and have a sound knowledge on the whole manufacturing procedure, from obtaining the raw material after checking its quality and releasing a product to the market following the standard procedures of quality checking, Even though our organization is not SLS certified, we follow the standards and maintain the necessary quality parameters defined by SLSI.

What are the future prospects of your organization?

We hope to supply more coconut-related products to the market. We have already submitted our proposals to commence the manufacture of coconut water and coconut milk.

Mr. Jayantha Wickramasinghe *obtained his GIC qualification from the College of Chemical Sciences and is currently reading for his M.Sc. in Food Science and Technology at the University of Sri Jayawardenapura. He has been working at BCC Lanka Limited since 2006, and currently serves as the Acting Production Manager and Assistant Quality Controller.*

Contemporary Feature

Aflatoxins

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Department of Chemistry, The Open University of Sri Lanka

Nowadays, "Aflatoxin and Coconut oil" has become a provocative topic in Sri Lanka. However, **aflatoxins (AFs)** were first discovered in England, around 1960s, after the outbreak of turkey X disease. In 2012, the International Agency for Research on Cancer (IARC) categorized aflatoxins (B_1, B_2, G_1, G_2 and M_1) as a "Group 1" **mycotoxin**, which means that they are **carcinogenic** to humans.

What are mycotoxins?

All living organisms inherit their own, natural, self-defense system. Mycotoxins are toxic secondary metabolites produced by fungi, which readily colonize on substrates. Secondary metabolites (that are not directly involved in the growth, development, or reproduction) of plants, bacteria and fungi often play specific and important roles for their survival/existence in the natural habitat. Bacteria produce endotoxins and exotoxins whilst molds (fungi) produce mycotoxins. Bacterial toxins are composed of proteins which destroy a specific target species or host cell, and toxins produced by molds are comprised of simple low molecular weight compounds. There are various types of mycotoxins: aflatoxins, ochratoxins, citrinin, ergot alkaloids, *etc*.

Genus *Aspergillus*

Aflatoxins are mainly produced by fungi belonging to a genus named *Aspergillus*. The separated hyphae which appear as branched filaments make up the mycelium structure of this fungus (Figure 1).

Figure 1: Mycelium of *A. flavus*

The end of the rough and colorless conidiophore (the hypha that bears conidia) swells to make the vesicle which bears the phialids (Figure 2). These phialids can be arranged in either one row (uniseriate) or two rows (biseriate). Conidiophores are asexual spores that are observed at the end of the phialids. Their mycelia excrete various chemical compounds, as they are saprophytic organisms. *Aspergillus flavus* and *Aspergillus parasiticus* are the main causative microbes that produce aflatoxins.

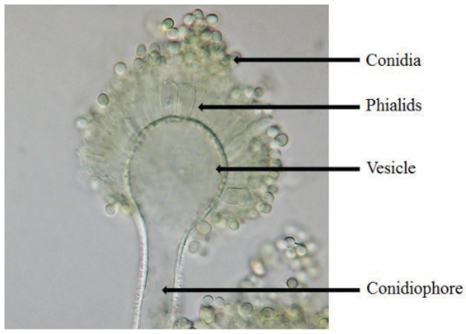


Figure 2: Morphology of *A. flavus*

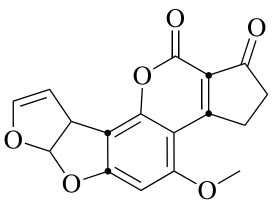
Their colonies can be visualized as **green** (dark green - *A. parasiticus*, light green - *A. flavus*) velvet mats (Figures 3 and 4).

Figure 3: Colony of *A. flavus*

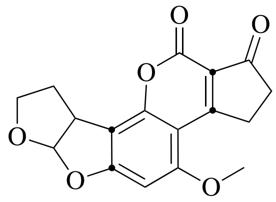
Figure 4: Colony of *A. parasiticus*

Chemical nature of aflatoxins

Aflatoxins (AFs) are stable polycyclic compounds, belonging to the **difurano coumarin** compounds and are resistant to roasting, extrusion and cooking. There are at least 20 types of AFs found in nature. AFB_1 is the most toxic compound that is produced by both *A. flavus* and *A. parasiticus*. *A. flavus* produces B-AFs, while *A. parasiticus* is responsible for the production of both type B-AFs and G-AFs. In nomenclature, English letters (**B** and **G**) stands for the **fluorescence color** under UV radiation (B for **blue** and G for **green**) and the number represents the relative chromatographic mobility.

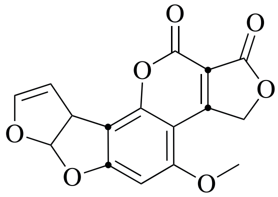


AFB_1

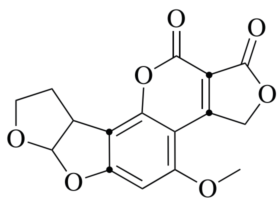


AFB_2

In both AFB_1 and AFG_1, there is a double bond between carbon atoms in the furan ring which allows them to form epoxides while, AFB_2 and AFG_2 lack that functional group.

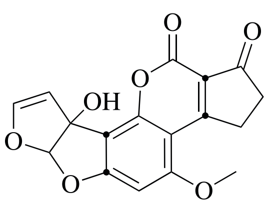


AFG_1

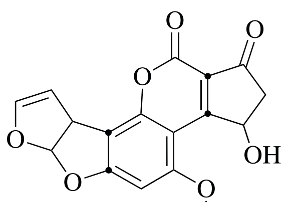


AFG_2

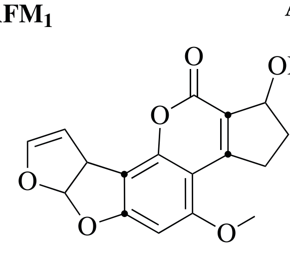
AFM and AFQ are metabolites of AFB types. For example, AFM_1 is a metabolite of AFB_1, in humans and animals and AFB_2 metabolizes to produce AFM_2, in milk of cattle fed on contaminated foods. AFQ_1 is another metabolite of AFB_1, which is prepared in the liver of other higher vertebrates. Aflatoxicol (AFL) is a reductive metabolite of AFB_1.



AFM_1



AFQ_1



AFL

A. flavus is also composed of other mycotoxins, such as sterigmatocystin, cyclopiazonic acid, kojic acid, glycotoxin, aspertoxin, *etc*.

Toxicity

AFs are acutely toxic, immunosuppressive, hepatotoxic, mutagenic, teratogenic (causing birth defects on an embryo and fetus) and carcinogenic compounds. AFs do not have any color, odor, or flavor. Therefore, it is easy to consume such contaminated food unknowingly. Ground nuts, maize, rice, cereals, dried foods, spices, crude vegetable oils and tree nuts can get easily contaminated, thus the *Aspergillus sp.* are saprophytic microbes. The contamination can occur in any stage of food processing, during pre-harvesting, harvesting, post-harvesting, storing, transporting, and consuming.

According to a recent review (Toxins, 2021), India and Sri Lanka are the leading countries that consume rice with a high content of AFB_1. Furthermore, it stated the maximum permissible limits for AFT (total) in food in the following countries as Singapore (5 μg/kg), Japan, Vietnam, Kenya, South Africa (10 μg/kg), Canada, Malaysia, Korea, Australia, Zimbabwe, Taiwan (15 μg/kg), US, Thailand, Philippine, Hong Kong, Brazil, Nigeria (20 μg/kg), and Sri Lanka, India (30 μg/kg).

According to the Health Ministry of Sri Lanka, the maximum permissible limit of AFs is 30 μg/kg (or ppb; parts per billion). However, Sri Lanka Standard states: - a product shall not exceed the level 5.0 μg/kg for aflatoxin B_1 and 10.0 μg/kg for total aflatoxins (AFT) when determined according to the method given in SLS 962. Acute exposure to a high dose of AFs causes vomiting, abdominal pain and even death. Global Cancer Observatory stated that chronic exposure to lower doses may lead to liver cancer which is the 6^{th} most common killer disease among all ages. The livestock may also get contaminated by consuming the feeds containing AFs.

Methods of detoxification

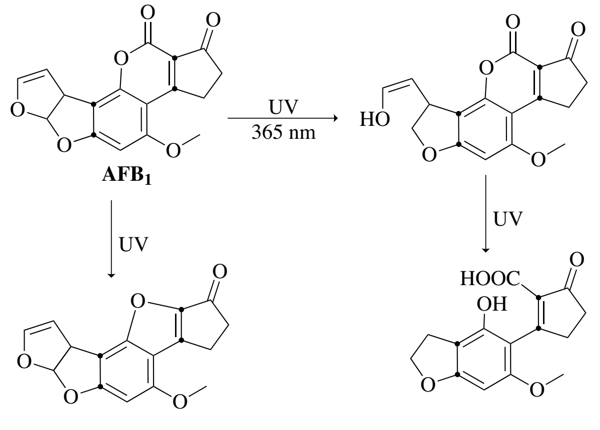
Low ventilation, ambient temperature and high moisture content are the best conditions to enhance the levels of AFs in food. Insects and other microbes, storage time, spore infection density, suitability of the fungal substrate also affect the contamination. Washing, drying and irradiation are the basic physical methods that can be practiced lowering the effect of AFs. Applying correct fungicides during a specific stage could minimize the contamination. But most of the time, these synthetic fungicides may lead to other adverse ecological and health problems.

The growth of AFs can be inhibited by adding essential oils (EOs). EO contains volatile compounds such as terpenes; they are naturally occurring secondary metabolites of some plants. These chemicals can degrade the cell wall of the fungi and alter the permeability of the membranes. EOs of apple-mint, anise, holy basil, betel, cinnamon, cardamom, lemon grass, coriander, cumin, turmeric, fennel, mint *etc.* can inhibit the effect of AFs. However, it is not practicable to apply EOs to protect foods from AFs, since they are very expensive as well as highly volatile.

As a bio control towards aflatoxins, nontoxic *A. flavus* strain AF36 is currently being used in Arizona, Texas, and Southern California, to substantially reduce the aflatoxin contamination in cottonseed. These strains compete with the toxic *A. flavus* strain and prevent the production of AFs.

AFs are soluble in organic solvents (*e.g.* chloroform and methanol) and slightly soluble in water. Detoxification can be carried out by degrading the structure of AFs. By applying different gases (*e.g.* ozone) or chemical agents (*e.g.* hydrogen peroxide, bases or acids), the chemical nature of AFs can be altered to make them harmless. Main drawbacks of these methods are the high cost and low aesthetic quality of treated foods.

AFs are destroyed when the sample is heated above 250 ^{0}C, but these elevated temperatures are intolerable to many food samples. Due to the photosensitivity of the AFs, the structure of them (especially more toxic AFB_1) can be degraded by sunlight or irradiating the sample with high energy photons. If 2 mm of the coconut oil layer is exposed to sunlight for 10 minutes, 75% of AFs that are present in that sample degrade due to the UV radiation of the sunlight. UV lamps with 365 nm wavelength and 6.4 mW intensity can also be used for this purpose. Gamma radiation (> 3 k Gy) is not very suitable to apply for food samples since it lowers the natural quality of the sample, even though it destroys AFs completely.



TiO_2 is an excellent low cost, eco-friendly photocatalyst, which can be used to degrade AFs. Bentonite, hydrated sodium calcium aluminosilicate (HSCAS), activated charcoal, grape pulp and shell, kaolinite clay are used as AFs absorption agents. Activated charcoal shows the maximum AFs absorption percentage (100%), while, bentonite clay shows 92.5% absorption. Nano materials such as magnetic graphene oxides (MGO) show high absorbance percentages for AFs.

The application of enzymes and microorganisms (yeast strains and lactic acid bacteria such as *Lactobacillus*) are the most convenient and safest methods to reduce AFs in foods (*i.e.* yeast cell wall can absorb about 92.7% AFs in a substrate).

Controversy of coconut oil

Coconut oil is one of major lipid sources used in Sri Lanka. Pure coconut oil is free from cholesterol and shows immense medicinal values. However, the true quality of this coconut oil is masked by adding other oils such as palm oil. The seed of African oil palm or *Elaeis guineensis* is rich in palm oil and its oil can be easily mixed with coconut oil. This adulteration can cause the elevation of AFs, as these nuts can get easily contaminated with *Aspergillus* molds. The other ecological problem caused by this palm plant is that it absorbs an excessive amount of water present in the soil. Therefore, the underground water level decreases, and other plants could die.

Detection of aflatoxins

Thin Layer Chromatography (TLC); Gas Chromatography (GC); High Pressure Liquid

Chromatography (HPLC); Enzyme-Linked Immunosorbent Assay (ELISA), Liquid Chromatography coupled to Mass Spectrometry (LC-MS); Immunoaffinity Column Assay (ICA) are the analytical methods that can be used to detect the AFs. ELISA is useful as it helps to find out whether the antibodies that are related to certain infectious conditions are present in the blood.

In conclusion, the maximum permissible levels of AFs for human consumption vary from 5 to 30 μg/kg (depending on the food type). In Europe, the maximum limit for AFT is 15 μg/kg and for AFB_1, 12 μg/kg. According to the standards of SLSI, the maximum level for AFs in coconut oil is considered as 10 μg/kg.

The health risks from AFs cannot be ignored as it can have a negative impact on human population. However, good practices during (food processing, pre-harvesting, harvesting, post-harvesting, storing, transporting) and public awareness are the best ways to avoid the intoxication of the society by AFs.

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Contemporary Feature

The Biochemistry and Cell Biology Behind Developing Vaccines Against SARS-CoV2 Virus

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The beta-Corona virus SARS-CoV-2 has caused a pandemic outbreak that has lasted for over a year and it still continues its impact in a global scale. The devastating loss of lives and livelihoods has caused socio-economic downfall across the world. The scientific community has since worked towards finding therapeutic strategies to mitigate adverse effects of the infection and vaccines to prevent the spread of the virus. The advancements and success in vaccine technologies have been tremendous and has led to the development of effective vaccine candidates under a remarkable time frame.

Pandemics and worldwide spread of viruses over the past several decades had prompted scientists to investigate more efficient alternative vaccine technologies. Beta coronaviruses have caused three outbreaks within the past 20 years: SARS-CoV (2002-2003), MERS-CoV (2012) and lastly SARS-CoV-2 (2019 till present). Since its emergence, SARS-CoV has mutated into few other strains that hold or surpass the high infection rate of the virus originated in Wuhan, China.

1. Biochemical features of SARS-CoV-2

Structurally, SARS-CoV-2 is a pleomorphic virus with a diameter between 50-200 nm. The whole viral genome is encoded in a positive-sense ssRNA, that carries a 5' cap structure and is polyadenylated at the 3' end. The polyadenylation of the genome and as well as the subgenomic mRNAs allow isolation of these molecules using oligo dTs. The whole viral genome of about 29.9 kB contains 5' and 3' untranslated regions of about 200-500 nucleotides. There are 14 open reading frames (ORFs) on the mRNA that transcribe 27 different viral proteins. Among these, non-structural proteins perform essential functions including genome unwinding, replication, capping, tailing, methylation, membrane rearrangement, etc. The structural proteins make the envelop, nucleocapsid, membrane and spike proteins. The spike protein (S) is a multifunctional trimeric transmembrane glycoprotein that plays essential roles is attachment, fusion and entry into the host cell. The S protein is where the initial mutation occurred that led to an outbreak and an eventual pandemic. The cleavage of the S protein trimer is a crucial step in the process of the viral infection. Sequence analysis of the virus had revealed insertion of 4 amino acids between S1 and S2 sub-units of the spike protein. These mutations introduce a new furin cleavage site on the S protein, that was absent in previous SARS-CoV and may have presumably led to the increased pathogenicity of the virus.

The SARS-CoV S trimer has two distinct conformations as shown by Cryo-electron micrography. The change in conformation between open and close forms, is believed to be crucial in its interaction with the human ACE2 (Angiotensin converting enzyme 2) receptors on the cell surface. The opened conformation presents the three hACE-2 recognition motifs on each of the sub-unit and renders it for interaction. ACE2 receptors are highly expressed in Type II alveolar epithelial cells, that explains the respiratory distress associated with the infection. In addition, these S proteins have an abundance of N-linked glycans that protrude out of the viral particle that play roles in protein folding, priming by host proteases and antibody recognition. Sequence analyses confirm the conservation of 20 glycosylation sequences across all SARS S proteins suggesting that antibody presentation and interactions are perhaps comparable among the viral strains. Recent data show that S protein is more exposed to the host than the other fusion proteins on the viral surface. This suggests that the S protein may present more to the machinery of the immune system making it an ideal target for vaccines against SARS-CoV-2.

2. Milestones in developing mRNA Vaccines against SARS-CoV2

The basis of a vaccine is to mimic the entry of the virus into the host by presenting a specific immunogen to initiate a cascade of immune response driven cellular processes. There have been few immunogens that have been the focus of the vaccines. In addition, there have been several strategies that have been explored in producing a vaccine including, inactivated or live attenuated virus, virus like particles, protein or protein subunits, DNA and novel mRNA technology. Between DNA and RNA based vaccines, the latter presents an advantage by not having to cross the nuclear envelop. Among these, although novel, RNA technology is ideal if successful as it is incapable of altering the genome and its expression is maintained in a transient manner by intrinsic cellular mechanisms. In addition, synthesis of RNA molecules allows a wide array of target proteins and epitopes as immunogens in contrast to the capabilities with traditional approaches.

RNA based vaccines have made major advances over the years and have proven promising in non-human primates. RNA is able to elicit a robust innate immune response and such vaccines have been tried for HIV infections in other non-human hosts and Zika in the past. They are well tolerated in preliminary studies and in some clinical settings. One of the strengths of RNA based vaccines is that it can be produced in a large scale, in contrast to traditional approaches which makes large scale production much feasible with escalated high demand during a pandemic.

Unprotected RNA molecules are highly unstable under physiological conditions. Optimizations on the RNA molecule in prophylactic vaccines have made great advancements by introducing a capped structure to enhance translation efficiency and increase stability. Addition of 5' untranslated regions to the sequence enhanced the translation efficiency. Both the leading mRNA-based vaccines, BNT162-01 and mRNA-1273, encode the full-length spike glycoprotein where the latter with modification at two residues to prolines. The mRNAs are transcribed in vitro using a DNA template and a cap structure is introduced to increase translation capacity and stability in vivo following intra-muscular administration.

One other main challenge that was overcome was advancing cellular delivery methods to circumvent the catalytic hydrolysis of RNA by cytosolic ribonucleases. A number of strategies have been developed for RNA delivery including RNA conjugates, modified RNA, viral vectors, microparticles and nanoparticles. Among these methods, tagged or conjugated RNAs, although increasing stability, present the challenge of non-targeted binding and interactions with cellular components perhaps leading to aggregation. Despite viral vectors being a viable choice, the challenges associated with packaging the virus with the mRNA, large scale production and low immunogenicity limit its use in a prophylactic setting. Packaging genetic material into non-viral vectors with lipids, polymers, peptides and inorganic peptides have presented promising technology with an easier production pipeline. Further, the size of these particles can be altered to carry a larger load of oligonucleotides. Delivery of genetic material in lipid nanoparticles (LNP) has been through major technological advancements over the past years. LNPs may contain ionizable amino lipids, phospholipids, cholesterol and polyethylene glycol (PEG) containing lipids in their formulation. The LNP-formulated mRNA must be able to induce a marked but transient increase in pro-inflammatory cytokines at the injection site. Change in cytokines contribute to chemotaxis, recruitment and activation of specific immune cells that activate a cascade of cellular events.

The mRNA-based vaccines essentially target antigen presenting cells (APCs), which are an heterogenous group immune cells including B-cells, macrophages and dendritic cells. APCs are primarily involved in ingesting the foreign antigen and presenting the partial peptides on the cell surface along with an antigen-presenting molecule. The immunogenicity of a peptide and therefore a mRNA molecule rely on efficiency of the immunogen to act on the cell surface of the APC to generate an immune response, generating antibodies against it.

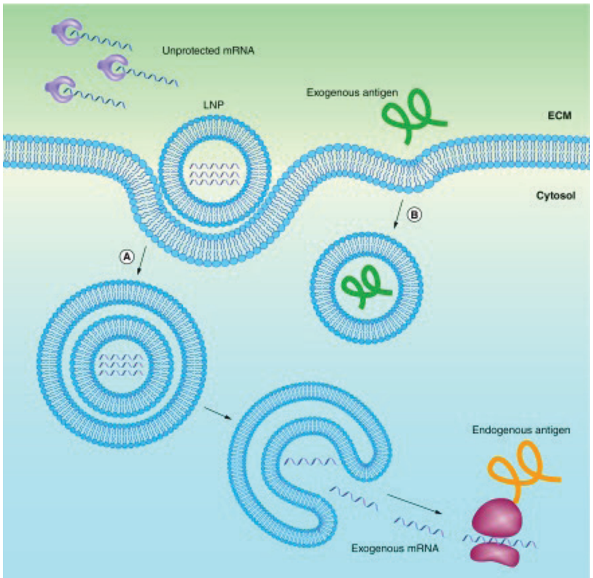

Figure 1 : mRNA molecules in lipid nanoparticles (LNP) are protected against degradation and facilitates endocytosis in to host the cell (Reichmuth et al., 2016, pp. 319–334).

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Guest Articles

Guest Articles

Chemical Aspect of Cannabis

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Cannabis spp. contains a highly complex mixture of compounds, and up to 568 unique molecules are identified in the cannabis.[5] Among these compounds, Δ^9-tetrahydrocannabinol (Δ^9-THC), cannabinol (CBN), and cannabinodiol (CBND) are known to be psychoactive (Figure 01). Because of that, Cannabis spp. plants and their derivative products are either regulated or banned in many countries. In some countries like Canada, cannabis has been made available for medicinal purposes since 1999.

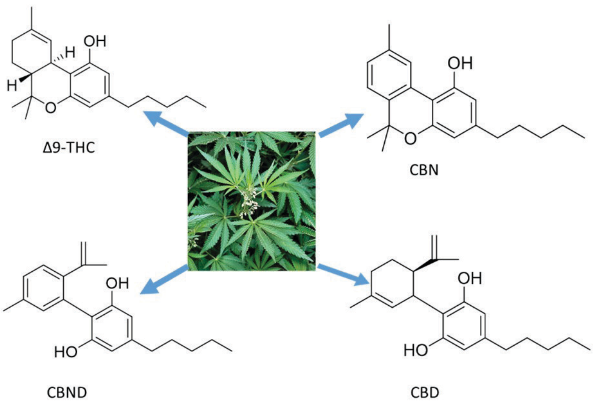

Figure 01: Chemical structures of psychoactive phytocannabinoids

Concentrations of all of these compounds may not even be at the detectable levels or may not be present in many commercial cannabis strains; hence, physiological significance of all of these compounds is irrelevant, except the ones that are present in detectable levels. Other cannabinoids such as cannabidiol (CBD) are nonpsychoactive compounds.

Cannabinoids exert their physiological effects through a variety of receptors including adrenergic receptors, cannabinoid receptors (CB1 and CB2), and a variety of other recently discovered G protein-coupled receptors (GPCRs) such as GPR55, GPR3, and GPR5. Patients consume medical cannabis, often with little medical evidence, for the treatment of or to seek relief from a variety of clinical conditions including pain, anxiety, epileptic seizures, nausea, appetite stimulation, and so on.

Cannabis-derived extracts (resins) are becoming commercially available popular products, and many of the patients prefer to use these extracts, as they do not involve smoking.

Phytocannabinoids in dried cannabis generally carry a carboxylic acid moiety and undergo spontaneous loss of this carboxyl moiety when subjected to high temperature (either direct sunlight, smoking, hot oven, and similar heat sources). Cannabinoid acids generally bind at the cannabinoid receptors, CB1 and CB2, with weaker affinity and exhibit weaker activity, but the corresponding decarboxylated phytocannabinoids exhibit higher potency at these receptors. Thus, dried cannabis in general is subjected to activation (*via* decarboxylation) prior to consumption by the patients for maximal *in vivo* efficacy.

Δ^9-THC characteristically produces, in a dose dependent manner, hypoactivity, hypothermia, spatial and verbal short-term memory impairment. But, CBD, does not affect locomotor activity, body temperature or memory on its own. However, higher doses of CBD can potentiate the lower doses of Δ^9-THC by enhancing the level of CB1R expression in the hippocampus and hypothalamus.[6] Literature depicts that the two main compounds, Δ^9-THC and CBD, whilst having similar effects in certain domains, also have almost opposite effects to one another in other aspects.[7]

Melissa et al. in 2017 has identified several phytocannabinoids extracted from dried cannabis using supercritical fluid extraction (SFE), which can be carried out at ambient temperature. They have identified several phytocannobinoids shown in figure 02.

As per their study, analysis of commercial medical cannabis extract in its native form and after subjecting it to heat to decarboxylate phytocannabinoids carboxylates into their active form, revealed 16 unique mass spectral signals representing upto 58 compounds in the decarboxylated cannabis extract, including various phytocannabinoids, flavonoids, terpenes, and miscellaneous compounds.[8]

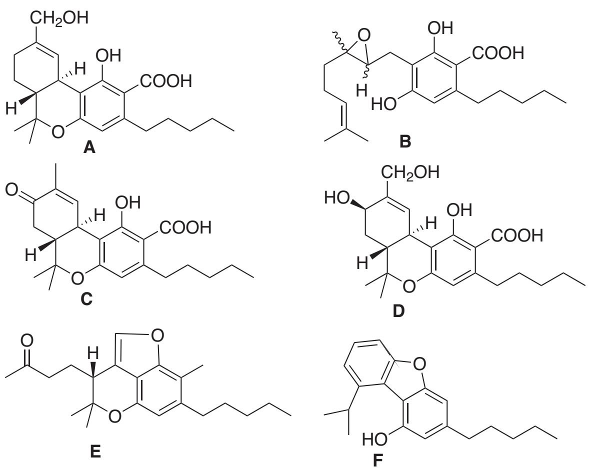

Figure 02: Chemical structures of the phytocannabinoids, (A) 11-hydroxy-Δ[9]-tetrahydrocannabinolic acid A, (B) (±)-6,7-*cis*/*trans*epoxycannabigerolic acid, (C) 8-keto-Δ[9]-tetrahydrocannabinolic acid A, (D) 8β,11-bis-hydroxy-Δ[9]-tetrahydrocannabinolic acid , (E) (−)-7R-cannabicourmaronic acid , and (F) cannabifuran.

Among these potential 58 compounds, up to 36 compounds are found to be in the native cannabis extract (prior to decarboxylation) as well, and did not change due to the decarboxylation process. The remaining 22 compounds in the decarboxylated cannabis extract were not present in the native cannabis extract (prior to decarboxylation), and admittedly, most of these new compounds are the decarboxylated forms of phytocannabinoid acids. The other categories of compounds in the activated cannabis extract includes sesquiterpene, β-caryophyllene oxide, and stearidonic acid. Two fatty acids, roughanic acid and α-linolenic acid, were observed in the native cannabis extract but were absent after subjecting the extract to heating for decarboxylation.[8]

When one correlates the above chemical changes, effect of controlled heating, changes in the chemical composition in addition to decarboxylated phytocannabinoids, and attempt to correlate the pharmacological effects, it is imperative to think that inconsistency in the extracts and decarboxylation could have profound effects for the patient. Furthermore, basic and clinical sciences supporting proper dosage forms yielding adequate pharmacological activity and outlining the potential adverse effects and risks of cannabis consumption, are also urgently needed; but these are immensely dependent on the chemical constituents of the extracts consumed by the patients. Healthcare practitioners would benefit from predictable dosing, a better understanding of the pharmacological activity and knowledge of the common adverse events. Given the inconsistency and misrepresentation of cannabis in the marketplace in general, new metered dosing modalities would be welcomed by healthcare practitioners and patients.

Relative to dried cannabis material, cannabis extracts and edibles pose a significant measurement challenge because of their high complexity and diversity. For instance, food products such as chocolate create difficulties with cannabinoid extraction due to the high fat content and also yield a multitude of interference peaks that can hinder accurate quantitation.

The White House recently completed its review of pending Food and Drug Administration (FDA) guidance on marijuana and CBD research—though it remains to be seen whether the draft document will ultimately be released to the public.[9] It is very important to develop guidelines for Sri Lankan researchers to carry on further studies under the guidance of government.

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Guest Articles

Chemical Constituents of Murunga Tree

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It is obvious to introduce ***Moringa oleifera*** (MO) or "Murunga" as the "**miracle tree**", since every part of it has a prodigious medicinal value. *Moringa* is a genus of medicinal plants that consists of 13 species. *Moringa* species show anti-inflammatory, anticancer, antioxidant, antidiabetic and antihyperglycemic properties; mainly owing to the high content of flavonoids, glucosides and glucosinolates. Traditional uses of MO are healing skin infections, anxiety, asthma, wounds, fever, diarrhea and sore throats.

MO is a fast-growing, slender trunked, deciduous plant native to tropical Asia but also naturalized in Africa and tropical America, with 10-12 m in height. It can be cultivated in any tropical or subtropical region of the world. People introduce MO as a "**never die tree**" because its uses seem to be endless and trees may survive despite high altitudes or very dry and arid deserts with annual rainfall less than 400 mm. This natural powerhouse can be used to achieve goals such as good health and well-being.

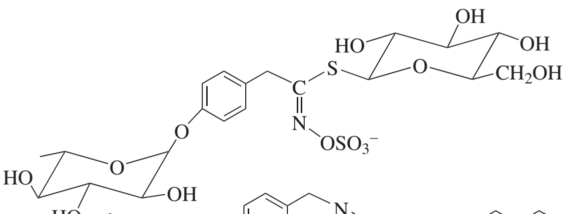
Chemicals present in *Moringa oleifera*

Phytochemicals are known as special chemical compounds, which are produced by plants through primary or secondary metabolic pathways. Phytochemicals (*e.g.* alkaloids, phytosterols, polyphenols, terpenoids *etc.*) play a vital role in improving the health due to their medicinal and pharmacological properties. Each part of this tree consists of a unique chemical composition; hence, the application of the plant component depends on the chemical nature of it. These compounds are mainly useful to build up a self-defense system against microorganisms and several diseases. Over 100 phytochemicals have been isolated from MO and some of them showed positive biological activities against various diseases.

Leaves

Most of the botanists and chemists pay more attention to carry out research on MO leaves relative to other parts because leaves are the centre of this powerhouse. Even though taste of the leaf is similar to spinach, MO leaves have more **iron** content than the same mass of spinach leaves; 7 times the **vitamin C** in orange, 4 times the **vitamin A** in carrots, 3 times the **potassium** in banana, 4 times the **calcium** in milk, and twice the **proteins** in yogurt. These leaves also contain other vitamins namely, B_1, B_2, B_3, D, E and K; minerals such as Cu, Zn, Fe, Mg, Ca and K; and **all essential amino acids**. High **selenium** content present in these leaves provides the successive way to work antioxidants and vitamins together.

Glucomoringin (GMG) or 4-(α-L-rhamnopyranosyloxy) benzyl glucosinolates (**1**) is the most abundant **glucosinolate** compound present in the leaves. Glucosinolates such as GMG derivatives react with **myrosinase enzyme** to form **isothiocyanates** (*e.g.* GMG-isothiocyanate or GMG-ITC (**2**)), which are very stable at room temperature compared to normal isothiocyanates. Hence, these compounds can be easily utilized as anticancer, antidiabetic, antimicrobial and anti-inflammation agents. **Nitrile glycosides** present in MO leaves are used as anti-hypertension drugs for pulmonary hypertension (*e.g.* **niazirin** (**3**), **niaziridin** (**4**)) and medicine for cancers.



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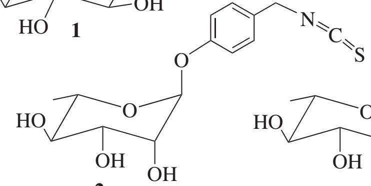

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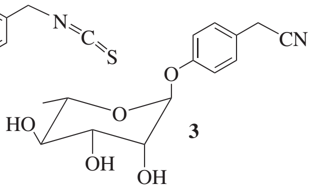

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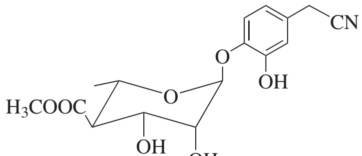

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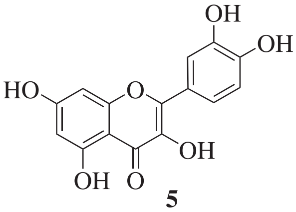
Flavonoids (*e.g.* **quercetin** (**5**), **kaempferol** (**6**), rutin, rhamnetin) play a vital role as antioxidants as they stabilize radicals produced in living cells. The concentrations of quercetin present in the leaves are as high as 100 mg/100 g, which is important to maintain the normal blood pressure.



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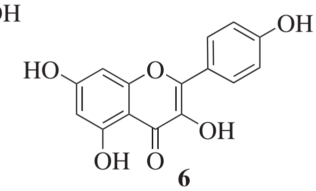

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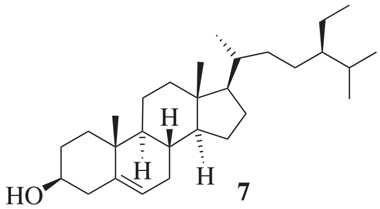
β-Sitosterol (**7**) (57%), **campesterol** (23%) and **stigmasterol** (8%) are the major phytosterols extracted from MO leaves.



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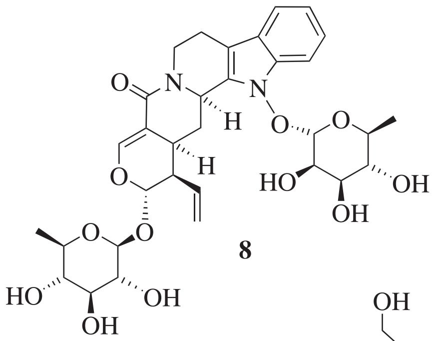
The bioactive alkaloids isolated from leaves include **vincosamide** (**8**), **marumoside-A** (**9**), **marumoside-B** (**10**) and a pyrrole-based derivative (**11**).



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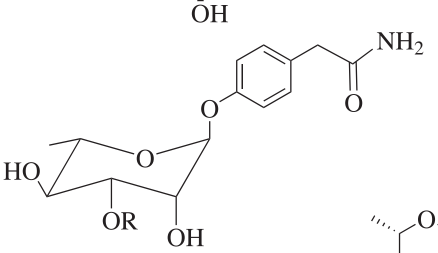
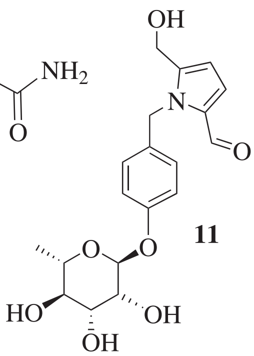


9 R = H
10 R = D-Glucose



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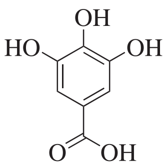
Phenolic acids are known to act as antioxidants. **Gallic acid** (**12**) is present in higher content in MO leaves. **Ellagic acid** (**13**), **ferulic acid** (**14**) and **caffeic acid** (**15**) are some of the other examples for phenolic acids.



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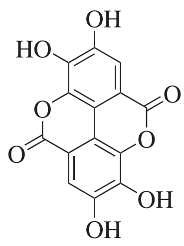

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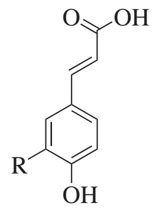
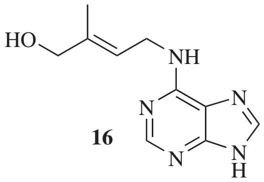


14 - R = OCH_3
15 - R = OH

Phytohormones are important to regulate the growth of plants. **Zeatin** (**16**) is an adenine based cytokinin hormone present in MO leaves. This substance is important in slowing down the aging process.



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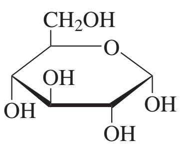
Although MO has the energy boosting ability, it does not contain caffeine. This property is empowered by NADH produced from niacin and vitamin B. Therefore, it increases the muscle, heart and brain functions. MO leaves act as a bio-cleaner in our body system by increasing the fecal excretion of cholesterol and flushing toxins from kidney.

Filipinos refer to MO as "**mother's best friend**" because its leaves increase the milk secretion in breast-feeding mothers.

Flowers

The flower of MO is yellowish white. It is bisexual and has a mild fragrant. This edible flower is composed of a remarkable content of **calcium** and **potassium**, as well as nine amino acids, sugars such as **D-glucose** (**17**), **sucrose** (**18**) *etc.*, waxes, and couple of flavanols (quercetin (**5**) and kaempferol (**6**)). It has a higher medicinal value and is used for curing inflammations, tumors, muscle pains, hysteria *etc.*



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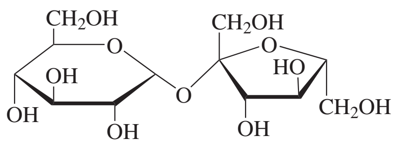

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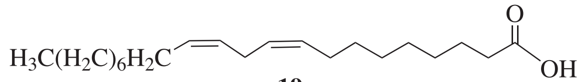
Pods

"**Drumstick**" is another name to introduce pods of MO due to its appearance. These edible pods are highly fibrous and mainly contain thiocarbamates, isothiocyanate glycosides and polyunsaturated fatty acids (PUFA) such as oleic acid, **linoleic acid** (**19**), palmitic acid and **linolenic acid** (**20**). Isothiocyanate glycosides help to maintain healthy blood sugar levels, while PUFAs elevate the healthy lipid level or HDL. **Arginine** and **histidine** are the amino acids present in pods.



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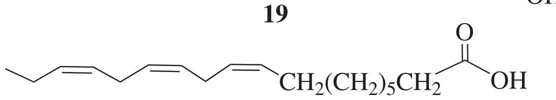

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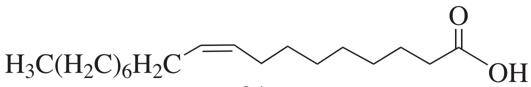
Seeds

"Ben oil" can be extracted from seeds and it contains fatty acids with sweet, non-sticking, non-drying and rancidity-resistant properties. This oil is composed of **oleic acid** (**21**) (major), **palmitic acid** (**22**), **stearic acid** (**23**) and **behenic acid** (**24**), hence it is used as a cooking oil and to produce cosmetic products such as perfumes, hair dressings and lubricants for machines.



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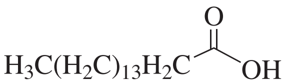

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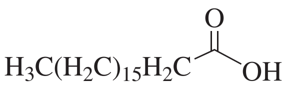

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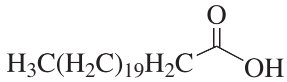

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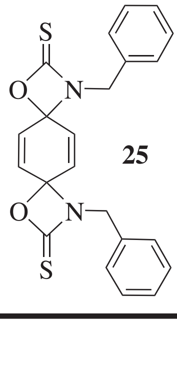
Pterygospermin (**25**) is a special compound present in the seeds, which has anti-microbial properties. Due to its disinfection nature, MO seeds are used in wastewater treatment processes, instead of Alum. These seeds act as bio sorbents; hence, they remove heavy metals such as Cu, As, Cr and Cd from water bodies.



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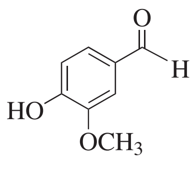
Most people consume MO seeds the same way as peas or roasted nuts since they contain high levels of vitamin C, moderate amounts of B vitamins, amino acids and dietary minerals. The presence of tannins, saponins, phenolics, phytates, flavonoids, terpenoids and lectins also play different favorable roles to improve the health of the body.

Root and stem

Root and stem are composed of a mixture of phytochemicals such as flavonoids, alkaloids, phytosterols, phytohormones, glucosinolates, waxes, resins and traces of essential oils with a pungent smell.

Root extract shows favorable impact on neuro-transmittance as well as sex-hormone related properties. Juice or extracts taken from MO root is a good medicine for asthma, liver and spleen expansion. At lower concentrations, it produces a dose-dependent positive inotropic effect, and at higher concentrations, produces a dose-dependent negative inotropic effect as a hypotensive toxin. Filipinos use the juice of scraped trunk to treat cuts in their skin.

Various sugars such as L-arabinose, L-galactose, L-rhamnose, L-mannose, L-xylose and L-mannose, and **vanillin** (**26**) are other compounds that can be found in the gum of the stem. The chemical composition in the bark of MO has antifungal and antibacterial properties.



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It is important to know how to consume these edible parts (leaves, flowers, seeds and pods) without destroying the nutritional value of them. For example, boiling of leaves can destroy the medicinal value of bioactive compounds. Doctors' advice is to consume leaf powder with hot liquid drinks. The recommended dosage for an adult per day is 3 g (*ca*. one teaspoon) of leaf powder or 1.5 g of seed powder or root powder. However, excessive use of these herbal parts can cause unknown side effects.

In conclusion, MO contains bioactive compounds. It is an excellent source of nutrients and used as a medicinal plant to cure wounds and various diseases, for purification of water, production of biodiesel and as a biopesticide. The leaf is the most widely used part of the plant and it is rich in vitamins, carotenoids, polyphenols, phenolic acids, flavonoids, glucosinolates, isothiocyanates, tannins, alkaloids and saponins.

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Young Scientists' Circle

Semiochemical approach to control Brinjal Fruit and Shoot Borer-*Leucinodes orbonalis* Guenee : A novel approach to global insect pest management

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Modern day, there are so many challenges for the farmers in agriculture including both biotic and abiotic stressors such as climate change, diseases and pest control. Brinjal plant (*Solanum melongena*) is an economically important plant grown in Asian countries. It contains various bioactive secondary metabolites which provide significant health benefits for the consumers.[1] In recent years, production of brinjal is under imminent threat due to the increased management cost of insect pest *Leucinodes orbonalis* Guenee- Brinjal Fruit and Shoot Borer (BFSB), which is considered to be the key insect pest that attacks brinjal plant. At present, farmers are completely dependent on chemical insecticides to control this pest and attempt to produce damage-free marketable brinjals.[2] Insects such as BFSB, which has extremely diverse adaptations such as hidden and protected lifestyles in adult stage and concealed habits in the larval stage cannot be easily controlled with cover sprays of insecticides. Indiscriminate use of synthetic chemicals causes many unwarranted problems.[3] Therefore, there is an urgent need to develop an environmentally friendly method that can be used to control the BFSB in brinjal plant. Crop protection through semiochemical approach has gained wide popularity in the present-day demand for safe, pesticide-free products. Semiochemicals are considered as safe and eco-friendly molecules due to their natural origin and low persistency in the environment. Contrary to chemical insecticides, insects find it difficult to develop resistance against volatile semiochemicals as semiochemicals work by a non-toxic mode of action through modifying the insect pest's behavior.[4] Semiochemicals are defined as chemicals that are emitted by living organisms which could induce a behavioral or physiological response in other individuals. Semiochemical communication is divided into two broader classes: (a) pheromones mediated intraspecific communication which occurs between individuals of the same species (b) allelochemicals mediated interspecific communication which occurs among individuals of different species.[5]

Previous studies reported that female BFSB produced sex pheromone-baited traps attracted the male insects of BFSB in the field and achieved significant reduction in the pest population.[6] There is evidence suggesting that ecological interaction, especially odours between insect pest and their host will aid in the development of most effective insect pest control strategies.[7] Plants synthesize and emit a wide range of volatile organic compounds which act as chemical signals and produce a wide range of behavioral responses in insects. Some studies reported that the behaviour of the larvae or adult or both stages of the insects can be influenced by plant volatiles.[8] Further, a large number of attractive volatile organic compounds released by plants can pose a challenge for herbivore insects to navigate towards their host plants. Therefore, the relationship between the insect pests and volatile semiochemicals of the host plants have been studied well and recognized as an important communication system within insect species, which can modify the insects' behavior.[9] In some plants, these volatile organic compounds are the key compounds that are involved in the attraction of insect pests. In addition, the synergism between insect pheromones and plant volatiles can increase the attraction of insect pest, offering new strategies for the development of more effective and reliable pest control programs. Volatile mediated foraging behavior is important in insect pests when they target host plants. In my research, we combined both sex pheromone from the insect pest and the volatiles from the host plant to synergize the *L. orbonalis*' attraction to the sex pheromone. No research has described the *L. orbonalis*' response to host plant volatiles. Our goal was to improve a trap catch of the adult *L. orbonalis* by using host plant volatiles with the combination of pheromone as a new formulation.

Initially, samples of brinjal plant ("Lena iri" variety) leaves, shoots, fruits and flowers were collected separately from an unsprayed brinjal field at Agriculture Research Station, Kandakuliya, Kalpitiya. Insects were rare at the laboratory using infested brinjal fruits collected from the market. Host plant volatiles from the different parts of brinjal plant were collected using steam distillation method and insects' volatiles were captured on Super Q. We evaluated the effects of host plant volatiles obtained from different parts of brinjal plant on the behavioral responses of adult *L. orbonalis* males, virgin females and gravid females separately in the absence of visual cues or pheromone signals using two-choice and multiple-choice bioassay methods. Further, we identified the male *L. orbonalis* attraction to the female produced sex pheromone blend. Subsequently, we evaluated the synergism between the host plant volatiles and the sex pheromone in the attraction of *L. orbonalis* males in laboratory level. Furthermore, we analyzed the volatile chemical constituents present in different parts of the host plant brinjal as well as in the sex pheromone extracted from the virgin females using GC-FID and GC-MS. Finally, we conducted a green-house assay to show the synergism between the host plant volatiles and sex pheromone in the attraction of *L. orbonalis*. The simple water bottle trap was used to catch the insects in our greenhouse experiments. Sex pheromone was used alone and in combination with host plant volatiles for possible enhancement of attraction.

The present bioassay guided study conducted in a short-range Y-shaped olfactometer revealed that adult male and female insects were attracted to the volatiles of brinjal fruits, leaves and shoots but not for the volatiles from flowers. *L. orbonalis* feed primarily and oviposit solely on shoots and leaves. Therefore, it is possible that the attractive compounds present in the leaf and shoot are absent from flowers, alternatively, the amount of volatiles being released from the flowers may have been below the behavioral threshold for response. Gravid female insects are highly attracted to the host plant volatiles than virgin female and male insects. The multiple-choice bioassay revealed that all three types of adult insects are highly attracted to the volatiles from fruits. This study reports for the first time the entire volatile profile of different parts of the brinjal plant. GC-MS analysis of plant volatiles showed that the volatile compounds belonging to different classes of organic compounds: hydrocarbons, green leaf volatiles (aldehydes, esters), alcohols, fatty acids and other volatiles. Chemical investigation of the pheromone emitted by adult females revealed the presence of (E)-11-hexadecenyl acetate as major compound while tracer amounts of (E)-11-hexadecen-1-ol; which attracted the adult male insects. Further, two-choice olfactometer experiments showed that all three types of volatiles from the host plant increased the attraction of male insects to the sex pheromone blend. In addition, the volatiles from brinjal fruits significantly increased the male attraction to the pheromone blend. Preliminary green-house experiments using host plant volatiles and sex pheromone blends as lure incorporated in a water bottle trap identified that the host plant volatiles individually not effective as field attractants while the combination of pheromone showed high activity in the greenhouse experiments. Combination of sex pheromone and host plant fruit volatile blend successfully lured male insects as well as female insects to this trap. This could be explained in terms of synergetic action of the above attractants. This study revealed that the chemical investigation of female produced sex pheromones of *L. orbonalis* and entire volatile chemical profile of various parts from the host plant brinjal.

The present study has led to identify an ecologically friendly control system for the brinjal fruit and shoot borer; *L. orbonalis*. Although this is a preliminary study, our result supports the idea that the interaction between host plant volatiles and insect pest should receive more attention. Results of this study will be helpful in designing research studies to develop integrated pest management due to the impact of these host plant volatiles on insect pests. Additionally, further studies need to be conducted to elucidate the synergism between insect pheromones and host plant odours in natural field conditions to increase the attraction of insect pest and it would offer new strategies for biological control of this insect pest. New research in this area will shed light on this and other issues relevant to the development of eco-friendly trapping systems for the monitoring and management of *L. orbonalis*.

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Young Scientists' Circle

Unraveling the bioactivity of peptide-based nano systems in tumourgenesis

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Antimicrobial peptides (AMPs) are known as natural antibiotics produced by animals, plants, and bacteria. Even though AMPs have been identified as the most promising alternative to conventional molecules used against infections, some of them may have other activities such as defense mechanisms, or even regenerative. Moreover, the reported studies show the broad spectrum of cytotoxic activity against various types of cancer cells by these peptides. When considering the cell targets, some peptides active against microbial and cancer cells while not being active against healthy mammalian cells, such as magainins.[1] Some are active against all three types of cells including microbial, normal, and cancerous such as human neutrophil defensins HNP-1.[2] Although ACPs are expected to be selective toward tumor cells without impairing the normal cells, the development of a selective ACP has been regarded as a therapeutic strategy to explore.

From a structural point of view, the peptide with anti-cancer activities (ACPs) contain 5–50 amino acid chains and are generally composed of α-helices, β-sheets, or both.[3] Concerning the ACPs anticancer effects, it may generally occur by membranolytic mechanisms.[4] The anticancer activity is dependent on the peptide amphipathicity, hydrophobicity, as well as on the target membrane features such as protein receptors,[5] which in turn modulate the peptides' selectivity and toxicity.

However, the use of peptides as therapeutics has been limited by low bioavailability, poor stability to proteolytic degradation, low permeability across barriers, and short biologic half-life in the circulatory system. Encapsulation of these peptides on nanocarriers may improve the potential of these therapeutic molecules to create a novel environment for therapeutics, disease diagnosis, fluorescent microscopy, imaging, and other life science devices.

Peptide nanotherapeutics have been reported useful tools in targeting and deliver the drug *in situ* to selectively target cancer cells, decreasing toxicity on healthy cells. Nanoparticles (NPs) offer the possibility to encapsulate poorly soluble anticancer drugs, enhance the stability of therapeutic molecules, and modify their blood circulation. The present study was focused to develop and characterize an *in vitro* sustained release formulation for peptide-based drugs using nanomaterials. The study focused to optimize a nanohybrid for a peptide.

In this study, a naturally derived 6-mer peptide was synthesized by the Solid Phase Peptide Synthesis (SPPS) method and characterized using nuclear magnetic resonance spectroscopy (NMR) and mass spectrometry (MS). The synthesized peptide was screened for *in vitro* cytotoxicity against Muscle rhabdomyosarcoma (RD) and Kidney normal (Vero) cell lines using 3, 4, 5-(dimethylthiazol-2-yl)-2-5-diphenyl tetrazolium bromide (MTT) cell viability assay. The native peptide effectively inhibited the survival of the rhabdomyosarcoma cell line in a dose-dependent manner with less cytotoxicity effect on a normal healthy cell line.

Furthermore, the undergoing molecular mechanism was studied using computational approaches. The *in silico* study revealed that the tumor inhibition by the peptide involves inhibition of an intracellular molecular pathway known as the serine/threonine kinase Akt signaling pathway, which is hyperactivated in rhabdomyosarcoma. The present study used docking and (un)binding simulation analyses to identify peptide interacting residues of the human target protein. The results proved that peptide is an allosteric inhibitor of the respective protein and exerts its inhibitory mechanism by binding to the allosteric site of the protein and engaging the functionally important residues in various interactions. The exact binding mode of the peptide-based on the computational approach is presented and various interacting residues within the allosteric site of this protein were identified and characterized. The docked peptide-protein conformation is expected to serve as a suitable model for understanding the amino-acid environment mediating molecular interactions and thus, providing details for the inhibitory mechanism of the peptide. In the future, this study will help to design novel peptidomimetics for human target protein isoforms and it will help experimental biologists in testing and designing better inhibitors.

In addition to the cytotoxicity and undergoing inhibitory mechanism of the peptide, we proved that it could increase the efficacy of the peptide against RD cells when it is encapsulated with drug carriers such as functionalized HNT (fHNT). The induced cytotoxicity effect permits the use of relatively low concentrations of peptides and drugs to achieve significant anticancer effects *in vitro*. This dose reduction minimizes drug side effects on normal cells and enables an effective apoptosis-mediated anticancer effect. Our present study has implications in that the peptide may become a promising anticancer therapeutic agent with high anticancer selectivity and a strong induced effect in combination therapy. Our studies mainly illustrate the mechanism of peptide-induced cell death and may be helpful in the design of chemotherapeutics against RMS cell lines.

In the future, the bioavailability of the peptide after release from fHNT composites can be confirmed by *in vitro* studies using kinetic assays. The research can be taken further to the next level with *in vivo* studies on different animal models. Further, the tubular ends and surface of drug-loaded fHNT can be modified with pH-sensitive polymers, followed by the preparation of oral tablets for gastrointestinal drug delivery.[6,7] Such aminosilane functionalized nanomaterials have been used in some previous studies, and they displayed no toxicity upon oral consumption.[7] These milestones by aminosilane modified nanomaterials indicate the promising usage of the peptide-loaded fHNT.

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Young Scientists' Circle

In Silico Study of potential drug leads for inhibition of angioensin converting enzyme using Sri Lankan Natural Products

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Almost fifty percent of the active ingredients present in modern medicine is derived from natural products. Natural products were widely used in the past for drug discovery before high-throughput screening and genomic sequencing were practiced. These natural product-based drugs are mostly derived from different organisms, such as plants, microbes and animals as well as a few synthetic or semi-synthetic compounds that are derived from natural products, including tigecycline, everolimus, micafungin and caspofungin.[1] These natural product-based drugs have been used for a range of medicinal indications and they have a wide diversity of chemical structures. Approximately half (49%) of the 877 small-molecule New Chemical Entities (NCEs) introduced between 1981 and 2002 were natural products, semi-synthetic natural product analogues or synthetic compounds based on pharmacophores of natural products.[2]

Studies show that natural products usually have a higher number of chiral centers than either synthetic drugs or compounds derived from combinatorial libraries, and they have increased steric complexity. While a slightly higher number of nitrogen-, sulphur- and halogen-containing groups appear to be present in drugs and combinatorial molecules, natural products on the other hand, carry a higher number of oxygen atoms[3]. Multivariate statistical study of molecular descriptors shows that the ratio of aromatic ring atoms to total heavy atoms (lower in natural products), the number of solved hydrogen bond donors and acceptors (higher in natural products) and higher molecular rigidity of hydrogen bond donors and acceptors (higher in natural products) differ significantly from synthetic drugs and combinatorial libraries in natural products.[4] Scientific publications on compounds extracted from Sri Lankan medicinal plants during the period of 1970-2014 were analyzed, and about 480 compounds published within this period were selected for virtual screening.

Angiotensin Converting Enzyme (ACE) was chosen as our protein of interest. It plays a major role in the management of blood pressure, cardiovascular function and diabetic kidney disease. In most tissues of the body, ACE is always expressed. However, a high level of expression is found in the lungs, kidneys, testes, duodenum, choroid plexus and placenta. Since ACE is expressed in multiple cell types, it cleaves different substrates, such as endothelial cells, renal tubular epithelial cells, gut epithelial cells and myeloid-derived cells. ACE is best characterized by its function in the cleavage of two carboxy-terminal (C-terminal) amino acids of angiotensin I, thereby generating angiotensin II, a vasoconstrictor. ACE also cleaves bradykinin, a vasodilator, releasing an inactive product of 7-amino acids. The enzyme can cleave substrates as small as 3 amino acids and as large as 42 amino acids, but most ACE substrates are only 15 amino acids in size or less.[5]

The human ACE has two functional domains N and C, each of which has a zinc-ion binding site at its active site. In their substrate specificities, physiological forms, and inhibitors, the N and C domains have several variations. On the one side, the hydrolysis of substrates with similar efficiencies is catalysed by the N and C domains.[6] However, inhibition of the N domain of ACE has been reported to have no effect on blood pressure regulation. It was found that targeting the C domain was adequate for blood pressure regulation, and hence, all inhibitors target this site. An important catalytic component of ACE is zinc. As shown in Fig 1, alpha13 has two histidine (His383 and His387) zinc-binding motifs coordinated with a Zn^{2+} ion. ACE has many substrates and can also be used as a neurotensin. The half-life of bradykinin is extended by ACE inhibition and can lead to accumulation and activity. Angiotensin-converting inhibitory enzyme drugs have for decades been first-class therapeutics.[7] Captopril, lisinopril, enalapril, and ramipril are examples of drugs that are ACE inhibitors. Adverse side effects such as dizziness, coughing, and angioneurotic edema may, however, be caused by prolonged use of these drugs. New alternatives have been widely investigated as substitutes for ACE inhibitors. The main focus of this study is on bioactive compounds obtained from Sri Lankan natural products.

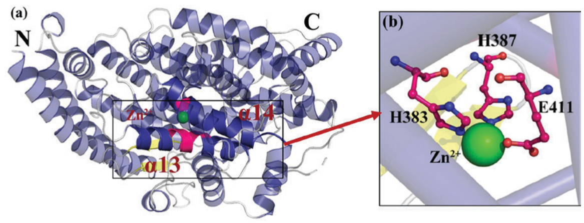

Figure 1: Active sites of angiotensin-converting enzyme; (a) Organization of the ACE protein. The active sites located in α13 and α14 of ACE are indicated by a black rectangle. (b) Zinc-binding motif; The residues that surround Zn^{2+} are represented by pink sticks.

To classify the possible targets for different ligands, computational and bioinformatics tools have become very important resources. Modern drug research and development (R&D) relies on the discovery of low-molecular weight compounds that interact with disease-related biological macromolecules, known as receptors or molecular targets, in a selective way. The use of structural information of molecular targets to improve aspects related to ligand binding is a core approach in the pharmaceutical industry, and it is commonly known as structure-based drug design (SBDD).[8] Methodologies for SBDD play a growing role in the development of drugs, and are important for the cost-effective identification of promising drug candidates. These computational methods of analysis are important in restricting the use of animal models in pharmacological study, they support the rational design of novel and potent drug candidates and in the repositioning of marketed medicines, and provide invaluable support for medicinal chemists and pharmacologists throughout the process of drug development. Lately, increasing attention has been paid to the concept of using direct or indirect structural knowledge on specific antitargets to enhance ligand selectivity and minimize off-target interactions, leading to increased protection and even improved pharmacokinetic profiles. *In silico* screening, which is generally combined with drug design, typically relies on exploration of the established chemical universe for the identification of new active motifs.[8] The objective of virtual screening is to uncover an unexplained or concealed interaction between known chemicals and a given biological activity, and not in the chemistry of the emerging hits as this information is most likely available. Advances in SBDD over the past two decades have been achieved by the integration of spectroscopic data and other methods. These include X-ray crystallography, and in silico techniques such as molecular dynamics, homology modeling and molecular docking. The combined use of these methodologies has made it possible to determine the 3D structures of many biological macromolecules along with the precise characterization of their binding site features, such as steric and electrostatic properties. The understanding of ligand-receptor molecular recognition phenomena has been extremely useful. SBDD has successfully assisted the development of pioneering treatments for highly complex and prevalent disorders by combining these data with current technologies in pharmaceutical R&D.

The use of SBDD strategies enables the conception of ligands with specific steric and electrostatic properties that will effectively interact with a target pharmacological receptor. SBDD consists of a cyclic process that begins with the resolution of the 3D structure of the molecular target, in this case angiotensin converting enzyme.[9] The x-ray crystallographic 3D structure can be found on the RCSB protein databank. Each PDB entry contains information on experimental details, related literature, the biological relevance of the macromolecule, and statistical indicators on the quality of the 3D model. Next, molecular modeling investigations are performed to find putative ligands. Molecular docking is prominently used for structure-based virtual screening. The binding event is simulated, and a scoring function is used to predict, for the most probable binding poses, the free energy difference due to the binding of the screened compounds to the target starting from the experimental structure of the target. A homolog from other organisms or another protein belonging to the same family may be used if the structural information of the desired protein is not available, and this is referred to as comparative or homology modeling. Both rigid and flexible approximations are possible. Though the rigid approach is computationally less demanding, the more accurate flexible approximation is computationally challenging. Molecular docking, compared to ligand-based approaches, can be considered a computationally demanding virtual screening approach. To produce a variety of ligand-binding orientations which are rigid body approximations, a search/sampling algorithm is used.

There are currently various software programs and instruments available for use at each point of the molecular docking process. Of all the molecular docking software currently available, AutoDock Vina[10] is one of the most cited software. An effective stochastic conformational search algorithm, and precise and well-rated force-field and empirical scoring functions are combined in AutoDock Vina[10]. Moreover, AutoDock Vina[10] has the capability to combine its productivity and competency in order to produce parallel computational results with a low computational cost. This makes AutoDock Vina[10] an ideal tool for structure based virtual screening against large compound libraries. Free-energy simulations, which employ molecular dynamics or Monte Carlo simulations, provide a more rigorous solution to binding free-energy estimation. Molecular dynamics (MD) simulations can be used to explore the dynamics of the target protein. This method has become popular for studying protein structures and in extracting conformational ensembles of these targets. These simulations can be carried out in the context of the solvent, ions, and various physiological parameters. In this way, one will not only able to identify and understand the flexibility of a given binding site but will be also able to explore its interaction with water molecules and ions.[11] Moreover, by analyzing the MD trajectory, one can also measure the persistence of the binding site, duration of the hydrogen bonds, and varying depth and width of the binding site.

In this study, promising compounds that are identified by in silico studies are thereafter commercially purchased or synthesized, and evaluated for potency, affinity, and selectivity against the receptor, ACE. Once active molecules are identified by wet studies, the 3D structure of the ligand–receptor complex is determined, enabling the identification of the intermolecular interactions that drive the molecular recognition process. Additionally, determining the structure of the ligand–receptor complex enables the construction of relationships between biological activity and structural features. Finally, taking these results into account, molecular optimization efforts may be conducted to improve the ligand properties, mainly those related to affinity, selectivity, and efficiency.

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Metal Hydrides

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We know that main group hydrides such as $LiAlH_4$ and $NaBH_4$ are the common reducing agents used by organic chemists to reduce aldehydes, ketones and carboxylic acids. Transition metal hydrides act as good catalysts for hydrogenation, isomerization, hydroformylation and hydrocyanation of olefins. The coordination modes of the hydride ligand are as follows.

(i) **Terminal** (M-H) - *e.g.* $K_2[ReH_9]$, $[CoH(CO)_4]$, *trans* $[PtHCl(PEt_3)_2]$.

(ii) **Doubly bridging** (M-H-M) or (μ_2-H) - *e.g.* $[(OC)_5W(\mu\text{-}H)W(CO)_5]^-$.

(iii) **Triply bridging** (μ_3-H) - It bridges three metals or one triangular face of the tetrahedral metal cluster, *e.g.* $[Re_4(CO)_{12}(\mu_3\text{-}H)_4]^-$.

(iv) **Interstitial** - The H atom is placed at the centre of the metal cluster, *e.g.* octahedral complex ion, $[HCo_6(CO)_{15}]^-$.

Polyhydrides

Transition metal hydrides containing three or more hydride ligands per metal atom are called multihydrides or polyhydrides. Some examples include $[WH_6(PR_3)_3]$, $K_2[ReH_9]$, $[ReH_5(PR_3)_3]$, $[ReH_7(PR_3)_2]$, $[OsH_4(PR_3)_3]$, and $[IrH_3(PR_3)_3]$. The presence of phosphine or cyclopentadienyl (Cp) ligands tend to stabilize these 18e-complexes. Most of the polyhydrides are fluxional at room temperature.

Properties of metal hydrides

- A metal hydride can be a H^+ donor to a base, H atom ($H^·$) donor to an olefin, and H^- donor to a cation.
- Acidity of a metal hydride depends upon the other co-ligands. $[HCo(CO)_4]$ is a strong acid with a pK_a value of zero.
- A metal hydride exerts a strong *trans*-effect on the opposite ligand (L) and weakens the M—L bond, *i.e.* it labilises the *trans*-ligand.
- The proton chemical shift (δ_H) of a metal hydride appears in the range of 0 to -25 ppm with respect to TMS. For example, the chemical shift (δ_H) of the hydride ligand of $[HW(Cp)(CO)_3]$, $[HMn(CO)_5]$, $[H_2Fe(CO)_4]$ and $[HCo(CO)_4]$ are -7.5, -7.5, -11.2 and -10.7, respectively.
- The IR absorption frequency of the M—H bond, ν(M—H), appears in the region of 1500-2200 cm^{-1}; it can be identified by converting it into a M—D group with D_2O. $\nu(M—D) = \nu(M—H) \div \sqrt{2}$

Synthesis of metal hydrides

Metal hydrides can be synthesized in various methods.

Using a hydride source – In order to form a stable metal hydride, stabilizing ligands such as PR_3, CO and Cp^- groups are generally added. L = PPh_3

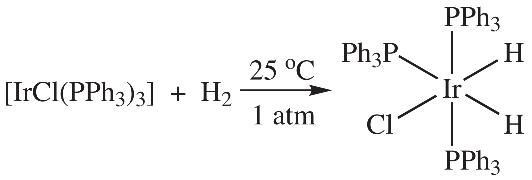
$$WCl_6 + NaBH_4 + NaCp \rightarrow [Cp_2WH_2]$$
$$WCl_6 + Li[BEt_3H] + L \rightarrow [WH_6L_3]$$
$$[RhCl(CO)L_2] + NaBH_4 + L \rightarrow [RhH(CO)L_3]$$

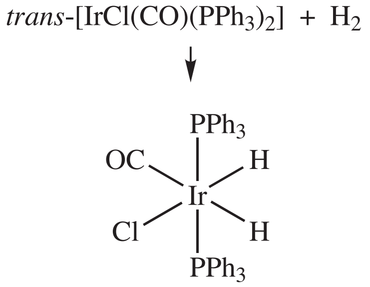
By protonation with acids - Basic metal centres and metal centres bonded with good electron donating ligands can be easily protonated with acids. Anionic complexes give neutral metal hydrides, while neutral complexes often yield cationic hydrides.

$$[Fe(CO)_4]^{2-} \xrightarrow{H^+} [HFe(CO)_4]^- \xrightarrow{H^+} [H_2Fe(CO)_4]$$
$$[Cp_2MoH_2] + H^+ \rightarrow [Cp_2MoH_3]^+$$
$$[Fe(CO)_3(PPh_3)_2] + H_2SO_4 \rightarrow [FeH(CO)_3(PPh_3)_2]^+$$
$$[CpCo(PMe_3)_2] + NH_4PF_6 \rightarrow [CpCoH(PMe_3)_2]PF_6$$

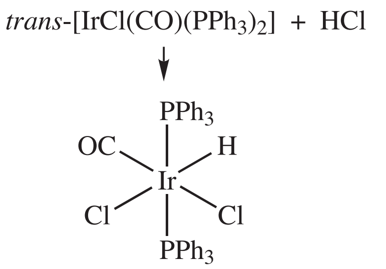
By oxidative addition of H_2 or HY - (Y= X, -CN, $-SiR_3$, $-B(OR)_2$, $-NR_2$, -SR group)

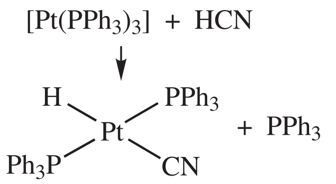
Addition of H_2 gives *cis*-dihydrides.



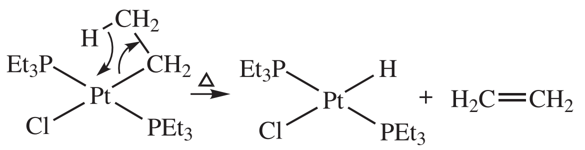


The HY addition gives *trans*-products.





By β-hydride abstraction - Metal alkyls give metal hydrides and olefins, *e.g.*

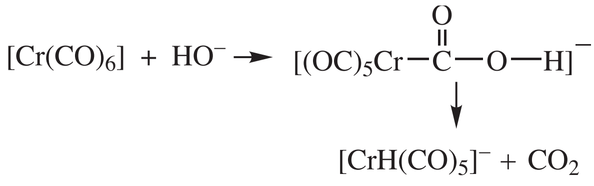


Metal alkoxides give metal hydrides with a loss of a ketone or aldehyde.

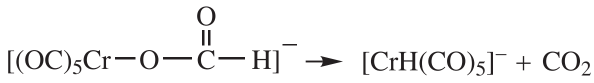
$$[RuCl_2(PPh_3)_3] + 2\,KOCHMe_2 + PPh_3 \downarrow [RuH_2(PPh_3)_4] + 2\,Me_2C{=}O + 2\,KCl$$

$$[K_2IrCl_6] + HOCD_2Me + \text{excess } PPh_3 \downarrow [IrDCl_2(PPh_3)_3] + MeC({=}O)D$$

By reacting metal carbonyls with HO^- - Initially formed hydroxycarbonyl group loses CO_2 molecule to give the metal hydride.



Metal formate loses a CO_2 molecule to give the metal hydride.



General reactions of metal hydrides

Metal hydrides undergo deprotonation ($-H^+$), dehydrohalogenation (-HX), migratory insertion reactions with olefins, and protonation ($+H^+$) as given below.

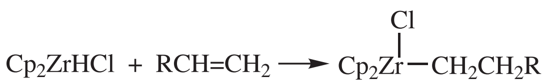
1. *Deprotonation and dehydrohalogenation*
   A metal hydride can be deprotonated by a base such as Et_3N, Bu_3N, pyridine and sodium ethoxide.

$$[IrHCl_2(CO)(PPh_3)_2] + \text{base} \downarrow trans\text{-}[IrCl(CO)(PPh_3)_2] + \text{base}\bullet HCl$$

   A base can be used to dehydrohalogenate a halogenohydride.

$$[Cp_2MoH_3]^+ + \text{base} \downarrow [Cp_2MoH_2] + \text{base}\bullet H^+$$

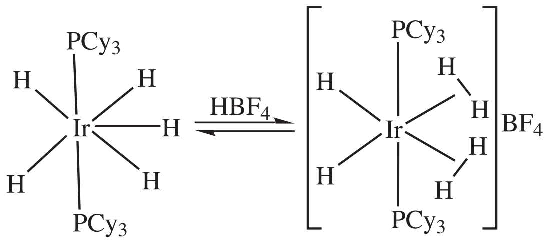
2. *Migratory Insertion*
   Hydride can migratory insert into an unsaturated molecule (*i.e.* the reverse of β-hydride abstraction and elimination of an olefin). For example,



3. *Hydrogen atom donation* - The Co(III) complex $[CoH(CN)_5]^{3-}$ transfers a hydrogen atom ($H^\cdot$) to the activated double bond of cinnamic acid giving the 17e complex $[^\cdot Co(CN)_5]^{3-}$.

$$[CoH(CN)_5]^{3-} + PhCH{=}CHCO_2H \downarrow [\dot{C}o(CN)_5]^{3-} + [Ph\dot{C}HCH_2CO_2H]$$

4. *Preparation of dihydrogen complexes* - HBF_4 reversibly protonates $[IrH_5(PCy_3)_2]$ to give $[IrH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]BF_4$.



Problems

1. Suggest the product(s) formed from the following reactions.

(i) $[(\eta^5\text{-}C_5Me_5)ZrHCl] + HC\equiv CH \rightarrow$

(ii) $[(\eta^5\text{-}C_5Me_5)WH(CO)_3] + HBF_4 \rightarrow$

(iii) $[Fe(CO)_5] + KOH \rightarrow$

(iv) $[RhEt(CO)_3] \rightarrow$ (heat)

(v) $[Co_2(CO)_8] + H_2 \rightarrow$

(vi) $[(\eta^5\text{-}Cp)Co(PMe_3)_2] + HBF_4 \rightarrow$

2. $[(PhCH_2CH_2)Pt(OCH_2CH_3)(dppe)]$ gives an alkane (**A**), alkene (**B**), alcohol (**C**) and aldehyde (**D**) when it is heated in toluene at 100 °C. Identify (**A**), (**B**), (**C**) and (**D**). dppe = $Ph_2PCH_2CH_2PPh_2$ is a bidentate ligand.

Student Corner

Hydrogenation of olefins

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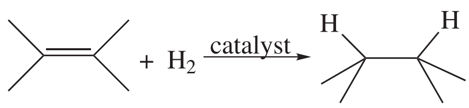
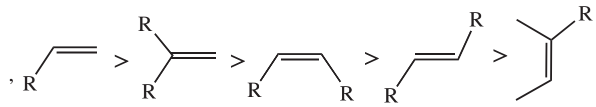
Hydrogenation of olefins is one of the simplest reactions, where two hydrogen atoms add across a carbon-carbon double bond to give an alkane.



The ease of this reaction decreases with the increasing steric hindrance at the olefin as shown below.



Heterogeneous hydrogenation catalysts

They are present in a phase different from that of the reactants. Here, the reaction takes place at the surface of an insoluble solid catalyst. Some examples are 1% platinum on activated carbon or alumina, 5% ruthenium on activated carbon, and Raney nickel. When homogeneous catalysts are chemically attached to a solid surface, they are called heterogenized homogeneous catalysts.

Homogeneous hydrogenation catalysts

The activity of homogeneous catalysts can be adjusted by changing the type and size of the ligands around the metal. Some simple homogeneous hydrogenation catalysts or precursors include: $[M_2(cod)_2Cl_2]$ (M = Rh, Ir), $[Ir(cod)(pyridine)(PPh_3)]PF_6$, $[RhClL_3]$, $[RuHClL_3]$ and $[RhH(CO)L_3]$, where L = PPh_3 and cod = cyclooctadiene.

Asymmetric hydrogenation can be achieved by using chiral ligands such as DIOP, binaphthyl (BINAP), ferrocenyl (PPFA), phosphinooxazoline (PHOX) ligands *etc*. Some commercial processes of asymmetric hydrogenation are the synthesis of (i) L-Dopa (dihydroxy phenylalanine), used in the treatment of Parkinson's disease; (ii) the pain reliever Naproxen; (iii) N-acetyl L phenylalanine, the synthetic precursor to the sweetener aspartame *etc*.

Sources of hydrogen

Hydrogenation is one of the most extensively studied reactions using homogeneous catalysts. Dihydrogen (H_2), BH_4^-, HX and HCO_2H are the sources of hydrogen. Here, we will consider reduction reactions of olefins with **dihydrogen** in the presence of a suitable catalyst.

Dihydrogen can be activated *via* three methods. They are, (i) **oxidative addition** (ii) **heterolytic activation** & (iii) **homolytic activation**. General reactions for these methods (i), (ii) and (iii) are given below. You should be able to determine the change in oxidation state of M; B is an external base and X is an internal monoanionic ligand.

$$\text{(i)}\quad L_nM + H_2 \longrightarrow L_nM(H){-}H$$

$$\text{(ii)}\quad \text{(a)}\ L_nM + H_2 + B \rightleftharpoons L_nM{-}H + HB^+$$

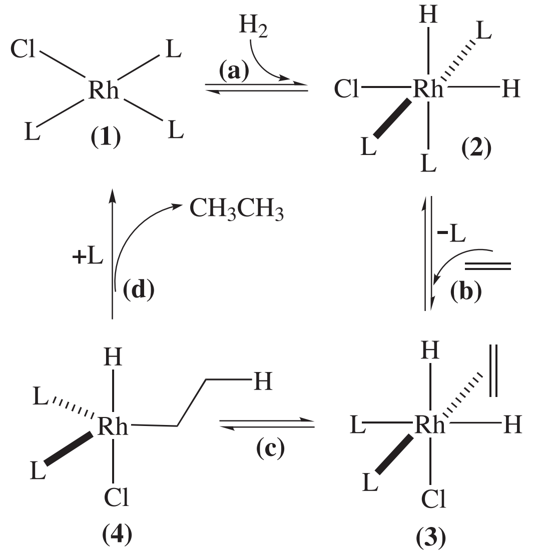
$$\text{(b)}\ L_nM{-}X + H_2 \rightleftharpoons L_nM{-}H + HX$$

$$\text{(iii)}\quad 2\,[L_nM] + H_2 \longrightarrow 2\,[L_nMH]$$

In ii(b), the heterolytic activation of H_2 occurs in a single step without oxidising the metal. One can argue that this process involves oxidative addition of H_2 followed by the reductive elimination of HX.

Hydrogenation *via* oxidative addition

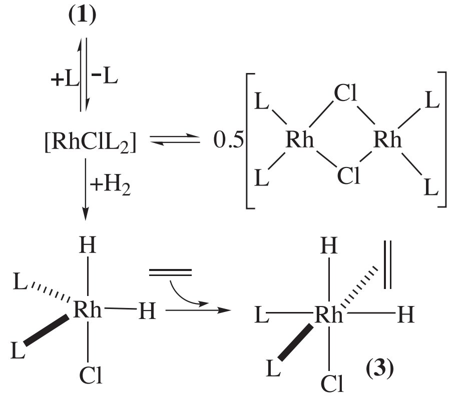
Hydrogenation of an olefin using the well-known 'Wilkinson's catalyst' $[RhCl(PPh_3)_3]$ proceeds *via* this route as shown in scheme 1. (L = PPh_3)



Scheme 1 A possible mechanism for the hydrogenation of ethene by $[RhCl(PPh_3)_3]$. Note that other mechanisms/ pathways exist.

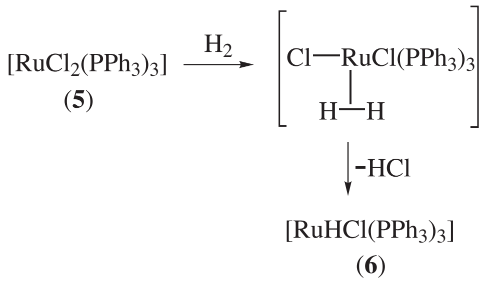
It is believed that the initial *cis* addition of H_2 to the Rh(I) centre (**step-a**) gives the Rh(III)-dihydride (**2**). Dissociation of PPh_3 and coordination of ethene (**step b**) gives (**3**). Insertion of ethene (**step c**) gives the alkyl derivative (**4**). Irreversible reductive elimination of ethane and coordination of PPh_3 (**step-d**) regenerates the catalyst (**1**).

Generation of other intermediates such as $[RhCl(PPh_3)_2]$, the dimer $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ and $[RhH_2Cl(PPh_3)_2]$ are also possible as shown below.



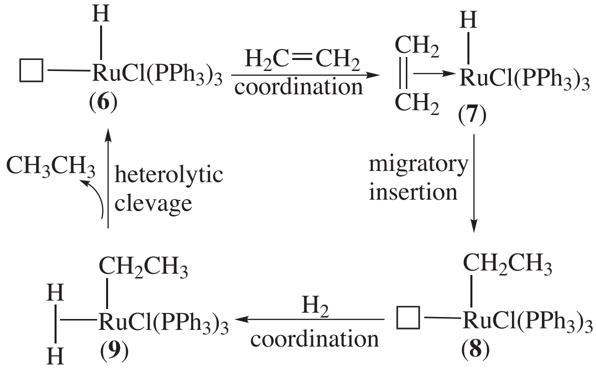
Hydrogenation *via* heterolytic activation

It is found that $[RuCl_2(PPh_3)_3]$ (**5**) activates H_2 heterolytically as shown below.



(**5**) is a coordinatively unsaturated complex; H_2 coordination to (**5**) and the cleavage of H—H bond takes place rapidly to give the monohydride, $[RuHCl(PPh_3)_3]$ (**6**). During this process, the oxidation state of Ru does not change and remains as +2.

The active catalyst (**6**) is also a coordinatively unsaturated complex and it catalyzes the hydrogenation of olefin as shown in scheme 2. The square (□) corresponds to a vacant site or a weakly coordinated solvent molecule.



Scheme 2 A possible mechanism for the hydrogenation of ethene by $[RuHCl(PPh_3)_3]$.

The first step involves coordination of ethene to the vacant site of the catalyst (**6**) to give the alkene-complex (**7**). Migratory insertion of ethene gives the ethyl-complex $[RuCl(Et)(PPh_3)_3]$ (**8**). Coordination of H_2 gives the η^2-H_2 complex (**9**). This complex undergoes a heterolytic cleavage of H_2, eliminating ethane and regenerating the active catalyst (**6**).

Hydrogenation *via* homolytic activation

The 17e Co(II)-complex $[Co(CN)_5]^{3-}$ activates dihydrogen homolytically to give the Co(III) complex $[CoH(CN)_5]^{3-}$.

$$2\,[Co(CN)_5]^{3-} + H_2 \longrightarrow 2\,[HCo(CN)_5]^{3-}$$

This 18e-complex $[CoH(CN)_5]^{3-}$ does not have a vacant site. However, it can transfer a hydrogen atom ($H^\bullet$) to an activated olefin, cinnamate (*trans* $PhCH{=}CHCO_2^-$), giving a moderately stable benzyl radical, $Ph^\bullet CHCH_2CO_2^-$ which abstracts another hydrogen radical ($H^\bullet$) to give 3 phenyl propionate ion, $PhCH_2CH_2CO_2^-$.

$$2\,[HCo(CN)_5]^{3-} + \textit{trans}\text{-}PhCH{=}CHCO_2^- \longrightarrow 2\,[Co(CN)_5]^{3-} + PhCH_2CH_2CO_2^-$$

Problems

1. The catalyst $[MCl(PR_3)_3]$ reacts with H_2 to give the octahedral M(III) dihydride (**A**). Replacement of PR_3 by $MeCH{=}CH_2$ in (**A**) gives the olefin-complex (**B**). In the presence of PR_3, (**B**) undergoes migratory insertion to give the octahedral alkyl-complex (**C**). (**C**) reductively eliminates the alkane (**D**) to regenerate the catalyst $[MCl(PR_3)_3]$. Write the molecular formulae of (**A**), (**B**), (**C**) and (**D**).
2. The active catalyst $[RuHBr(PPh_3)_3]$ coordinates with $MeCH{=}CH_2$ to give the olefin-complex (**P**). (**P**) undergoes migratory insertion to give the alkyl-complex (**Q**). (**Q**) reacts with H_2 to give the dihydrogen- complex (**R**) which eliminates (**S**) to regenerate $[RuHBr(PPh_3)_3]$. Identify (**P**), (**Q**), (**R**) and (**S**).

Student Corner

Introduction to Radiochemistry

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An **atom** consists of a very small (about 10^{-10} m in radius), dense and positively charged nucleus and negatively charged **electrons**. The **nucleus** consists of **protons** (p) and **neutrons** (n); these two particles are collectively known as **nucleons**. An element (X) with the atomic number (Z) and the mass number (A) is represented as $^{A}_{Z}X$, *e.g.* uranium-238 = ^{238}U = $^{238}_{92}U$.

Chemical reactions occur by transferring **electrons** between atoms, ions or molecules. Some unstable nuclei radiate energy and/or small particles to form a new element(s); these are called **nuclear** reactions. During these reactions A and/or Z of an element **may change**. Emission of particles is a nuclear property and it is not affected by the physical state of the element, its chemical composition, temperature or pressure of the system. Henry Becquerel noticed this phenomenon of **spontaneous disintegration** and named it as **radioactivity**.

Radioisotopes or radionuclides are the unstable nuclei (mainly with Z > 83) which emit radiation and undergo spontaneous decay or disintegration. The three main types of radiation are α, β and γ. Charge and mass of particles are given below.

Name and Symbol	Charge	Mass (amu)
α (Alpha) ($^{4}_{2}He$)	+2	4.0015
β (Beta) ($^{0}_{-1}e$)	-1	0.00055
Neutron ($^{1}_{0}n$)	0	1.0089
Proton ($^{1}_{1}p$ or $^{1}_{1}H$)	+1	1.0074
Deuterium ($^{2}_{1}H$)	+1	2.014
Positron ($^{0}_{1}e$)	+1	0.00055
γ (Gamma)	0	-

Nuclear stability

Components in a nucleus are strongly attracted to each other; in stable nuclei, the ratio of neutron to proton is one. With increase of the n/p ratio, more neutrons are required to reduce the proton-proton repulsion forces. Extra stability is associated with nuclei having the following magic numbers for p and n.

p = 2, 8, 20, 28, 50, 82

n = 2, 8, 20, 28, 50, 82, 126

e.g. $^{4}_{2}He$, $^{40}_{20}Ca$, $^{208}_{82}Pb$

Binding energy

The energy required to decompose a nucleus into protons and neutrons is defined as the binding energy. The binding energy can also be considered as the energy associated with the formation of the nucleus from its constituent protons and neutrons. When a nucleus is formed, some of the mass of its constituents is converted into binding energy.

Actual mass of a He nucleus or α particle is 4.0015 amu. But expected mass is 4.0326 amu (2p+2n). Thus, **mass defect** (Δm) is 0.0311 amu.

$$1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$$

The average binding energy per nucleon for an α particle can be calculated by using the Einstein's equation ($E = mc^2$), which is 7.245 MeV, ($c = 2.99776 \times 10^8$ m s^{-1}). For most of the stable nuclei it varies between 6-9 MeV.

$$1 \text{ MeV} = 1.60210 \times 10^{-13} \text{ J}$$

Nuclear reactions

Nuclear equation symbolizes a nuclear reaction where one element is transformed into another element(s). The sum of Z and A on one side of the arrow should be equal to those on the other side. For example,

$$^{238}_{92}U \rightarrow ^{234}_{90}Th + ^{4}_{2}He$$

Examples for some nuclear reactions are as follows.

1. **α emission**: The α particle is identical to a helium nucleus. It carries a charge of +2 but the charge is omitted from its symbols. It can be deflected by electric and magnetic fields.

$$^{222}_{86}Rn \rightarrow ^{218}_{84}Po + ^{4}_{2}He$$

Elements below atomic number 66 do not usually emit α-particles.

2. **β emission**: β-particle can be deflected by electric and magnetic fields. β emission decreases the n/p ratio since a neutron is converted into a proton.

$$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}e$$

$$^{1}_{0}n \rightarrow ^{1}_{1}p + ^{0}_{-1}e$$

3. **Positron emission**: The positron emission is equivalent to the conversion of a proton to a neutron.

$$^{1}_{1}p \rightarrow ^{1}_{0}n + ^{0}_{1}e$$

$$^{54}_{27}Co \rightarrow ^{54}_{26}Fe + ^{0}_{1}e$$

4. **Electron capture**: An unstable nucleus decays by capturing an electron from an inner orbital of an atom.

$$^{54}_{27}K + ^{0}_{-1}e \rightarrow ^{40}_{18}Ar$$

$$^{1}_{1}p + ^{0}_{-1}e \rightarrow ^{1}_{0}n$$

5. **γ emission**: There is no change of atomic number or mass number. Often γ emission occurs very quickly after a radioactive decay. Excited nuclei emit gamma photons ($\lambda \sim 10^{-12}$ m) in order to lower their energies. The reaction between positron and electron (annihilation collision) generate photons and energy (511 keV).

$$^{0}_{1}e + ^{0}_{-1}e \rightarrow 2\gamma$$

Rate of radioactive decay

The rate at which a radioactive element (isotope) disintegrates is proportional to the number of radioactive nuclei present. Radioactive decay obeys a first-order rate law.

$$-\frac{dN}{dt} \propto N \; ; \; -\frac{dN}{dt} = \lambda N$$

$$N = N_0 e^{-\lambda t}$$

N is the number of nuclei at time t and N_o is the initial number at t = 0. λ (Lambda) is the **decay constant**, which is a characteristic of that isotope. The rate of decay is generally expressed in counts per second. Thus, the unit of the decay constant (λ) is s^{-1}.

Radioactivity can also be expressed in term of activity (measured as disintegrations per second). A_o = initial activity, A = activity after time t.

$$A = A_0 e^{-\lambda t}$$

The older non-SI unit of radioactivity is Curie (C_i). One Curie is equal to the disintegration rate of 1 g of radium-226. That is equal to 3.7 x 10^{10} disintegrations per second (dps). *i.e.* 1 C_i = 3.7 x 10^{10} dps. The SI unit of activity is the Becquerel (Bq), where 1 Bq = 1 dps.

Half-life

The half-life ($t_{½}$) of a radioactive isotope is the time required for an isotope to reduce the number of initial radioactive atoms (or activity) by half of the initial value. *i.e.* when $t = t_{½}$; $N = N_o/2$.

$$\therefore \ln 2 = \lambda t_{½} \rightarrow \lambda t_{½} = 0.693$$

The half-life of Ra-226 is about 1600 y. Thus, 1 g of Ra becomes ½ g in 1600 y, and ¼ g in another 1600 y, and so on.

Radioactive decay series

The series containing all the elements starting with the **parent** element and all the decay products (**daughter** elements) is called the **radioactive decay series**. The heavy radioactive elements can be grouped into four decay series and in each series, α and β emissions take place until a stable isotope of lead or bismuth is formed.

a. Thorium (4n) Series (ends with lead 208) (the mass numbers 232, 228, 224,..............., 208 are multiples of 4).
b. Neptunium (4n+1) Series (ends with bismuth 209)
c. Uranium (4n+2) Series (ends with lead 206)
d. Actinium (4n+3) Series ends with lead 207)

Induced nuclear reactions

There are two main types of radioactive processes namely natural and artificial.

Natural radioactivity arises from naturally occurring radioactive isotopes such as ^{235}U, ^{232}Th and ^{238}U. Artificial radioactivity or nuclear transmutation is a process that produces radioactive elements by bombarding non-radioactive elements with a suitable particle.

1. **Bombarding with α particles**: *e.g.*

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{1}_{1}H + ^{17}_{8}O$$

The shorthand notion of the above reaction is $^{14}_{7}N\ (\alpha, p)\ ^{17}_{8}O$ representing, reactants (bombarding particle, ejected particle) products. Other examples include

$$^{27}_{13}Al(\alpha, n)^{30}_{15}P \ ; \ ^{10}_{5}B(\alpha, p)^{13}_{6}C$$

$$^{9}_{4}Be(\alpha, n)^{12}_{6}C$$

2. **Bombarding with protons**: *e.g.*

$$^{7}_{3}Li + ^{1}_{1}H \rightarrow 2\ ^{4}_{2}He$$

$$^{19}_{9}F + ^{1}_{1}H \rightarrow ^{20}_{10}Ne$$

3. **Bombarding with neutrons**: *e.g.*

$$^{31}_{15}Li + ^{1}_{0}n \rightarrow ^{32}_{15}P + \gamma$$

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{1}_{1}H + ^{14}_{6}C$$

Nuclear fission

Nuclear fission is a process in which bombardment of neutrons breaks a suitable radioactive nucleus into several nuclei, neutrons and energy.

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{139}_{54}Xe + ^{95}_{38}Sr + 2\ (^{1}_{0}n)$$

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{143}_{56}Ba + ^{90}_{36}Kr + 3\ (^{1}_{0}n)$$

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{135}_{53}I + ^{97}_{39}Y + 4\ (^{1}_{0}n)$$

Nuclear fusion

Nuclear fusion is a process in which two light nuclei are joined to form a heavier nucleus.

$$^{2}_{1}H + ^{3}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n + \text{energy}$$

Applications of radioisotopes

We are aware of the destructive aspects of nuclear energy; nuclear bombs have been used to destroy cities and millions of people. Many nuclear power stations generate electricity at a lower cost. Scientists use radioisotopes as "tracers" or "labels" to follow the pathways in many physical, chemical or biological reactions: *e.g.* to find out leaks in hidden pipelines, study the uptake of phosphorus by a plant, preserve food and estimate the age of rocks or archaeological objects (*e.g.*: radiocarbon dating). Radioisotopes are widely used in medicine; use of radiation (Co-60) to treat cancer. Some of the medicinal uses of them are given below.

X	Importance	X	Importance
^{74}As	Locate brain tumours	^{60}Co ^{226}Ra	Treatment for cancer
^{51}Cr	Determine total blood volume	^{131}I	Treatment for thyroid cancer
^{58}Co	Determine uptake of Vitamin B_{12}	^{24}Na	Detect obstructions in the blood circulation

Detectors used for measuring radiation

The interaction of nuclear radiation with matter is used to identify different types of radiation and their quantitative analysis. Geiger Muller counter, semiconductor detector, proportional counter and scintillation counter are some of the common devices used in this regard.

Problems

1. Write complete nuclear equations for each of the following notations:

   (a) $^{59}_{27}Co(\text{n}, \alpha)$ (b) $^{31}_{15}P(\text{n}, \;)^{32}_{15}P$

   (c) $^{7}_{3}Li(\text{p}, \;)^{4}_{2}He$

2. $^{225}_{88}Ra$ decays with a half-life of 15 days to produce $^{225}_{89}Ac$.
   a) Identify the type of decay involved in the above process.
   b) Calculate the decay constant (λ)
   c) Calculate the percentage of Ra-225 that will remain after 5 days.
   d) Calculate the time taken to decay 75% of the original sample.

3. Given below is a part of the (4n+2) decay series

$$^{238}_{92}U \xrightarrow{-\alpha} X \xrightarrow{?} {}^{234}_{91}Pa \xrightarrow{-\beta} Y \xrightarrow{?} {}^{230}_{90}Th \xrightarrow{-\alpha} Z$$

   Identify the missing particles, and X, Y and Z.

4. Calculate the binding energy per nucleon in MeV for iron–56 which has an atomic mass of 55.9349 amu.

5. Calculate the energy released in the following nuclear reaction.

$$^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \rightarrow 2\,{}^{4}_{2}\text{He}$$

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