EXPLORATION AND MODIFICATION FOR BETTER UTILISATION: ADDING VALUE TO PLANT BASED RESOURCES FOR NUTRITIONAL, MEDICINAL, AND INDUSTRIAL APPLICATIONS

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DEDICATION

To God, our Heavenly Father, who created man in His own image and likeness, breathed into him, and he became a living being. Indeed, the psalmist says in Psalm 8 (*The Psalms: A new translation. Collins. 1963*) concerning the nature of man:

… You have made him little less than a god;

with glory and honour you crowned him,

gave him power over the works of Your Hand,

put all things under his feet …

To my parents, uncles, and aunts, for their love and dedication to the upbringing of their children and others.

To my siblings, cousins and friends, for life-long relationships, which have made all the difference

To my students, past and present, for their trust and willingness to learn.

To all my teachers (especially my mother, my first teacher) for their dedication to duty, the evidence of which I am.

To my children Osahon, Oseyi and Amenawon, and my wife Ijeoma, the love of my life. I thank you for being there for me always.

And to the Blessed Mother,

Maria nẹn bhọn ulukhọ

“Totus Tuus”

The President

The Vice Chancellor

The Deputy Vice Chancellor

Principal Officers

Deans and Directors

Heads of Departments, and Units

Professors and Colleagues

My dear Students, past and present

My Lords, Spiritual and Temporal

Eminent Guests

Gentlemen of the Press

Distinguished Ladies and Gentlemen

1.1. Preamble

Mr Vice Chancellor Sir, I thank you sincerely for the opportunity and indeed the great priviledge to deliver this lecture, the 17th in the history of Benson Idahosa University. Please, allow me to say a few things about myself.

1.2. Early Life and Education

My name is Frederick Omonkhegbe Joseph Oboh. I was born at the Zuma Memorial Hospital, Irrua, Western Region, Nigeria, on the Feast of the Immaculate Conception, Sunday, the 8th of December, 1957, at 4.50 pm. I attended St. Joseph's Catholic Primary School, Igueben (founded in 1918) from 1964 to 1968, and Edo College, Benin City, from January 1969 to May 1973 (ours was the first set to write the West African School Certificate Examinations in May-June, and spent only about five or 6 months in form 5, depending on the subjects taken). I then proceeded to higher

school in September of the same year, and in the same school, but subsequently secured admission to read science at the University of Benin, Benin City. I resumed there in January 1975 for the 5-term predegree programme. At the end of our predegree studies, we were asked to choose from among the following - biochemistry, chemistry, industrial chemistry, optometry, geology, and the biological sciences – botany, microbiology, and zoology. I chose biochemistry, because I was interested in the study of natural products, and their utilisation.

Growing up in Nigeria before the oil boom, agriculture was the mainstay of the regional economies. Palm produce (palm oil and palm kernel), cocoa, and rubber were the cash crops produced in our part of the Midwestern Region of Nigeria. In my hometown, it was a common sight to see these commodities being processed for export. Except for palm oil, which apart from being produced for export was also utilised locally, the other commodities were mainly for export. I often wondered how these exports were processed into products at their destinations. Primary and secondary school geography focussed on production and export of agricultural and mineral commodities. However, not much was taught about their further processing and conversion into various products. I often wondered how these products came about. By reading biochemistry, I felt I would find answers to these questions, so I chose biochemistry and graduated in 1979, with a BSc (Hons) degree in the discipline.

I was posted to Niger State, for my national service, and did my primary assignment at the General Hospital, Minna. At the end of my service, I was interviewed for, and appointed to the position of Research Officer-in-Training (ROT), at the Nigerian Institute for Oil Palm Research, and was expected to go back to university after one year, to earn an MSc in biochemistry or any related discipline. I settled for biochemistry.

I resumed at the University of Benin sometime in 1981, but lectures were delayed due to the strike embarked upon by the university teacher's union. While there I took in addition to the compulsory biochemistry courses, electives related to food science and brewing (i.e., Industrial Biochemistry and Elements of Brewing) in the hope that I would do research in these areas in future. These courses were taught by Professor Campbell an expert in brewing and food fermentations, from Heriot Watt University, the late Dr. Aisien, a food scientist, Dr. Andy Opoku, a biochemical engineer, and the late Dr. Chris Iyayi, an applied microbial biochemist. Initially, for my project, I designed something in the area of biodegradation of fats and oils. But on giving my

pre-project seminar, the consensus was that there was very little by way of novelty, and that furthermore, the proposed project was more microbiological than biochemical. I was assigned a new supervisor, a food scientist, and found myself in the area of fat modification by fractionation. I earned the MSc in biochemistry in 1984, and was promoted by NIFOR to the rank of Research Officer 1.

When I got back to NIFOR, I designed a PhD project, which I took to the University of Ibadan, and it was accepted. I was admitted to the MPhil/PhD programme in Industrial Chemistry and Dr. Rotimi Oderinde (as he then was) was my supervisor. I earned a PhD in Industrial Chemistry in 1994, with specialization in the Chemistry and Technology of Fats and Oils.

What occasioned my transition from biochemistry to the chemistry and technology of fats and oils? My MSc project involved analysis and modification of palm oil. In the course of the project, I acquired the skills required for fats and oils research. These aspects of palm oil research, though quite new in Nigeria, were advancing by leaps and bounds in Malaysia and the UK. In designing my PhD work, I decided to work on other fats and oils that were quite obscure, being mainly of local and regional importance in their areas of origin in South America. The palms that I chose, based on my literature survey and visual observation of their fruits were part of the palm collection in the NIFOR palmatum Through exploratory studies using Official Methods of analysis of fats and oils, it would be possible to identify the fats and oils with sufficient prospects to warrant modification for commercial exploitation. Thus, my studies were no longer biochemical, but decidedly chemical in nature, being focused on the chemistry and technology of fats and oils.

I also came to realize that fatty oils are eminently suitable for the synthesis of a broad spectrum of specialty chemicals known as oleochemicals (section 1.11).

1.2.1. Encounter with "Giants of the Past" in the chemistry and technology of fats and oils

In scientific enquiry, one builds on the foundations laid by others. In chemistry and biochemistry, there are Official Methods and other experimental procedures, which have been accepted (within certain limits) as reliable. These may be modified from time to time to adapt them to suit the differences in the materials under study, and conditions (such as temperature, time etc.) that prevail during the determination of the values which serve to characterise the material under study. Also, for the same materials, there should be agreement between values from various laboratories. This

suggests that there must be a body of knowledge (scientific literature) already present for scientists to compare emerging information with. However, wide differences in the results for the same material between different laboratories may suggest forgery of data and/or experimental error.

As I delved into the literature on fats and oils, and their utilisation, I discovered that the field was dominated by chemists. Great names in the study of fats and oils, past or present, who have been recognised for their immense contributions and are referred to as "Giants of the Past" include Michel Chevreul (1786-1889), Thomas Percy (T.P.) Hilditch (1886-1965), Frank Denby (F.D.) Gunstone (1923-2021), Carter Litchfield (1932-2007), Enzo Fedeli (1928-2016) and K.G. Berger (1923-2018), who were all chemists. I therefore migrated to Industrial Chemistry, with my MSc project a sure foundation to build upon. Furthermore, I was interested in oleochemistry, an area of chemistry that involves the synthesis of fat-based chemicals. Another reason was that NIFOR had the facilities (laboratories, equipped with the required equipment and reagents, as well as a library with a vast collection of books and journals on lipids, especially fats and oils) required for such research. My head of Division at that time, Dr. D.A. Okiy, also happened to be an oil chemist/food technologist, and he placed his vast collection of books and journals at my disposal.

Isaac Newton (Wikiquote. http://en.wikiquote.org/wiki/Isaac_Newton), in a letter to Robert Hooke in 1676, wrote – *If I have seen a little further than others, it is by standing upon the shoulders of giants.*

The dynasty (permit me to refer to it that way) of these "giants" started with Michel Chevreul (1786-1889), regarded by some as the father of lipid chemistry. List (2021) provides an excellent history of the man and his contributions to the chemistry and technology of fats and oils. Michel Chevreul was born in Angers, France in 1786, and was descended from a long line (dating back some 200 years prior to his birth) of apothecaries, physicians, or surgeons. In 1799 Chevreul entered the l'Ecole Centrale in Angers, where he studied languages, botany, minerology, mathematics, physics, and chemistry. He finished his studies in 1803, and had to make a career choice. In this, he departed from the family tradition, and chose chemistry instead. In pursuit of this goal, Chevreul went to the National Museum of Natural History in Paris to study under the noted chemist, Louis Vauquelin (1763-1829), who discovered beryllium and chromium, and was

the first chemist to separate biological materials into fats, proteins, and starches and sugars (now called carbohydrates).

Chevreul began his investigation into the nature of fats in 1811, when Vauquelin assigned him to the task of examining a sample of soap. He soon discovered that upon dissolving soap in water and treating the solution with HCL, the insoluble organic acids (long chain carboxylic acids) separated, forming a floating layer. He then demonstrated that this layer was composed of distinct fatty acids. He demonstrated also, that when fats were heated in the presence of bases, glycerol remained in solution. In 1823, Chevreul demonstrated that lard contains two types of triacylglycerols, one which remained solid at room temperature, which he named "stearine" and the second, a liquid which he named "elaine". He went further to unravel the nature of the saponification reaction, and demonstrate that fats and oils are esters of fatty acids and glycerol, and identified oleic, butyric, capric, "stearic" acids and cholesterol as constituents of animal fats.

In 1825, Chevreul and Joseph Louis Gay-Lussac took out a patent for the manufacture of stearic acid-based candles. For this he was awarded a prize of 12,000 francs in 1855 by the Society for the Advancement of Industry, and a medal was struck honouring the occasion. In 1824 Chevreul was appointed director of the dyeing department of Manufacture Royale des Gobelins in Paris. This effectively ended his work as an oil chemist.

I am particularly grateful to the following "giants of the past" who have wielded great influence since the 20th century and whom I stood on their shoulders, for their publications, which I found very useful, for their willingness to reply to enquiries, and their encouragement.

1. Professor T.P. Hilditch, for his book "The Chemical Constitution of Natural Fats". 4th Edition. London, Chapman and Hall (with assistance by P.N. Williams). First published in 1940, as "The Chemical Composition of Natural Fats", with later editions in 1947, 1956, and 1964 (the edition I read). This is a very important book, containing the compositions of numerous (including obscure) fats and the methods used for their analysis (back in his time, these methods were very laborious and time-consuming), with data dating back to the early 20th century. Professor F.D. Gunstone, who was one of Professor Hilditch's students, wrote in a tribute some years ago (Giants of the past. Thomas Percy Hilditch 1886-1965, *Inform* May 2003. Volume 14 No. 5) had this to say about his supervisor and

mentor – " Hilditch will be remembered for contributions to three areas: His research into the composition of oils and fats and into methods of studying these compounds, his books summarizing our understanding of oils and fats, and the graduate students that he trained and who went on to make their contribution in this field of science" Professor Gunstone went on to write "Any successful academic extends his influence through the training of graduate students, some of whom continue to work in the same area of science. Fifty to 80 years on, there are not many of us left, but we carried the torch for 50 years after his death and passed it with his and our enthusiasm to another generation. Hilditch had over 80 research students …".

2. Professor F.D. Gunstone, for his books, which over the years have served as introductory material for those entering into the study of fats and oils, and for his numerous journal articles and book chapters on various areas of fats and oils. He was a prolific writer of scientific literature well into his nineties, and like his mentor, Hilditch, trained many postgraduate students, who have also made their mark in academia and industry.

   Professor F.D. Gunstone passed away on 30th October, 2021. In his tribute Marcel S.F. Lie Ken Jie, his former student and mentee states (*Marcel S.F. Lie Ken Jie 2022. A tribute to Frank Denby Gunstone - The father of lipid chemistry Eur J Lipid Sci. Technol.* 2200148) – "Our gratitude goes to Frank Gunstone on whose shoulders we stand, which has given us a better view of lipid chemistry. When Frank started out in 1940 to investigate the oxidative properties of edible oils, the Chemistry of Fats and Oils was a forgotten field of Organic Chemistry. Nothing was mentioned in textbooks about this class of organic compounds. Nothing." Jie goes further "It is hard to appreciate just how brutally labor-intensive and time-consuming it was for him to isolate and identify a novel unsaturated epoxy fatty acid from the seed oil of *Vernonia anthelmintica* (*F.D. Gunstone, J. Chem. Soc. 1954, 1611*), even when the basic separation tools, such as gas-liquid and thin-layer chromatography were not available to him in the early 1950s, not to mention NMR and mass spectrometry."

3. Carter Litchfield for his seminal work on the analysis of triacylglycerol composition *(Litchfield, C. 1972. The Analysis of Triglycerides. Academic Press*), which back in the day was a priceless resource for those interested in the determination of triacylglycerol

composition of food fats and oils. Of equal importance are his other research findings published in journal articles, for example, his taxonomic studies reporting the correlation between seed fat content, fatty acid composition and distribution in triacylglycerols, and botanical sub-families within the Palmae (Arecaceae) family to which the palms belong. Dr. Litchfield demonstrated a strong passion for the study of lipids.

Carter Litchfield earned a B.S. in chemical engineering from Rensselaer Polytechnic Institute, New York, and began his career as a chemist in Procter and Gamble (P&G), where he developed an interest in the history of fatty oils, including vegetable seed oils as well as lard, tallow and other animal fats. Litchfield left P&G in 1960 to take a job as a research scientist at Texas A&M University, where he later received a doctorate in organic chemistry. He then spent nine years as a biochemist at Rutgers University, where he worked on lipids in marine mammals and sponges.

While at Rutgers, Litchfield started Olearius Editions, under which name he published works on the history of vegetable oil and fat production. Litchfield retired from Rutgers in 1979 to devote his time to historical research, publishing, and collecting. Remarkably, by the time of his death on May 9, 2007, Litchfield had assembled a comprehensive collection of 5,000 books and pamphlets, advertisements, and other memorabilia and photographs documenting the history of fatty oils over a period of 500 years.

4. Enzo Fedeli, Professor, and former chief executive of SSOG (Stazione Sperimentale degli Oli e dei Grassi) Milan, Italy, and Editor for decades of the journal *La Revista Italiana Delle Sostanze Grasse,* for accepting the first article which I wrote (I appreciate here, also, the contributions of Dr. Oritsejafor (my senior) and Mr. Okpala-Jose (my junior), colleagues in NIFOR for proof-reading the manuscript and their suggestions and corrections prior to submission). This article was *Oboh F.O.J. (1987). The composition of Bactris major kernel and kernel oil. Riv Ital. Sostanze Grasse 64: 355 – 365.* From that moment on, Professor Fedeli, in his correspondence to me, always addressed me as doctor (Dr.), a title I earned only years later. Due to the high quality of the journal, I sent more articles which were published. My last article submitted to the journal was published in 2009 bringing the total to seven. Sometime in 1988, he offered me a place in his laboratory to undertake fats and oils research.

5. Kurt G. Berger, for decades, dominated research into the utilisation of palm oil, and was largely responsible for its global acceptance in food applications. He started his career as an Oil Chemist/ Food Technologist at Lyons, a large UK conglomerate with interests in ice cream, cakes, biscuits, and pastries, which had a string of famous corner cafes. There, he had a state-of-the-art laboratory, equipped with GLC (Gas Liquid Chromatography), NMR (Nuclear Magnetic Resonance, and X-ray diffraction, among other state-of-the-art equipment, and with staff from all over the world, who were interested in food applications of oils and fats. One of them was a certain chemist, by name Margaret Thatcher, who going on to the less interesting job of politics, became Prime Minister of the UK.

On his retirement from Lyons, Berger accepted the job of Chief Executive of PORIM (the Palm Oil Research Institute of Malaysia) and his name became synonymous with palm oil, being in the forefront, and the major spokesman for the global development and utilisation of this oil. He even appeared before the US congress to refute misinformation being spread about palm oil by the soybean lobby. I met him in NIFOR sometime in 1988, when I had the good fortune to take him on an inspection tour of our research facilities. He asked me about what my current project was, and I gave him a progress report. We discussed analytical methods and he offered suggestions, which turned out to be very useful. Before he left, he delivered a lecture on food applications of palm oil and its nutritional implications, and the production and utilisation of oleochemicals based on palm oil. In demonstration of the high regard, he had for my work, he cited my first two journal articles (Oboh, 1987; Oboh and Oderinde, 1988b) in a book chapter which he wrote on fats and oils from lesser-known oil bearing palms (Berger, 1994).

1.3. My Career in Academia

Research was my only work when I was a research scientist. Now, as a university lecturer, I have to mix research and teaching, a combination which sometimes (depending on my teaching load) may lead to too little attention being paid to research.

My career as a university teacher started in January 2002, when I was appointed to the position of Senior Lecturer in the Department of Chemical Sciences, Igbinedion University, Okada. The work-

load was heavy, and there was no promotion in the period (from January 2002 to October 2006) that I was there.

Sometime, early in 2006, I asked my friend Prof. McDonald Iduh, who was at the time on sabbatical as the Dean, Faculty of Basic and Applied Sciences at Benson Idahosa University, if there was a vacancy for a chemistry lecturer of my status in the Department of Chemistry, thinking that there was such a department in Benson Idahosa University. He said there was no chemistry programme, and the chemistry lecturers there were servicing programmes with chemistry content. He said however, that since I had my BSc and MSc degrees in biochemistry, I was eminently qualified to teach the subject and could apply for a position in biochemistry. I did, and was invited for an interview, which was successful. I was subsequently employed to the position of Senior Lecturer in April 2006. I did not accept the appointment at that time but stayed on at Igbinedion University, in the hope that I would be promoted to the position of Associate Professor for which I had been qualified for over a year. I finally accepted the BIU job in October 2006, but told the registrar (Mr. Igbinovbanhia, of blessed memory) that the position of Senior Lecturer was less than I was qualified for. He told me I did not have to wait for long as there was an interview coming up soon and I could apply for the position of Associate Professor. I did, and was successful. That was how I came in as a Senior Lecturer and was appointed (subsequently adjusted to promotion) an Associate Professor, a month and ten days later. I was promoted to the position of full Professor of Biochemistry in October 2010. To God be the Glory.

Mr. Vice Chancellor Sir, the role of the utilisation scientist, it is said, **"is making the known better, and exploring the unknown, to discover the potential therein"**. This informed the title of my inaugural lecture:

"Exploration and Modification for Better Utilisation: Adding Value to Plant Based Resources for Nutritional, Medicinal, and Industrial Applications"

My inaugural lecture consists of three parts, as follows:

1. **The characterisation of fats and oils and their modification for rational utilisation, which is the longest,**
2. **The analysis, medicinal properties, and preservation of green leafy vegetables**
3. **Palm sap utilisation studies**

1.3.1. A spiritual perspective

To the Christian, value addition is a spiritual imperative, and indeed a duty, the dereliction of which bears grave consequences. The parable of the talents (Matt. 25: 14-30 RSV) serves to illustrate this: - Those who (by the grace of God) have the capacity to add value are loved by the Master. For these, the reward is great. The timid and wicked servant, with the wrong attitude, who buries his talent, is cursed, and the little that he was given is taken from him and given to he who has "the capacity" to add value - "For to everyone *who has,* will more be given, and *he will have abundance*; *but from him who has not*, even what he has will be taken away"- and woe betide that fellow, for it is written- "*and cast the worthless servant into the outer darkness, where men will weep and gnash their teeth*" (italics mine). Such can be likened to the fate of countries which export their commodities as raw materials to others, without adding value. Such amounts also, to the loss of the jobs required to covert these commodities to finished products, and the value that would have accrued to the exporting country if these materials were processed locally.

1.4. My Research Effort

1.4.1. Characterisation of fats and oils and their modification for rational utilisation

My research efforts in the area of oleaginous (fat bearing) materials, oils and fats, involved the characterisation, modification and utilisation of mesocarp and kernel oils of the African oil palm (*Elaeis guineensis*) and the Amazonian palms *Attalea cohune*, *Astrocaryum vulgare* Mart, *Arecastrum romanozoffianum* and *Bactris major* Mart.

Over the years, many species of domestic and exotic palms had been planted at NIFOR and the research institute's palmatum included a sizable collection of palms. As of April 1971, this collection consisted of 112 domestic and exotic palms (Obasola, 1971). These were largely still in place at the time I started my exploration in 1985, It was from this collection that I selected the exotic species listed above. Obasola (1971) reports further, that in the 1970-1971 research period, some oil-like substances were extracted from wet and dried mesocarp and kernels of some of these palms, and the extracts were sent to the Tropical Products Institute in London, for chemical analysis. Subsequent examination of the seed oils from some of these palms was carried out, and the results published (Opute, 1979). But there was still a great deal to be done, a task which I embraced fervently.

My exploration consisted of the examination (where possible) of palm fruit yield, the proportions of fruit mesocarp, shell and kernel, and proximate composition of the mesocarps and kernels. The composition, oil yield of mesocarp (pulp) and kernels, as well as the composition and physico-chemical characteristics of their oils and residues from oil extraction, were determined as a guide to their exploitation. Such information would then enable the rational utilisation of these resources by indicating what kind of modification (i.e., processing) should be undertaken to make them better suited for various applications. Such knowledge would also indicate to what use the residues from their modification could be put (if suitable), or their proper disposal (if required).

However, before embarking on the examination of the produce of these exotic oleaginous palms, I had undertaken the characterisation of palm (*Elaeis guineensis*) oil by determination of its composition, and its physico-chemical properties. It was with the knowledge of its composition as a guide that, I carried out suitable modification with a view to making palm oil better suited for a range of food and non-food applications. This research was undertaken in partial fulfilment of the requirements for an MSc (Biochemistry) degree at the University of Benin, and is recorded in my dissertation titled "*Fractionation and Biochemical Characterisation of a Nigerian Palm Oil*" dated June 1984, and the publications derived from this work (Oboh, 2004abc; Oboh, 2007ab).

This project (undertaken in 1983/84 and sponsored by The Nigerian Institute for Oil Palm Research) was carried out in partial fulfilment of the requirements for the award of an MSc degree in Biochemistry in the University of Benin, Benin City.

1.4.2. Aims and Objectives

This work was undertaken to:

i. Standardize a process for the fractionation of locally produced palm oil to yield a free-flowing oil (the olein) retaining the full nutritional value of the starting material. and a hard fraction (the stearin).

ii. Study the composition and distribution of the fatty acids in the triacylglycerols of palm oil and its fractions.

iii. Determine the characteristics of palm oil available in Benin City and surrounding areas, with a view to improving the quality (by way of recommendations for adequate fruit harvesting and processing, and oil handling and storage) of locally available oil.

iv. To study the effects of the combined use of citric acid and butylated hydroxyquinone (BHT) for the prevention of oxidative deteriorate

v. ion of palm oil during handling and storage.

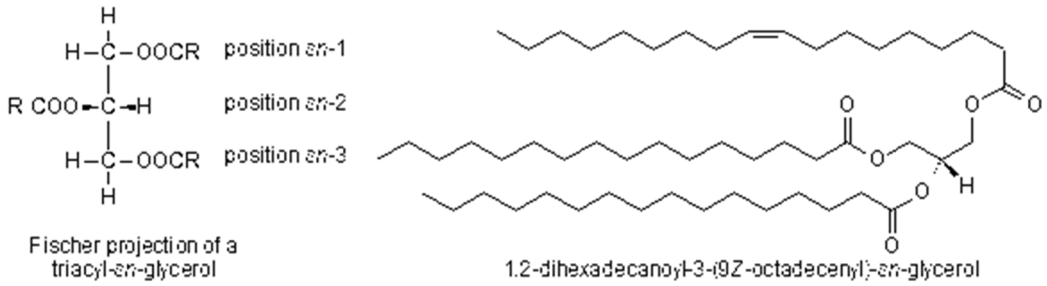
1.4.3. Some useful definitions and structures

Mr. Vice Chancellor Sir, please allow me at this point, to define some key terms in the chemistry of fats and oils.

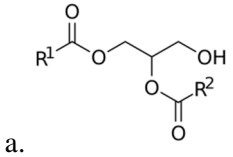
Acylglycerols

Acylglycerols, esters of fatty acids with the trihydroxyl alcohol, glycerol are constituents of oils and fats. They have the following structures (Fig. 1.1):

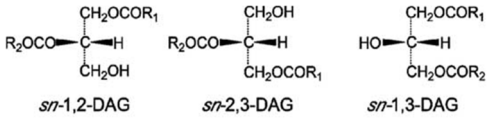
A. Triacylglycerol



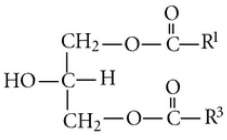
B. Diacylglycerols



a.



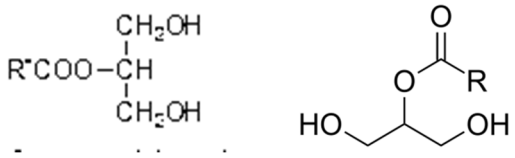
b.



c.

Diacylglycerol structures: a. 1, 2-diacylglycerol; b. *sn*-1, 2-, 2, 3- and 1, 3-diacylglycerols; c. *sn*-1, 3-diacylglycerol

C. Monoacylglycerol



2-monoacylglycerol structures

Where R = Fatty acyl groups

Fig. 1.1: Structures of acylglycerols: A. Triacylglycerols; B. Diacylglycerols; C. Monoacylglycerols

Fatty acids

The common fatty acids of plant tissues are C_{16} and C_{18} straight-chain compounds with zero to three double bonds of a *cis* (or *Z*) configuration. Such fatty acids are also abundant in animal tissues, together with other even and odd numbered acids with a somewhat wider range of chain-lengths and up to six *cis* double bonds separated by methylene groups (methylene-interrupted double bonds). The systematic and trivial names of those fatty acids encountered the most, together with their shorthand designations, are listed in Table 1.1 below:

Table 1.1. Dietary fatty acids*

Common name	Systematic name	Abbreviation	Fatty acid family
Caproic	n-hexanoic	6:0	
Caprylic	n-Octanoic	8:0	
Capric	n-Decanoic	10:0*	
Lauric	n-Dodecanoic	12:0	
Myristic	n-Tetradecanoic	14:0	
Palmitic	n-Hexadecanoic	16:0	
Stearic	n-Octadecanoic	18:0	
Arachidic	n-Eicosanoic	20:0	
Behenic	n-Docosenoic	22:0	

Lignoceric	n-Tetracosanoic	24:0	
Palmitoleic	9-Hexadecenoic	16:1	n-7***
Oleic	9-Octadecenoic	18:1	n-9
Gadoleic	11-Eicosaenoic	20: I	n-9
Cetoleic	11-Docasaenoic	22:1	n-11
Erucic	13-Docasaenoic	22: 1	n-9
Nervonic	15-Tetracosaenoic	24:1	n-9
Linoleic	9,12-Octadecadienoic	18:2	n-6
α –linolenic	9,12,15-Octadecatrienoic	18:3	n-3
γ-linolenic	6,9,12-Octadecatrienoic	18:3	n-6
Dihomo-γ-linolenic	8,11,14-Eicosatrienoic	20:3	n-6
	5,8, 11-Eicosatrienoic	20:3	n-9
Arachidonic	5,8,11,14-Eicosatetraenoic	20:4	n-6
EPA	5,8,11,14,17-Eicosapentaenoic	20:5	n-3
Adrenic	7,10,13,16-Docosatetraenoic	22:4	n-6
	7,10,13,16,19-Docosapentaenoic	22:5	n-3
DPA	4,7,10,13,16-Docosapentaenoic	22:5	n-6
DHA	4,7,10,13,16,19-Docosahexaenoic	22:6	n-3

*Other dietary fatty acids are butanoic (4:0), found in milk fat, hexanoic (6:0), found in milk fat and palm kernel and coconut oils, octanoic acid (8:0) found in all three fats. Also, minor quantities of the odd number carbon chain fatty acids, pentadecanoic acid (15:0) and heptadecanoic acid (17:0) are found in milk and ruminant fats. **a: b: a=carbon chain length, b= number of double bonds. ***Also referred to as ω-; indicated the position of the first double bond when counting from the methyl end of the fatty acid molecule.

As a class, the fats and oils are insoluble in water, but soluble in non-polar solvents. The solubility is greater and the melting point lower the richer the fat is in short chain and unsaturated fatty acid residues.

Triacylglycerol structure and composition

The triacylglycerols (TAGs), triesters of fatty acids with glycerol, their slip melting points, melting and cooling profiles, and solids content at critical temperatures), their oxidative stability, and their metabolic fate and functions in organisms are all influenced by the molecular structure of their TAGs (Hannewijk *et al.*, 1968, Timms, 1985; Iwasaki and Yamane, 2000). Parameters such as the degree of unsaturation of fatty acid chains, fatty acyl chain length, and positional distribution of the fatty acids esterified to the glycerol backbone determine the structure of the TAGs.

The cooling/heating, time-temperature history applied to the system, and the presence of certain factors, for example free fatty acids and partial acylglycerols (especially diacylglycerols), are

additional variables that affect the molecular organisation of TAGs, and therefore their phase change properties (Okiy, 1978; Hernqvist and Anjou; 1983; Timms, 1985).

Palm oil and the various fats and oils obtained from it by fractionation, hydrogenation, and/or interesterification are used in a broad range of edible (Berger, 1975; Young, 1985; Pease, 1985), pharmaceutical products, and cosmetics (Kalustian, 1985). Detailed knowledge of the intramolecular distribution of fatty acids in the TAGs, and the TAG composition of palm oil is therefore vital for the understanding the molecular basis of the functional properties and oxidative stability of this oil in food systems, pharmaceuticals and cosmetics, and also its digestion and absorption in organisms. Such knowledge would provide a scientific basis for the modification of palm oil triacylglycerols, in order to improve its performance in various end-use applications.

In this study, the distribution of fatty acids in the TAGs of palm oil, and their composition were determined. The implications of the results with regards to the functional properties of the oil - its oxidative stability, its digestion and metabolism, and its fractionation into liquid and solid fractions - are discussed.

1.4.4. The Characterisation and Fractionation of Palm Oil: The Nutritional, Functional and Industrial Implications

TABLE 1.2. Distribution of fatty acids in triacylglycerols of palm oil (Oboh, 1984; 2004a)

	Fatty Acids[b] (mol %)					
PALM OIL	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Triacylglycerols (TAGs)	0.3	1.8	49.0	5.1	36.7	7.1
2-monoacylglycerols	0.7	2.4	13.6	1.1	62.5	19.7
Proportion in 2-position	77.7	44.4	9.3	7.2	56.8	92.5
Proportion in 1, 3-position	22.3	55.6	90.7	92.8	42.2	7.5
Preferential esterification	2-	2-	1, 3-	1, 3-	2-	2-

[*]**Fatty acids: 12:0, lauric; 14:0, myristic; 16:0, palmitic; 18:0 stearic; 18:1, oleic; 18:2, linoleic.**

The positional distribution of fatty acids in TAGs of palm oil is presented in Table 1.2. The major fatty acids found in palm oil TAGs were palmitic (49.0%) and oleic (36.7%); other fatty acids

were linoleic (7.1%), stearic (5.1%), myristic (1.8), and lauric (0.3%). Lauric, myristic, oleic, and linoleic acids were preferentially esterified at the 2- positions, while palmitic and stearic acids exhibited preference for the 1, 3-positions.

1.4.5. Implications of the distribution of fatty acids in palm oil TAGs

Resistance to oxidative deterioration

The oxidative stability of oil is dependent on its fatty acid composition and distribution in its TAGs, as well as on the presence of non-acylglycerol constituents, for example tocopherols, sterols and carotenoids. The preferential esterification of unsaturated fatty acids at the 2-position of TAGs could serve to stabilise them (and therefore the oils to which they belong) against oxidative deterioration (Rachuveer and Hammond, 1967). Correlation of fatty acid composition, TAG structure, and oxidative stability has been reported (Konishi *et al*., 1995). The preferential esterification of 18:1 and 18:2 at the 2- position of palm oil TAGs therefore suggests a *regio*-selective protection of these acids resulting in their stabilisation against oxidative deterioration.

Digestion of palm oil and absorption of its fatty acids

Pancreatic lipase hydrolyses dietary TAGs at their 1- and 3- positions, to yield free fatty acids and 2- monoacylglycerols with the preferential absorption of the latter. Mattson and Volpenhein 1962) observed that palmitic acid (16:0) was best absorbed when fed as 1, 3-dioleoyl 2-palmitoyl-glycerol, and least when fed as the free acid; 1- or 3-palmitoyl-dioleyl-glycerol occupied an intermediate position. Filler *et al*. (1969) found that butter oil was poorly absorbed by newborn infants while human milk was well absorbed. In butter oil, the 16:0 in TAGs exhibits a near-random distribution, but is preferentially esterified at the 2-position in human milk TAGs. The difference in absorption was attributed by the authors to the preferential esterification of 16:0 at the 2-position in the latter. Mattson (1983), using a series of stearic-oleic model TAGs observed that the 18:0 in the 1-, and 3- positions was hydrolysed to the free acid, and in the presence of calcium, the soap formed was poorly absorbed. If, however, the digestion product was 2-monostearoylglycerol, the 18:0 was well absorbed.

Structured fats: The possibility of improvement of nutritional and functional quality

Palm oil, and fats and oils derived from it by fractionation, hydrogenation and/or interesterification find application in a broad range of edible applications, due to their excellent functional properties. However, it is obvious from the foregoing that the preferential esterification of palmitic acid at the

1, 3- positions of their triacylglycerols could result in poor absorption of this fatty acid. This preference of 16:0 can be modified by chemical esterification, which would result in a random distribution of this acid among the three 1-, 2-, and 3-, positions. This process would however also randomise the 18:1 and 18:2, resulting in an increase in their susceptibility to oxidation and a decrease in their absorption. *Regio*-selective interesterification, the interchange of fatty acids or their esters with fatty acyl groups at the 1- and 3-positions of TAGs (which is catalysed by *sn*- 1, 3-specific lipases) can be used to structure palm oil TAGs for improved nutritional and functional properties without altering the composition of the fatty acids at the 2-position (Iwasaki and Yamane, 2000; Akoh *et al*., 1998; Latta, 1990).

The constituent TAGs of palm oil are shown in Table 1.3.

TABLE 1.3. Composition (mol %) of palm oil triacylglycerols (Oboh, 1984; 2004a)

Triacylglycerols	**Palm (*Elaeis guineensis*) oil[c]**
SSS[a] (PPP[b])	10.1(6.1)
SSU (PPO)	6.6 (4.3)
SUS (POP+PLP)	46.7 (27.8+8.8)
USU	1.1
UUS (OOP)	30.7 (19.8)
UUU (OOO)	4.9 (3.5)
SSS	10.1
SSO	6.4
SSL	0.2
SOS	35.5
SLS	11.2
OSO	1.0
LSL	-
OOS	22.4
LOS	0.8
OLS	7.1
LSO	0.1

LLS	0.2
OOO	3.5
OOL	0.2
LOL	-
LLL	-
OLL	0.1
OLO	1.1

P=palmitic acid, S =saturated fatty acids, U=unsaturated fatty acids, O= oleic acid, L= linoleic fatty acids *() In parenthesis: dominant triacylglycerol

Structure-function relationships

For convenience of calculation, saturated fatty acids have been grouped as saturated (S, mainly palmitic, unsaturated fatty acids as U, mainly oleic (O), and lesser amount of linolenic (L). The major TAGs of palm oil are SSU (53.4%) and SUU (31.7%), consisting mainly of SOS (35.5%) and OOS (22.6%) respectively. The trisaturated TAGs (SSS) constitute 10.1%, and SLS 11.2% of crude palm oil TAGs.

Trisaturated TAGs of palm oil have an average melting point of 66^{o}C (Berger, 1976). They therefore provide structure i.e., physical structure (solidity) as well as the structural characteristics needed for performance, for example creaming properties in bakery applications (Wiederman, 1978). The disaturated TAGs SSU (average melting point of 38.8^{o}C), provide both structure and lubricity. They are solid at room temperature but melt at body temperature (Berger, 1975, Wiederman, 1978). The lower melting acylglycerol types SUU and UUU (average melting points of 19.8 and 5.0^{o}C respectively) can provide only lubricity and nutritional properties, for example essential fatty acids and improved digestibility and absorption of the oil. Lubricity describes imparted tenderness, for example, to bread. It adds to the richness, and improves the eating property (i.e., palatability) of foods, and provides a feeling of satiety after eating (Wiederman, 1978). Thus, palm oil differs from most vegetable oils in possessing both structure and lubricity. In this respect it resembles the animal fats tallow, lard and butter, and tucum palm fruit pulp oil (Oboh and Oderinde, 1988b, 1988d).

Triacylglycerols being long chain compounds display the phenomenon of polymorphism i.e., they crystallise in more than one form (Hagemann, 1988). The different forms are classified as α, ß', and ß, with increasing stability and melting point in that order (Larsson, 1994). Triacylglycerols

go through the monotropic sequence α→ ß'→ ß. Each transition from one state to another is slow for acyl chains of different chain lengths and for asymmetric TAGs. As these are typical of butter oil (Deffense and Tirtiaux, 1989), this fat generally shows a stable ß'– form, with little tendency for polymorphism. Transitions are fast, however, for fatty acids of same length and for symmetric TAGs, for example PPP, PLP, and POP, which constitute 6.1, 8.8, and 27.8% respectively of palm oil TAGs (Table 3). Due to this high proportion of symmetrical solid acylglycerols, palm oil is expected to exhibit a high tendency to polymorphism (i.e., a fast α→ ß'→ ß transition leading to formation of the stable ß polymorph). But palm oil is usually stable in the metastable ß'-2 form (Timms, 1985; De Souza, 1990; Dian *et al.,* 2003). The TAG POP cannot exhibit its stable ß-3 form in the presence of PPO and PLP. Also, PPP forms a solid solution with POP and does not seem able to exhibit its stable ß-2 form.

The metastable ß' polymorph is the most desirable for fat-rich products such as margarines, table spreads, and cake shortening. The ß' crystals are relatively small and needle-like; such fats appear smooth, provide good aeration and can incorporate a large amount of liquid in their crystal network (Wiederman, 1978; Charteris and Keogh, 1991). The ß' crystals result in good spreadability, smooth texture, and glossy surface in margarines and table spreads, and good creaming properties in bakery fat (DeMan, 1998).

Palm oil is unique among the vegetable oils of commerce because of its high saturated acid content with significant amount (10-17%) of the saturated acids at the 2- position of its triacylglycerols. In consequence, palm oil consists of three main types of TAGs: trisaturated (mainly PPP), disaturated (mainly PPO), and monosaturated (mainly POO). Palm oil also contains appreciable amounts of diacylglycerols (5-8%) and free fatty acids, which can have a substantial effect on its physical properties, including retardation of the of ß'→ ß transition (Okiy, 1978).

1.5. Fractionation of palm oil

Fractionation is a thermo-mechanical process where constituents triacylglycerols of fats and oils are crystallised from a melt. This is accomplished by solidification of certain triacylglycerols, which are separated from the oil by filtration.

In the fractionation process, the oil is cooled from the ambient to a predetermined (i.e., from laboratory bench studies) temperature of crystallisation.

In the Dry Process, the slurry which results is maintained at this temperature and subjected to liquid-solid separation by filtration (Puri *et al*, 1980, Deffense, 1985, Deffense and Tirtiaux, 1989). In the Solvent Fractionation Process, fractionation of the oil is carried out in an appropriate solvent, e.g., acetone (Oboh, 1984, 2007a; Oboh and Oderinde, 1988cd). The solvent process allows a clean separation of stearin from the olein, due to less entrainment of the latter in the former (Rossel, 1985). In the third process, The Detergent (Hydrophilization) Process, the partly crystallised mass is mixed with an aqueous solution of a surface-active substance. By the action of this surface-active agent, the crystals are wetted by, and dispersed in the aqueous phase, while their surface is being washed free from the liquid (olein) component.

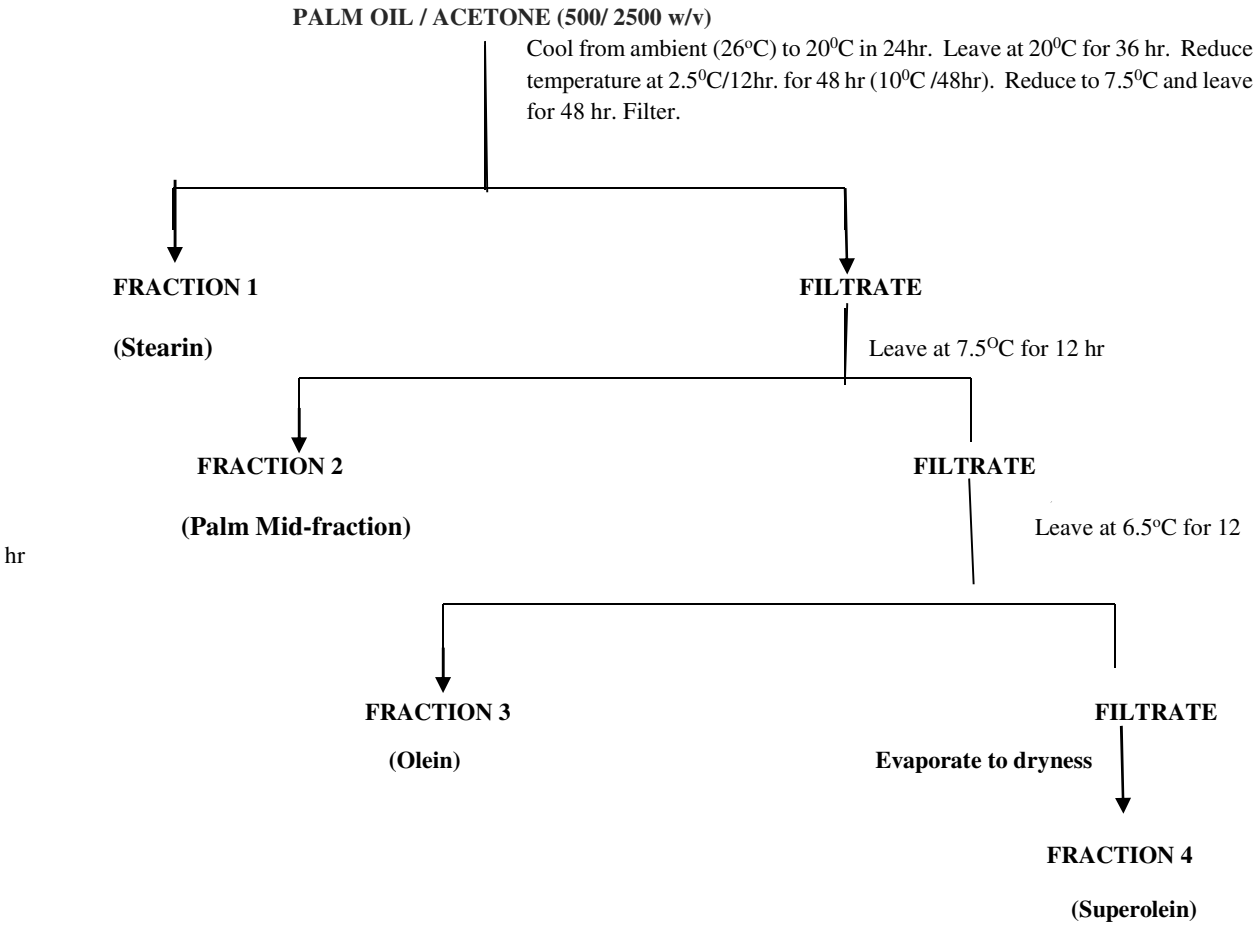


Fig. 1.2: Fractionation of palm oil (Oboh, 1984; 2007a)

The solid fraction (stearin) consists mainly of the higher melting triacylglycerols and the liquid fraction (olein), mainly of the low melting triacylglycerols. On fractionation of a complex mixture of triacylglycerols (as is found in natural fats and oils), a portion of the higher melting triacylglycerols will be found with the lower melting liquid fraction, as a result of eutectic formation and equilibrium solubility (Rossel, 1967).

The Molecular basis for the fractionation of palm oil

Under normal ambient conditions (20-30^{o}C), palm oil appears as a heterogeneous slurry of crystals (mainly PPP+POP) in liquid oil (mainly POO+POP). The separation of these phases forms the basis of the large–scale fractionation processes applied to palm oil. These fractionation processes are relatively easy to operate, because the phases are more distinct than in other fats of commercial importance. If the fractionation process uses a solvent, three fractions roughly corresponding to the three main types of TAGs (i.e., the stearin, mid-fraction and olein) may be separated easily (Oboh, 1984; Timms, 1985).

Fractionation of palm oil at the Nigerian Institute for Oil Palm Research was first reported by Eapen (1971), who subjected a crude palm oil sample to laboratory scale dry fractionation overnight at a temperature of 26^{o}C to produce a solid and a liquid fraction, with the following results (Table 1.4):

Table 1.4. Bench-scale dry fractionation of palm oil (Eapen, 1971).

Characteristics	**Liquid fraction**	**Solid fraction**
Carotene (ppm)	941	748
Iodine value	56.63	49.01
Saponification value	193.54	197.75
Unsaponifiable matter (%)	0.509	0.313
Residual colour (10R+Y) 14 cell	3.4	3.4
Moisture %	0.38	0.49
FFA %	4.00	3.43
Peroxide value	1.13	1.21
Density at 60^{o}C	0.876	0-.901

The author commented that "The higher iodine value coupled with the lower saponification value of the liquid portion is a clear indication that it contains higher proportions of the two unsaturated namely oleic and linoleic acids than the solid fraction. The fact that it remains a liquid at ambient temperatures and also contains a higher proportion of carotene should weigh in its favour as an oil preferred for local consumption. It may also be mentioned here that there is an increasing demand for unsaturated oils in (sic) the world market".

1.5.1. Results and implications

In our study (Figure 1.2), there was an increase in the β-carotene content of the fractions according to their order of emergence (Table 1.5). The β-carotene content of the stearin was 150 mg/L; the mid-fraction and first olein fraction had 804 mg/L and 972 mg/L respectively. These were lower than that of the whole oil (1479 mg/L). However, compared with the whole, the superolein which contained 1968 mg/L, was enriched in β- carotene by 33.06%. Whole palm oil had a tocopherol content of 0.73 mg/g. The stearin contained by far less (0.08 mg/g). Tocopherol content of mid-fraction was 0.78 mg/g (similar to that of the whole palm oil), while the olein and superolein contained 0.63 mg/g and 0.34 mg/g respectively. Thus, the liquid fractions had lower tocopherol concentrations than whole palm oil, with this material concentrated in the mid-fraction.

TABLE 1.5: Physico-chemical characteristics of crude palm oil and its fractions (Oboh, 1984; 2007a)

Characteristics	Palm Oil	Fraction 1 (Stearin*)	Fraction 2 (Palm Mid-Fraction)	Fraction 3 (Olein*)	Fraction 4 (Superolein)
Slip point (°C)	35.0	51.0	24.0	19.5	12.0
Refractive Index (40°C)	1.4577	1.4532	1.4562	1.4582	1.4592
Iodine Value (Wij's)	51.9	30.6	43.3	51.1	63.5
β-carotene (mg/kg)	1479	150	804	972	1968
Total Tocopherols (mg/g)	0.73	0.08	0.78	0.63	0.37
Yield (%)	-	20.9	7.9	6.8	63.6

Consistency at ambient temperature (27°C)	Semi-solid	Solid	Semi-solid	Liquid	Liquid

*Stearin and olein are technical names for fats that are solid and liquid respectively at ambient temperature

Our results were in agreement with reported values for fatty acid compositions of the stearin, palm midfraction, and oleins from industrial commercial processes (Tables1.6 and 1.7).

TABLE 1.6. Fatty acid composition (wt %) of palm oil and its fractions (Oboh, 1984; 2007a)

Fatty Acid	Whole Palm Oil	Fraction 1 (Stearin)	Fraction 2 (Mid-fraction)	Fraction 3 (Olein)	Fraction 4 (Superolein)
12:0	0.9	-	-	0.1	0.3
14:0	4.3	1.4	1.2	1.2	1.5
16:0	54.9	66.2	48.5	47.8	36.8
18:0	2.8	6.2	6.6	5.4	4.7
18:1	30.2	24.5	36.4	37.1	43.8
18:2	6.9	1.7	7.3	8.4	12.9

TABLE 1.7. Palmitic, stearic, oleic and linoleic acids content, analytical values, and yields of stearin and superolein from various sources

	STEARINS			SUPEROLEINS			
Fatty Acid	**Nigeria**	**Indonesia[b]**	**Malaysia[b]**	**Nigeria[a]**	**1[c]**	**2[c]**	**3[c]**
16:0	66.2	68:8	66.2	36.8	35.6	34.9	37.3
18:0	6.2	5.1	4.8	4.7	4.0	3.7	4.1
18:1	24.5	19.1	21.6	43.4	44.2	46.9	43.8
18:2	1.7	4.5	5.1	12.9	13.4	12.1	12.3
Yield (%)	20.9	20.2	17.0	63.	-	-	-
IV[d] (Wij's)	30.6	24.9	28.0	63.5	62.9	62.7	60.7
SMP[e] (°C)	51.0	55.9	55.3	12.0	16.0	15.0	18.2

[a]Solvent fractionation in acetone (Oboh, 1984, 2007a). [b]Single stage fractionation, Alfa-Laval detergent process (Deffense, 1985). [c]Double stage fractionation (Deffense, 1985). [d]IV=Iodine Value. [e]SMP =Slip Melting Point

Fatty acid distributions in the triacylglycerols of the fractions were similar to that of palm oil triacylglycerols: Palmitic acid was preferentially esterified to the 1, 3- positions, and oleic and linoleic to the 2-position (Table 1.8A, B, C and D).

TABLE 1.8. Fatty acid distribution in the triacylglycerols of palm fractions

A. Distribution of fatty acids in palm stearin triacylglycerols (Oboh, 1984; 2007b)

	Fatty acids (mol %)					
STEARIN	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Triacylglycerols	0.1	1.4	63.8	6.3	24.6	3.8
2-monoacylglycerols	0.3	1.6	32.7	3.7	52.3	9.4
Proportion in 2-position	100	38.1	17.1	19.6	70.9	82.5
Proportion in 1, 3-position	0	61.9	82.9	80.4	29.1	17.5
Preferential esterification	2-	2-	1, 3-	1, 3-	2-	2-
Iodine value (Wij's)	30.6					
Slip melting point	51.0					

B. Distribution of fatty acids in triacylglycerols of the palm mid-fraction

	Fatty acid (mol %)					
PALM MID-FRACTION	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Triacylglycerols	0.1	1.4	53.5	5.9	33.1	6.0
2-monoacylglycerols	0.2	0.3	9.9	0.7	74.8	14.1
Proportion in 2-position (%)	66.7	7.1	6.2	2.9	75.1	78.3
Proportion in 1, 3-position (%)	33.3	92.9	93.8	97.1	24.9	21.7
Preferential esterification	2-	1, 3-	1, 3-	1, 3-	2-	2-
Iodine value (Wij's)	43.3					

Slip melting point ºC	24.0

C. Distribution of fatty acids in the triacylglycerols of the olein fraction from palm oil

	Fatty acids (mol %)					
OLEIN	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Triacylglycerol	0.4	2.8	47.9	5.1	36.9	6.9
2-Monoacylglycerol	1.0	6.6	11.2	1.1	64.3	15.8
Proportion in 2-position	83.3	79.2	7.8	7.2	58.1	76.3
Proportion in 1, 3-position	6.7	20.28	92.8	92.8	41.9	23.7
Preferential esterification	2-	2-	1, 3-	1, 3-	2-	2-
Iodine value (Wij's)	51.1					
Slip melting point	19.5					

D. Distribution of fatty acids in the triacylglycerols of the superolein fraction

	Fatty acid (mol %)					
SUPEROLEIN	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Triacylglycerols	0.4	1.7	40.5	4.3	41.6	11.5
2-Monoacylglycerol	1.1	1.7	12.5	0.9	61.0	22.8
Proportion in 2-position	91.7	33.3	10.3	7.0	48.9	66.1
Proportion in 1, 3-position	8.3	66.7	89.7	93.0	51.1	33.9
Preferential esterification	2-	Random	1, 3-	1, 3-	2-	2-
Iodine value (Wij's)	63.3					
Slip melting point	12.0					

The triacylglycerol compositions of palm oil and its fractions are shown in Table 1.9.

TABLE 1.9. Triacylglycerols of palm oil and fractions

Triacylglycerols (mol %) [a]	Palm oil	Fraction 1 (Stearin)	Fraction 2 (Palm Mid- Fraction)	Fraction 3 (Olein)	Fraction 4 (Superolein)
S_3	**10.2**	**29.9**	**8.3**	**11.8**	**6.3**
S_2U	**53.6**	**55.9**	**67.6**	**50.7**	**40.3**
SSU	6.6	8.0	2.8	8.6	7.6
SUS	47.0	47.9	64.8	42.1	32.7
SU_2	**31.8**	**13.5**	**22.2**	**32.2**	**41.0**
SUU	30.7	12.9	21.9	30.7	39.6
USU	1.1	0.6	0.3	1.5	1.4
U_3	**4.9**	**0.8**	**1.9**	**5.6**	**12.0**

[a] Calculated according to the 1, 3-random- 2-random hypothesis (Coleman, 1961).

1.5.2. Utilisation of Palm Fractions

Palm oleins and stearin

Palm oleins are used, with or without blending as components of cooking oils, while stearins are used as hard stocks for shortening and margarine manufacture. Table 10 shows examples of such formulations. Palm oleins and stearins are usually refined, bleached and deodorised before they are employed in these formulations. This means that the micronutrients they contain in their crude forms are largely lost during processing to yield bland oils and fats. Some of these micronutrients are then added when the oils and fats are formulated for various food applications.

TABLE 1.10. Zero-*trans*-formulations for a tropical market using palm stearin, palm olein, and groundnut oil (de Graft, 1976).

Product	Palm stearin	Palm olein	Groundnut oil	Palm oil
Table/Cooking oil Grade A	-	50	50	-

Table/Cooking oil Grade B	-	75	25	-
Table/Cooking oil Grade C	-	100	-	-
Bakery Fat (Shortening)	70	-	-	30
Premium Table Margarine (m.p. 29-31°C)	45	-	15	40
Standard Table Margarine (m.p. 37°C)	20	-	-	80

Palm olein in dairy substitutes

Due to cost, performance, availability and nutritional factors, the replacement of milk fat with vegetable oils (single or blends) is undertaken by food processors. Palm oils or their blends, when substituted for milk fat, offer good taste stability, improved nutritional value, desired crystallisation behaviour and favourable cost. Vegetable oil processing technologies offer refined, bleached, and deodorised palm oils and fats (both mesocarp and kernel) of highest quality, opening up possibilities for their application as milk fat replacer in dairy products (Oboh, 2012). Some commercial products containing vegetable fat as dairy fat replacer are shown in Table 1.11.

Table 1.11. Product formulations containing vegetable fat as milk fat replacer (Halliday, 1968; Oboh, 2012).

Formula	**Filled milk %**	**Imitation milk%**	**Coffee whitener%**	**Imitation sour cream%**	**Whipped topping: with milk solids%**	**Whipped topping: with sodium caseinate**
Vegetable fat	3.5	3.5	8-11	14-18	23-28	24-28
Corn syrup	-	1.5-3.0	9-11	-	3-5	-
Sucrose	-	3-5	-	-	7-10	10-15
Stabiliser	-	0.3-0.6	0.3-0.5	0.5-0.75	0.2-0.4	0.2-0.4
Skim milk solids	10.0	-	-	8-10	5-7	-
Sodium caseinate or soy protein		1.0-3.5	1-2	-	-	1-2
Phosphates		0.1-0.2	0.25-0.4	-	-	-
Emulsifiers	0.1-0.2	0.1-0.3	0.2-0.5	0.2-0.5	0.5-1.0	0.5-1.0
Water	To 100	To 100	To 100%	To 100	To 100	To 100

Palm Mid-Fraction (PMF)

Palm mid-fraction (PMF) resembles cocoa butter in its SUS content (Table 1.12), but lacks the stearic acid content of the latter (Table 1.13). PMF is used, after further modification by transesterification with high-stearic content hydrogenated fat using a chemical catalyst, or by the use of a *regio*-specific lipase for replacement of some of the palmitic acid in its 1, 3- positions with stearic acid (Maragoni and Ghazani, 2012) (Fig. 1.3).

TABLE 1.12. Cocoa butter triacylglycerol compositions [a-]

Cocoa Butters	**Composition: Types***				**Composition: Isomers***			
	S_3	**S_2U**	**SU_2**	**U_3**	**SUS**	**SSU**	**USU**	**UUS**
Main Accra[a]	7.0	75.4	16.7	0.9	73.8	1.6	0.1	16.6
Season's Arriba[a]	12.5	71.1	15.8	0.9	68.4	2.7	0.2	15.6
Superior Bahia[a]	6.5	68.3	23.3	1.8	66.1	2.2	0.2	23.1
Youngs[b] – Found	5.0	73.0	23.0	1.0	66.0	7.0	3.0	20.0
Calculated	5.0	71.0	27.0	2.0	69.0	2.0	0	22.0
Vander Wal[c]	7.1	67.5	23.3	2.1	65.0	2.5	0.2	23.1
Coleman[d]	2.7	81.3	15.3	0.7	80.8	0.5	0	15.3
Palm Mid-Fractions								
Oboh[e]	8.3	67.6	22.2	1.9	64.8	2.8	0.3	21.9
Deffense[f]	2.1-6.7	62.1-74.6	16.7-31.5	2.0-4.3	62.1-74.6	-	-	16.7-31.5

[a]Chacko and Perkins (1964); [b]Youngs (1961); [c]VanderWal (1960); [d]Coleman (1961); [e]Oboh (1984, 2007b); [f]Deffense (1985). *S = Saturated fatty acids (composed of stearic and palmitic in cocoa butter, but mainly palmitic in palm mid fractions). U= Unsaturated fatty acids (mainly oleic)

Table 1.13. Fatty acid composition of cocoa butter and palm mid-fraction (PMF)

Fatty acids	**Cocoa butter (Gordon *et al.*, 1979)**	**PMF (Oboh, 1984)**
8:0	-	-
10:0	-	-
12:0	-	
14:0	Trace	1.2
16:0	25	48.5
18:0	35	6.6
18:1	37	36.4
18:2	3	7.3
Others	<1	-

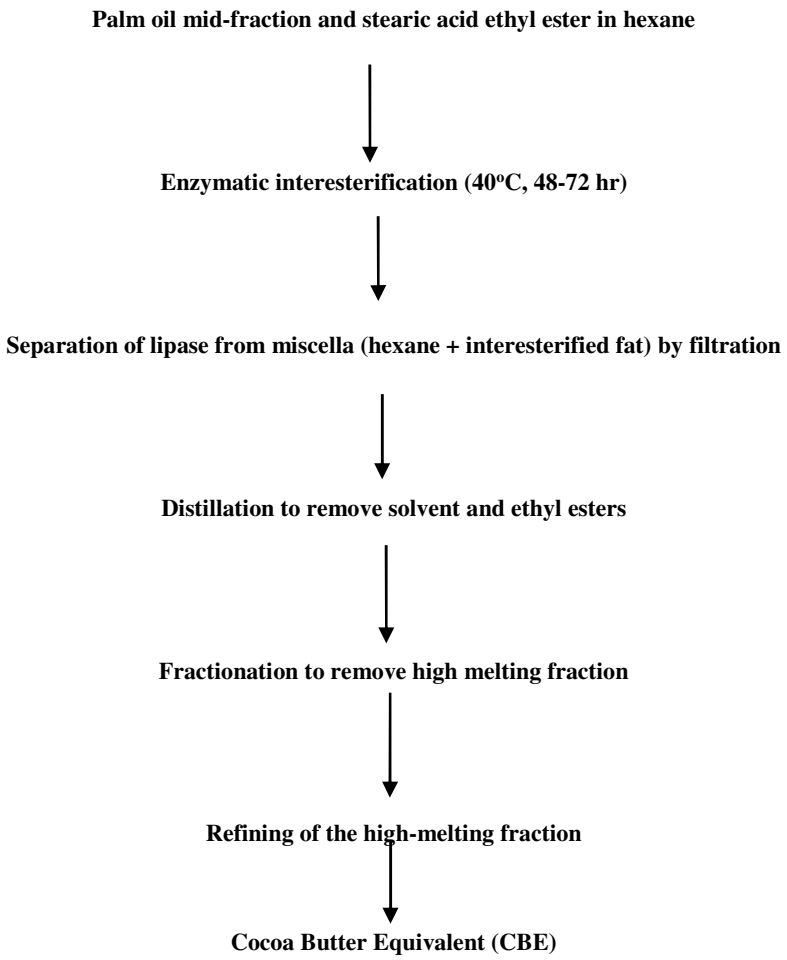


Figure 1.3: Preparation of CBE from PMF by interesterification catalysed by regio-specific lipase (Maragoni and Ghazani, 2012)

1.6. Crude Palm Oil: Some Aspects of Quality

1.6.1. Factors affecting extracted oil quality

The quality of oil from the extraction process depends on the handling of the oil-bearing material prior to processing. Four basic considerations serve to guide any good fat recovery operation and process selection. These are:

Time: Raw material quality usually falls with time.

Temperature: Unless placed under strict control, temperature accelerates raw materials deterioration. Generally, every 10°C rise in temperature doubles raw material hydrolysis. Particularly destructive to oleaginous (oil-bearing) material, product and by-product quality, is the temperature range in which lipolytic and proteolytic organisms thrive.

Microorganisms and enzymes: Poor harvesting schedules, handling and storage of oleaginous materials, their products and by-products can lead to loss of quality. Unhygienic handling may result in infection of oleaginous material by spoilage microorganisms. Over ripening of fruits or bruising may bring endogenous oil and enzyme together, resulting in hydrolysis of the former and the development of off-flavours.

Moisture: Raw materials for oil extraction, if not properly dried, will undergo deterioration during storage due to microbial infection. Also, excessive moisture may impair oil extraction.

Palm oil is the dominant cooking oil in Nigeria. Its production surpasses by far, that of other locally produced oils, such as groundnut, cottonseed, coconut, and palm kernel oils. In addition to its fatty acid composition, which consists of an excellent mix of saturated, monounsaturated, and diunsaturated fatty acids, palm oil has high content of ß-carotene (provitamin A), and tocopherols and tocotrienols (vitamins E). These characteristics confer on palm oil, nutritional and functional properties, and high resistance to oxidative deterioration.

The quality of palm oil can be vitiated, however, by inadequate harvesting schedules, leading to over-ripening of fruits and long storage times of the harvested fruit bunches prior to milling, the latter resulting also in over-ripening, and the proliferation of lipolytic fungi on the fruitlets. Contamination by Cu and Fe during milling of fruits and storage of oil can also result in oil of poor quality. This study was undertaken to determine the quality of palm oil from different sources, and to relate this to mill practices and oil storage methods.

1.6.2. Results and implications

Palm oil samples were taken from the various sources and analysed. Samples 1-4 were obtained from markets in Benin City. Sample 5 was taken from the Stork Amsterdam mill at the Nigerian Institute for Oil Palm Research (NIFOR), near Benin City, and sample 6 from the Oil Palm Company's Cowan Estate in Ajagbodudu, Delta State. The results of the analysis are shown in Tables 1.14 and 1.15.

Some chemical characteristics of the samples are presented in Table 1.14. Saponification value (200.8-205.0) and iodine values (54.2-57.1) were in agreement with literature values for palm oil (Cocks and van Rede, 1966). These values are related to the fatty acid composition, and are characteristic of the oil, varying only within narrow limits. They are therefore quick methods for

determining if oil is adulterated with other oil(s). The results indicate that that there was no admixture with other oils.

The FFA content of the oils varied from 3.8 for NIFOR oil to 17.3% for one of the market samples. With the exception of sample 2, all the market samples had high FFA values. Sample 6 also had a high FFA content; while 1-4 had been subjected to handling after production by middlemen and retailers, 6 was drawn straight from the mill, after extraction, but before storage. The high FFA was therefore present in the fruits before oil extraction and may have arisen from harvesting of over-ripe fruits and /or long storage of fruit bunches after harvesting, prior to milling leading to over-ripening of fruits. The mill from which the sample was taken was built in the 1930s and was experiencing frequent breakdowns resulting in delayed harvesting and accumulation and long storage of harvested fruit bunches prior to milling (Mr. Ighalo, Mill Manager, Oil Palm Company, Ajagbodudu, 1983. Personal communication). These factors obviously led to over-ripening of fruits, resulting in FFA build-up due to cell wall rupture resulting in mixing of intracellular lipase with oil stored in the fruit mesocarp.

A practice in many small mills is the quartering and gathering of FFB in heaps for long periods (up to 2 or 3 weeks) to aid the loosening of fruitlets from the bunches and also to soften them in order to facilitate digestion. Oil yield on milling is believed to be higher, but would have a high FFA content. If samples 1, 3, and 4 were produced under such condition they would be expected to have high FFA content. Contamination of the oil by water and dirt may also cause lipolysis and high FFA. Dirt may contain lipolytic organisms, the presence of moisture creating the right environment for their proliferation, and activity of the lipase, which they produce, to split the ester bonds of the oil triacylglycerols, with release of FFA. According to Eggins and Coursey (1968), lipolytic enzymes are responsible for the build-up of FFA during storage, the amount of FFA produced being dependent on the length of storage and the degree of microbial infection.

Table 1.14: Some chemical characteristics of crude palm oil (Oboh, 1984, 2004)

Characteristics	**SAMPLES**			**PORIM[c] (Stage, 1985)**
	Markets in Benin City	**NIFOR[a]**	**OPC[b] Ajagbodudu**	

	1	2	3	4	5	6	
Iodine value (Wij's)	57.1	57.1	57.1	56.6	54.2	55.6	52.9
Saponification value	201.0	205.0	200.8	202.0	200.8	201.0	195.7
Free fatty acid (FFA) (% palmitic)	10.1	5.3	14.0	17.3	3.8	7.4	3.15
Peroxide value (meq/kg)	3.5	4.3	2.0	4.8	0.8	2.0	3.9
Carbonyl value (mg/g)	0.42	0.23	0.68	0.17	0	0.05	-
Total monoacylglycerols (%)	0.52	0.56	0.76	0.86	0.54	0.33	
ß-carotene (mg %)	160.0	110.0	210.0	210.0	160.0	160.0	60.0
Total tocopherols (mg/g)	1.0	1.2	1.7	1.6	1.3	1.1	0.8
Cu (ppm)	0.50	0.50	0.88	0.88	0.70	0.13	0.04
Fe (ppm)	40.0	12.0	32.8	17.2	5.0	10.0	4.0

[a]Nigerian Institute for Oil Palm Research; [b]Oil Palm Company, Ajagbodudu; [c]Palm Oil Research Institute of Malaysia

For culinary application, crude palm oil of low FFA content is obviously not a requirement in Nigeria. On the contrary, there appears to be a preference for high FFA oil for the preparation of certain indigenous dishes. In palm oil processing however, a high FFA value is regarded as an indicator of bad harvesting, milling, handling, and/or storage practice, resulting in losses during the refining of the crude oil.

Peroxide values (PV) ranged from 0.8 meq/kg oil for sample 5 to 4.8 meq/kg for sample 3. Unless the history of a fat is well known, its peroxide value (which is a measure of the degree of primary oxidation it has undergone, must be accompanied by determination of the extent of secondary oxidation of the fat as well (the carbonyl value in this study). Samples 3 and 6 had the same PV (2 meq/kg). However, while sample 3 had a carbonyl value (CV) of 0.68 mg/g, sample 6 had a value of 0.05 mg/g, indicating that the latter had undergone far less oxidation than the former. Sample 5 had a low PV of 0.8 meq/kg, and a CV of 0, indicating that it had undergone very little oxidation.

Peroxide and carbonyl values measure the extent of primary and secondary oxidation respectively. They are dependent on the degree of contact of the fat with atmospheric oxygen and the extent of

its exposure to the agents that enhance autoxidation – light, heat, and transition metals (especially iron and copper). Also important in this regard are free fatty acids which serve to solubilise these metals (Sherwin, 1976). The secondary reaction, hydroperoxide decomposition, occurs readily in the presence of metal catalysts, and the rate of its decomposition eventually exceeds the rate of formation. Thus, peroxide value attains a maximum and then declines.

Iron and copper content of the samples were high, with values ranging from 5.0-40.0 ppm for Fe, and 0.23-0.88 ppm for Cu. Iron and copper are very active pro-oxidants even in trace amounts of less than 1 ppm, Cu being more pro-oxidant than Fe (Jacobsberg *et al*., 1978; Sherwin, 1976). Contamination with iron and copper derives mainly from wear of metal parts of processing equipment through contact with oil-bearing material. This can easily be observed in locally fabricated digesters, presses, and handling equipment (wheelbarrows and headpans) for the transfer of digested material from the digester to the press. To achieve low Cu and Fe content, it is important that the right grade of steel be used in the construction of milling equipment. By the use of stainless steel in specific areas in the milling process, it is possible to reduce the Fe content to 1 ppm (Stage 1985). Particulate iron can be removed by filtration or the use of magnetic pipeline inserts. These devices are not included in the small locally fabricated mills and low-quality steel is used for their construction. It is probable that the market samples (1, 2, 3, and 4) with high Fe content (40.0, 12.0, 32.8, and 17.2 ppm respectively) came from locally fabricated mills. The high FFA content of these samples would serve to solubilise the Fe, making it more active as a prooxidant.

In their role as pro-oxidants, the metals act primarily by facilitating decomposition of hydroperoxides (R-O-O-H) to additional free radicals (Holman, 1954). Although thermal decomposition of these compounds gives the radicals $RO^{\cdot}$ and $HO^{\cdot}$, both of which are active enough to attack the C-H bonds of organic compounds, the decomposition rate is slow (Bateman and Hughes, 1952). The ions of a number of transition metals, notably Fe and Cu are however effective as secondary catalysts of autoxidation and function as one electron donors to give $RO^{\cdot}$ radicals:

$$R\text{-}O\text{-}O\text{-}H + M^{2+} \rightarrow RO^{\cdot} + M^{3+} + OH^{-} \text{ (M = metal)}$$

The oxidation $M^{3+} \rightarrow M^{2+}$ is followed by a second radical producing reaction:

$M^{3+} + RH \rightarrow R\cdot + M^{2+} + H^{+}$ (RH = olefinic system) (Smith and Waters, 1969)

The hydrocarbon radical $R^{\cdot}$ is a good reducing agent. This has been demonstrated with both Fe^{3+} and Cu^{2+} (Collinson *et al.*, 1960; De laMare *et al.*, 1963)

$M^{3+} + R\cdot \rightarrow \mathbf{M^{2+} + R^{+}}$

$R^{+} + OH^{-} \rightarrow ROH$

Consequently, alcohols and their oxidation products, aldehydes and ketones, rather than hydroperoxides are the major products of metal catalysed autoxidation and the unpleasant odour of rancid oils and fats is due to these aliphatic compounds of fairly low molecular weight produced by the oxidative scission of long hydrocarbon chains of lipid molecules. As should be expected, from the foregoing, the samples 1 – 4, which had high Fe and Cu content, coupled with high FFA content acting to solubilise the metals, also had relatively high carbonyl values.

Monoacylglycerol content varied from 0.33 for sample 6, to 0.86% for sample 4, in agreement with Berger (1977) that the level of these compounds in crude palm oil (even oils of relatively high FFA) is usually not more than 1%. A disadvantage of high monoacylglycerol content (i.e., > 0.5%) in oil is the depression of its smoke point.

The ß-carotene (110.0-210.0 mg %) and tocopherol (1.0-1.7 mg/g) contents of the samples were relatively high. The high ß-carotene (pro-vitamin A) and total tocopherol (vitamin E) content of palm oil is very important from the nutritional standpoint. In addition, the tocopherols are potent antioxidants, and serve to stabilise oils and fats against oxidative deterioration. The relatively high stability of palm oil has been attr

ibuted largely to its fatty acid composition and distribution in the triacylglycerols, and its high tocopherol content (Sherwin, 1976; Hartley, 1988; Kamal-Eldin and Appelqvist, 1996).

Table 1.15 shows the fatty acid composition of the four palm oil samples obtained from local markets. Palmitic acid (41.1-52.0 wt %) and oleic (32.6-43.8) were the dominant fatty acids, followed by linoleic acid (6.7-9.4), and stearic (3.9-5.1). Lauric (0.3-3.4) and myristic (0.5-1.4 wt %) were minor constituent fatty acids. These findings were in agreement with reported values for palm oil (Rossel *et al*., 1985; Cocks and van Rede, 1966).

TABLE 1.15. Component fatty acids (wt %) of palm oil samples obtained from local markets

	Fatty acids					
Oil samples	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Sample 1	0.3	0.8	47.4	5.1	38.8	7.6
Sample 2	3.4	1.4	52.0	3.9	32.6	6.7
Sample 3	0.8	1.3	47.2	5.1	36.2	9.4
Sample 4	2.8	0.5	41.1	4.2	43.8	7.6

The susceptibility of palm oil to autoxidation, with or without antioxidant was determined, using the Schall Oven Method at 60±0.5^{o}C. The test oil had the characteristics given in Table 1.16, and the 2, 6-di-tert-butyl -4-methyl phenol (BHT) and citric acid were employed at concentrations of 0.02 BHT and 0.02 citric acid based on the weight of the oil. The result (Figure 1.4) indicates that when used in combination, both compounds were very effective for the protection of the oil against oxidative deterioration during handling and storage, even in the presence of a relatively high content of FFA, and Fe, a highly potent pro-oxidant, due to the effect of the citric acid which chelates pro-oxidant metals, rendering them unavailable for the catalysis of the oxidation process.

Table 1.16. Characteristics of the test palm oil (Oboh, 1984; 2004)

Characteristic	**Value**
Iodine value (Wij's)	55.6
Saponification value	201.0
Free fatty acids (as % palmitic acid)	7.4
Peroxide value (meq/ kg)	0.8
Carbonyl value	0.05
ß-Carotene (mg %)	160.0
Total tocopherols (mg/ g)	1.1
Cu (mg/L)	0.13
Fe (mg/L)	10.0

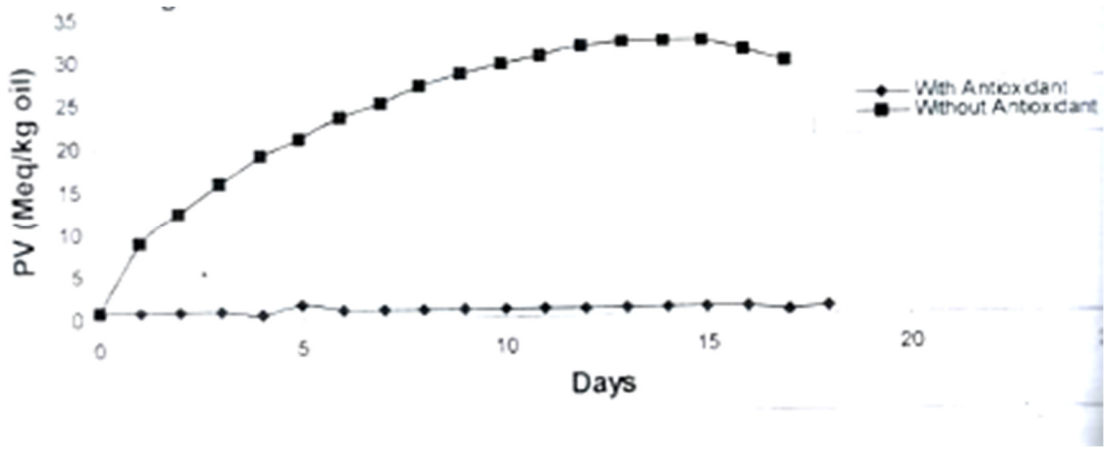


Fig. 1.4: Schall oven stability plots for crude palm oil [a]**Concentration of antioxidant mixture: 0.02% BHT, 0.02% citric acid based on wt of oil palm oil**

Conclusions

1. The palm oil samples did not come from adulterated sources, having satisfied all the characteristics typical of crude palm oil

2. The susceptibility of palm oil to oxidative deterioration could be minimised through treatment with BHT in combination with citric acid.

1.7. Post-MSc Research

I went back to my job as Research Officer 1 at NIFOR on the completion of my studies towards the MSc degree in biochemistry in 1984. I continued with my work on palm oil utilisation. In addition, I designed a project for the utilisation of fats and oils from the fruit coat and seeds of some exotic palms grown in the palmatum at NIFOR (Oboh, 1985), titled:

1.7.1. Novel sources of fat, protein and carbohydrate, a survey of the fruits of four Palmae species: *Attalea cohune, Bactris major, Arecastrum romanozoffianum* and *Astrocaryum vulgare.*

I gained admission into the University of Ibadan (for the MPhil/PhD), for which this project formed my research work.

The studies were undertaken at three levels:

1. Exploratory studies were undertaken by:

i. Physical observation of fruit yield and literature survey on the origin and utilisation of the plants in their areas of origin, and information (if any) on the composition and processing of their produce.

ii. Chemical taxonomy to confirm the recorded classification of the palms recorded by the planters.

iii. Determination of the yield characteristics of *Arecastrum romanozoffianum* and *Astrocaryum vulgare* palms.

2. Characterisation of kernels and kernel fats of the Nigerian grown *Bactris major, Attalea cohune, Arecastrum romanozoffianum,* and *Astrocaryum vulgare* palms, and the fruit pulp of the *Arecastrum romanozoffianum* (pindó) and *Astrocaryum vulgare* (tucum) palms, and tucum pulp oil. This was undertaken to determine their suitability for exploitation as oleaginous materials.

3. Refining of tucum pulp oil.

4. Modification, through fractional crystallisation of tucum kernel fat and pulp oil.

5. Possible use of kernel fats, tucum pulp oil, stearin, and tucum olein as food fats and oils, and other applications.

6. Synthesis of fatty derivatives (oleochemicals) from tucum kernel fat, pulp oil, and their oleochemical potential.

7. Possible utilisation of residues from oil extraction

1.7.2. Background to the study

The justification for this work, when it was undertaken (from 1985/86-1987/1988) was as follows:

"Nigeria possesses only five indigenous palm genera containing the following species:

i. *Elaeis guineensis* Jacq. (The African oil palm)

ii. *Phoenix* spp. (the date palms)

iii. *Raphia* spp. (Raffia palms)

iv. *Hyphaene* spp. (the doum palms)

v. *Borassus aethiopium* (Borassus)

The coconut palm (*Cocos nucifera*) is present as a migrant species.

Apart from *Elaeis guineensis* (and the migrant *Cocos nucifera*), the other indigenous species do not produce oil in reasonable quantity. In contrast, vast areas of Central and South America which are the climatic analogue of the Nigerian tropical rain forest and savannah contain a large number of palm genera and species, many of which are local sources of oil and oilseed cake in the area where they are found. The changes within the past few years in the Nigerian oil and fat sector have increased the demand for edible and industrial oils, and oilseed cake for which exotic palms offer a potential. Unfortunately, however, except for the cultivated palms of prime importance to man, the coconut palm (*Cocos nucifera*), the African oil palm (*Elaeis guineensis*), the date palm (*Phoenix dactylifera*), the arecanut palm (*Areca catechu*), and the carnauba wax palm (*Copernicia prunifera*), very little exists about the chemical composition of palm fruit coat and kernel, and the characteristics of the oils which they contain. Of the 225 genera and about 2,700 species of known palms, not more than 30 genera and 50 species have been studied in any detail (Opute, 1979).

In the case of the lesser-known oil palm fruits, kernels and oils for which knowledge is available, it has proved, in some cases to be inadequate for the full realisation of their potential in the light of the present-day technologies available for oilseed and fat utilisation. This situation necessitates more and detailed studies of Palmae fruit produce in order to increase their utilisation".

The guaranteed and continuous supply of raw materials is one of the key factors in the successful operation of a vegetable oil and fat industry. Poor linkage between industry and the producers of raw materials results in decrease both in quantity and quality, and further, to capacity under-utilisation in the industry (Figure 1.5).

To be competitive as a source of oil and fat, oleaginous vegetable material must have residues from oil extraction suitable for commercial exploitation. Thus, production and economics of extracting vegetable oils and fats from oleaginous materials are inextricably linked with the utilisation of residue in animal and human nutrition (Figure 1.5).

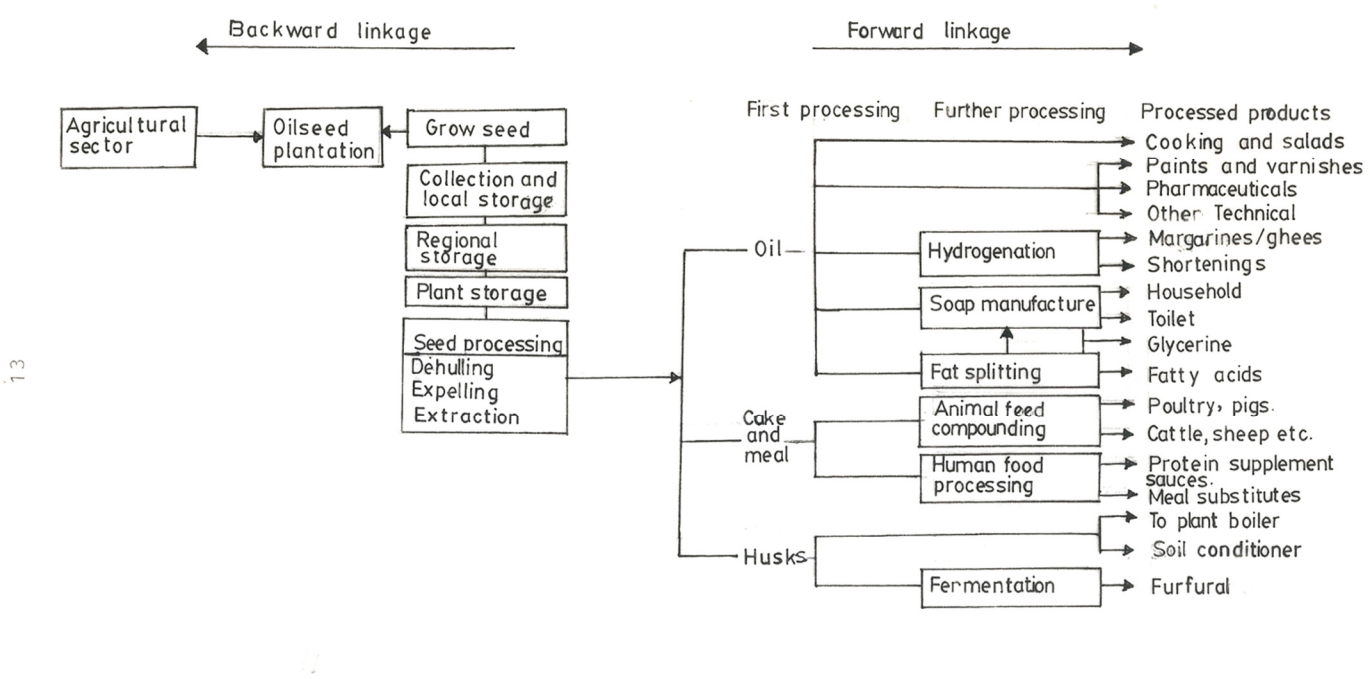


Fig 1.5: Intersectoral production linkages in the oilseed industry (UNO, 1977)

1.7.3. Criteria for Evaluating an Oil Extraction Process

The criteria are as follows (Rose, 1954):

"Having delivered the raw material to the processing unit with all the care and dispatch that economics will permit, the extraction procedure itself should meet, as much as possible, the following criteria:

- The process should deliver the theoretical yield of the products as determined in the raw material.
- The process should produce product quality equivalent to that known to be present in the raw materials received.
- The process must be sufficiently flexible to handle economically and efficiently all the classifications of raw materials to which it will be applied.

- The process must adequately maintain its efficiency and quality under variable load conditions from day to day and season to season, as the supply of raw material varies.

- The process must be inherently self-contained and clean, producing no nuisance and preferably no process discharge that is not a saleable product.

- The process should require a minimum of labour and of electrical, chemical and thermal energy.

- The process should be as simple as possible mechanically, to the end that capital investment, repair, replacement, taxes and insurance costs are kept at a minimum".

1.7.4. Vegetable Oil Extraction

Extraction of crude oil from vegetable raw material is done by mechanical pressing and/or solvent extraction. Both processes can be applied separately or in combination. Residual oil contents of 3-25% in expeller cakes are achieved by mechanical pressing compared with residual oil content of 0.5% or less in extracted meal from solvent extraction.

The solid, often protein rich component remaining after solvent extraction serves (after adequate treatment) as a high-grade animal feed. By modifying the process, these products can be turned into ingredients with high protein solubility for human consumption.

These studies were undertaken to provide the following:

1. Useful information on the fruits, fruit coat (pulp) and kernels as a guide to their improvement and utilisation.

2. A package of technologies for the utilisation, where worthwhile, of the kernel fat and/or pulp oil as raw materials for edible and oleochemical products.

1.8. Selected Palm Species Studied and their Produce

1.8.1. *Bactris major*

Bactris major (Figs. 1.6, 1.7 and 1.8) is a small to medium-sized (1–10 m tall) spiny palm which ranges from Mexico, through Central America into northern South America and Trinidad. The species is divided into three varieties (although the boundaries between varieties is not always clear) as follows (Henderson 2000):

- *Bactris major* var. *major*
- *Bactris major* var. *infesta* (Mart.) Drude
- *Bactris major* var. *socialis* (Mart.) Drude

The plant is sometimes harvested from the wild for its fruits and wood, which are used locally.

It is also grown as a hedge. The fruit pulp, which is sweet and juicy is fermented to yield an alcoholic beverage (Ramírez-Amezcua 2010).

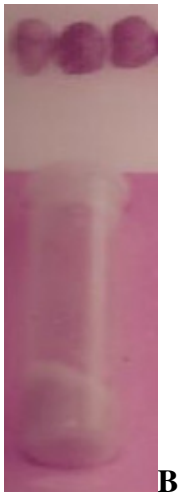
Fig. 1.6: *B. major* palms in the Palmatum of the Nigerian Institute for Oil Palm Research, 1985 (Oboh, 1994b).

A.  B. 

Fig. 1.7: A. Ripening *Bactris major* fruits (Fern *et al*. 2014)

B. Ripe fruits of *Bactris major* var. *major* (Ramírez-Amezcua 2010)

A



B

Fig. 1.8 A: The dried mature *B. major* fruit **B. *B. major* kernels and oil.**

Source: A. Environmental Sciences Program, Smithsonian Tropical Research Institute. © *Smithsonian Tropical Research Institute*. B. Oboh (1994b)

1.8.2. *Attalea cohune*

The cohune palm is a massive but slow-growing, single stemmed, evergreen palm, that can eventually grow to more than 20 m tall. The stem can reach up to 60 cm in diameter, topped by a crown of extremely long leaves that can measure up to 10 m long (Henderson *et al*. 1995). The wild cohune palm (Fig. 8A, B, and C) bears 1,000-2,000 fruits a year in bunches measuring about

1 m in length and weighing 20-25 kg. The fruits require a year to reach maturity. The tough outer fibrous layer (pulp) enclosing the nut contains 8-10% oil, but sometimes considerably more (Jamieson 1943).

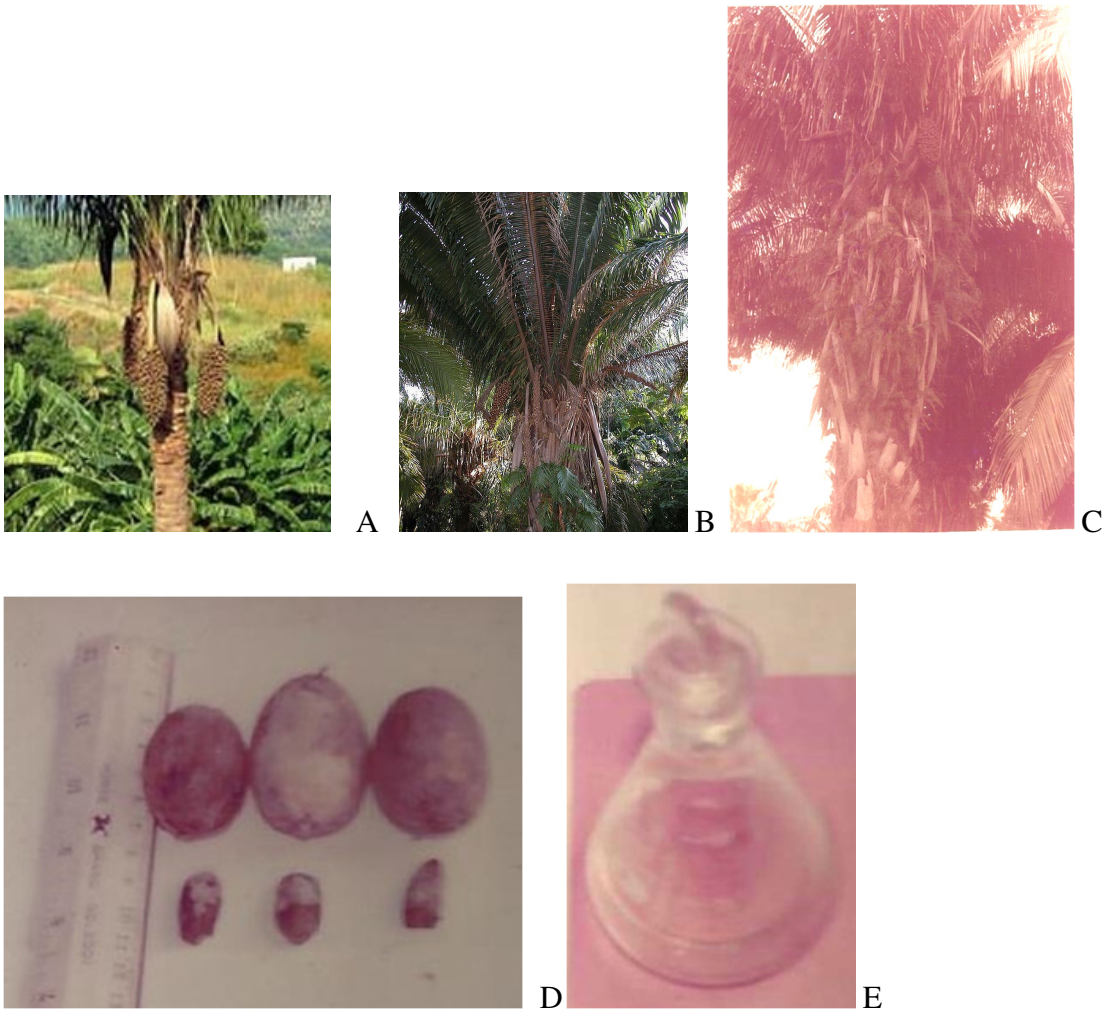


Fig. 1.9: A, B, and C: *Attalea cohune* palms.

A. Fruiting cohune palm in habitat, Mexico. B. In Hawaiian Tropical Botanical Garden (Palmpedia). C. In the palmatum of the Nigerian Institute for Oil Palm Research (NIFOR), near Benin City, Nigeria, 1985; D. Fruits (top) and kernels (below); E. Oil. (Oboh 1994b).

The oil has characteristics similar to those of *Elaeis guineensis* kernel oil, and is used for cooking and soap manufacture (Jamieson 1943, Williams 1966). The high fruit yield of the cohune palm

coupled with the presence of a considerable amount of oil in its fruit-coat provides additional incentives for its exploitation as an oleaginous crop.

1.8.3. *Syagrus romanozoffiana* (syn. *Arecastrum romanozoffianum*), the Pindó Palm


A


B


C


D


E

Fig. 1.10: A. Fruiting *A. romanozoffianum* palm (http:/www.plantsystemstics.org). B. Immature fruit bunch (*http://www.dpi.qld.gov.au*). C. Ripe fruits (palmpedia.net). D. An *Arecastrum romanozoffianum* palm in NIFOR 1985; E. Nuts (top), kernels (middle), and fat bottom (Oboh 1994b).

The *A. romanozoffianum* (syn. *Syagrus romanozoffiana*) palm (Fig. 1.10A and D), variously known as Queen's palm, plumy coconut or pindó palm, is indigenous to south eastern South America (Ruddle *et al*. 1978). The palm is a monotype, has an erect solitary slender trunk, 10-15 m long, and large pinnate leaves. It is a palm of both the tropical and sub-tropical forest and has an annual flowering and fruiting season. The cultivated *A. romanozoffianum palm* is a popular street palm in tropical and sub-tropical regions. The wild palm is utilised for its stem starch and palm heart (cabbage) (Ruddle *et al*. 1978).

The pindó palm bears 3-4 bunches annually, each weighing 25-40 kg, and containing numerous oval shaped fruits. Pindó bunch and fruit characteristics are shown in Table 1.17. The fruits weigh 12-19 g with a pulp: shell: kernel ratio of 67:23:10, and consist of a slimy, sweet and fibrous outer pulp, which is composed on a dry weight basis, mainly of carbohydrate (Oboh 1985, Oderinde and Oboh 1988). The shell encloses a hard kernel, which contains about 32-65% of a light-yellow fat (Earle and Jones 1962; Oboh 1985, Oderinde and Oboh 1988), similar in composition to palm kernel oil (Table 1.17). Kernel and kernel fat characteristics indicate that the *A. romanozoffianum* palm has potential as a commercial source of high lauric vegetable fat and high carbohydrate kernel cake. The latter could be of use as a high energy additive in livestock feed while the kernel fat is suitable for use as confectionery fat (Oboh and Oderinde, 1988c), as a component of margarine and shortening blends, and as a source of medium chain fatty acids for the production of oleochemicals (Oboh, 1985; 1987b).

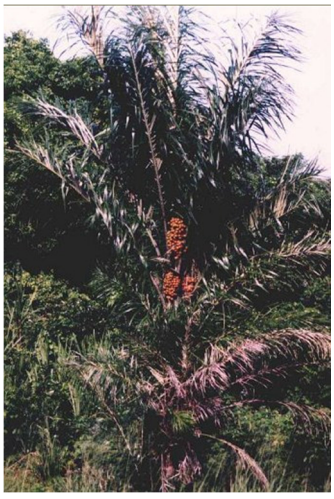
TABLE 1.17: Pindó fruit bunch composition, fruit gross composition and kernel composition (Oboh 1985, Oboh 1987b, Oderinde and Oboh 1988)

Bunch Characteristics	
Average bunch wt	28 kg
Bunch composition	% by wt
Fruits	90.0
Bunch refuse	10.0
Fruit characteristics	

		Pulley and von Loesecke (1941).
Pulp	67.0	23.0
Shell	23.0	69.0
Kernel	10.0	8.0
Average fruit weight (g).	12.0-19.0	-
Average kernel weight (g).	1.5	-

1.8.4. *Astrocaryum vulgare*

Astrocaryum palms belong to the genus *Astrocaryum,* which includes about 40 species of prickly cocosoid palms. They are indigenous to the evergreen rain forest of Central and South America up to an altitude of 2,000 ft., and are distributed in 12 countries being well represented in Brazil, Peru, Columbia, and in the Guianas, with 26, 14, 11 and 10 species, respectively. Eight species are endemic to Brazil, 4 to Colombia, and 4 to Peru. The habitat of these palms ranges from the flood plains of alluvial rivers and swamps that are under water for more than half the year (*A. jauari* and most varieties of *A. murumuru*) to well drained forests far above the level of high water (*A. tucuma* syn*: A. aculeatum* and *A. vulgare*) (Scultes 1977, Kahn 2008).


A


B


C


D

E

F

Fig. 1.11. A and B: Fruiting *A. vulgare* palms. Sources: A. Pallet (2007), B. Amazon Oil Industry (http://www.amazonoil.com.br/en/) **C. An *Astrocaryum vulgare* bush at the Nigerian Institute for Oil Palm Research Palmatum, with the author in the foreground, 1985 (Oboh 1994, 2009a). D. *Astrocaryum vulgare* halved fruits. E. *Astrocaryum vulgare* fruits, nuts, and oil. F. Kernel fat (Oboh 1994). Source:** https://en.wikipedia.org/wiki/Astrocaryum_vulgare

Figures for the *A. vulgare* fruit composition vary. Eckey (1954) gave a fruit weight range of 15-20 g, of which the pulp constituted 34%, shell, 46%, and seed (kernel), 20% for South American fruits. For Nigerian grown fruits, Oboh and Oderinde (1988b) gave fruit weight of 30-38 g (Table 1.18), with the pulp constituting about half (51%), the shell, about a third (36%) and the kernel, 13%. The following are some of my findings.

TABLE 1.18. *Astrocaryum vulgare* fruit composition (pulp: shell: kernel analysis (% fresh wt.)

Component	Oboh and Oderinde (1989)	Eckey (1954)
Pulp	51.0	34.0
Shell	36.0	46.0
Kernel	13.0	20.0
Fruit weight (g)	30.0-38.0	15.0-20.0

1.8.5. Oilseed (kernel) composition

The compositions of *Bactris major, Attalea cohune* (cohune), *Arecastrum romanozoffianum* (pindó), and *Astrocaryum vulgare* (tucum) kernels (seeds) are shown in Table 1.19.

Table 1.19. Proximate composition of palm kernels from sun-dried nuts

Characteristic	*Attalea cohune*[a]	*Bactris major*[b]	*Arecastrum rommanozoffianum*[c]	*Astrocaryum vulgare*[d]	*Elaeis guineensis*[e]
Moisture	2.8	6.0	6.0	5.1	8.0
Crude protein	1.5	12.7	6.6	5.6	8.5
Crude oil	65.8	21.4	33.0	41.1	49.0
Crude fibre	3.3	3.8	3.1	2.2	5.8
Ash	1.5	2.6	1.7	1.2	1.8
Nitrogen free extract	25.1	53.5	49.6	44.9	26.9
Texture of kernel	Hard	Hard	Hard	Hard	Hard

[a]Oboh (1985), Oboh and Oderinde (1988a). [b]Oboh (1985;1987) [c]Oboh (1985), Oderinde and Oboh (1988). [d]Oboh (1985), Oboh and Oderinde (1988b) [e]Halliday (1972)**.**

The kernels were of a hard texture and had oil content ranging from 21.1% (*Bactris major*) to 65. 8% (*Attalea cohune*). These kernel characteristics determine the mode of extraction of oil from them. Thus, palm kernels require seed preparation equipment of somewhat different design than those required for the processing of soft oilseeds, such as groundnuts and sunflower. For the harder oilseeds, harder wearing screws are utilised and expeller barrel design is slightly different. Seeds with high oil content may require a pre-pressing stage prior to final pressing or solvent extraction, while materials of low oil content, for example soybean (about 20%) and *B. major* oil (21.4%), or the press cakes from preliminary pressing of high oil content seeds can be subjected to a straight solvent extraction.

Figure 1.12 illustrates recommended large scale extraction procedures for the kernels.

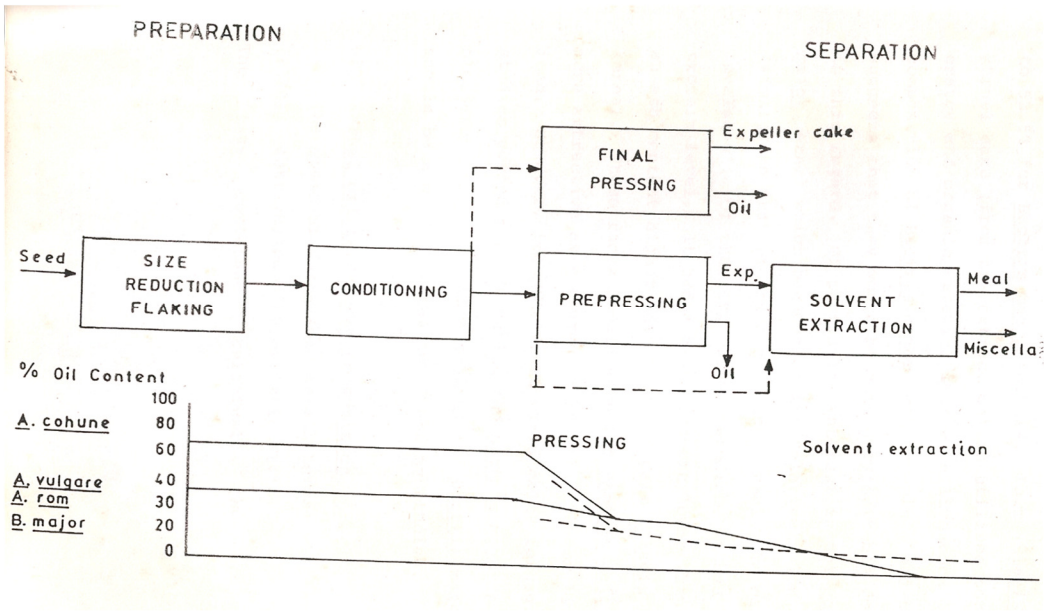


Fig. 1.12: Recommended extraction processes for oilseeds

To be competitive as source of oil of fat, oleaginous vegetable material must have residues from oil extraction suitable for commercial exploitation. Thus, production and economics of extracting vegetable oils and fats from oleaginous materials are inextricably linked with the utilisation of residue in animal and human nutrition (Figure 1.5). Palm (*E. guineensis*) kernel cake (from oil extraction) is utilised both as an energy and carbohydrate source in livestock feed.

The composition of *B. major, A. cohune, A. romanozoffianum* and *A. vulgare* suggest that they should be eminently suitable for use in this regard.

1.8.6. Fatty acid Composition and Physico-Chemical Characteristics of the Kernel Oils

The fatty acid composition and physico-chemical characteristics of the test kernel oils and oil palm (*Elaeis guineensis*) kernel oil and coconut (*Cocos nucifera*) oil are shown in Table 1.20.

Table 1.20: Fatty acid composition and physico-chemical composition of palm kernel oils

Fatty acids	*Bactris major*[a]	*Attalea cohune*[b]	*Arecastrum romanozoffianum*[c]	*Astrocaryum vulgare*[d]	*Elaeis guineensis*[e]	*Cocos nucifera*[f]
6:0						

8:0	2.9	4.0	1.7	2.0	3-4	5-10
10:0	4.7	6.0	2.9	2.4	3-7	4-15
12:0	41.6	42.4	55.5	45.5	46-52	37-51
14:0	21.3	18.7	20.4	20.2	14-18	7-19
16:0	8.5	8.3	6.6	5.6	6-9	2-11
18:0	3.1	2.1	1.7	5.6	1-3	1-3
18:1	13.6	14.9	10.2	12.7	10-19	5-8
18:2	4.4	3.6	1.7	6.0	0.5-1.5	1-3
Saponification value	242.6	241.0	237.0	232.1	246.0-249.0	254.0-258.0
Iodine value	16.5	18.9	13.6	14.5	14.5-19.0	7.5-7.9
Slip point	27.0	27.0	27.0	30.0	26.0-29.0	23-26
Free fatty acid% (as lauric acid)	0.4	0.9	1.6	1.85	0.5-10.0	1-6
Consistency at ambient temperature	Semi-solid	Liquid	Solid	Solid	Semi-solid	Liquid

[a] Oboh (1985;1987) [b] Oboh (1985), Oboh and Oderinde (1988a).[c] Oboh (1985), Oderinde and Oboh (1988). [d]Oboh (1985), Oboh and Oderinde (1988b) [ef]Williams (1966)

It is clear from Table 1.20 that the fatty acid compositions of the seed (kernel) oils bear more resemblance to palm kernel oil than to coconut oil in their lower content of the short and medium chain fatty acids (C8-14) and saponification values.

1.8.7. Lipid Composition

Triacylglycerols were the dominant lipid species in the kernel oils.

Table 1.21. Lipid composition of kernel oils

Species	**Lipid Classes (Mean±SD mol %)**						
	TAG[1]	**DAG[2]**	**MAG[3]**	**FFA[4]**	**ST[5]**	**SE/HC[6]**	**PL[7]**
Bactris major[a]	95.0±0.1	1.5±0.1	0.4±0.0	0.4±0.0	0.3±0.0	0.8±0.0	0.5±0.0
Attalea cohune[b]	95.6±0.1	1.8±0.1	0.6±0.0	0.9±0.0	0.4±0.0	0.8±0.0	0.4±0.0

Arecastrum romanozoffianum[c]	95.1±0.2	1.5±0.1	0.3±0.0	1.6±0.1	0.4±0.0	0.7±0.0	0.4±0.0
Astrocaryum vulgare[d]	94.76±0.04	1.40±0.01	0.22±0.00	1.85±0.01	0.73±0.01	0.66±0.01	0.39±0.01

[1]TAG =Triacylglycerols, [2]DAG=Diacylglycerols, [3]MAG=Monoacylglycerols, [4]FFA =Free fatty acids, [5]ST=Sterols, [6]SE/HC =Sterol Esters and Hydrocarbons, [7]PL=Phospholipids. [a]Oboh (1985;1987). [b]Oboh (1985), Oboh and Oderinde (1988a). [c]Oboh (1985), Oderinde and Oboh (1988). [d]Oboh (1985), Oboh and Oderinde (1988b).

1.8.8. Triacylglycerol Analysis

Fatty acid distribution in triacylglycerols

Table 1.22. Fatty acid distribution in triacylglycerols of kernel oils

Bactris major*	**Fatty acid composition (Mean±SD mol %)**							
Fatty acids	**8:0**	**10:0**	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Whole fat	4.3	6.5	45.7	19.6	6.5	2.2	10.9	4.3
TAG	4.5±0.0	8.5±0.0	54.5±0.2	14.2±0.1	5.8±0.0	1.3±0.0	8.9±0.1	2.4±0.0
2-MAG	0.1±0.0	2.4±0.1	73.6±0.2	8.4±0.2	3.4±0.0	0.0	10.1±0.1	2.0±0.0
Proportion in 2-Position	0.7	9.7	45.0	19.7	8.0	-	37.8	27.8
Proportion in 1, 3-Position	99.7	90.3	55.0	80.3	92.0	-	62.2	72.2

*[a] Oboh (1985;1987).

Attalea cohune*	**Fatty acid composition (Mean±SD mol %)**							
Fatty acids	**8:0**	**010:0**	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Whole fat	6.0	7.6	45.7	17.7	6.9	1.9	11.4	2.8
TAG	6.0±0.1	5.8±0.0	49.6±0.2	14.4±0.1	7.2±0.3	3.0±0.0	11.8±0.1	2.2±0.0
2-MAG	T	1.7±0.1	74.4±0.1	12.8±0.1	1.9±0.1	-	7.7±0.0	1.5±0.0
Proportion in 2-Position		9.8	50.0	29.6	8.8	-	21.8	22.7
Proportion in 1, 3-Position		90.2	50.0	70.4	91.2	-	72.8	77.3

*[b] Oboh (1985), Oboh and Oderinde (1988a).

*Arecastrum romanozoffianum**	Fatty acid composition (Mean±SD mol %)							
Fatty acids	**8:0**	**10:0**	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Whole fat	2.1	2.1	58.3	18.7	6.3	2.1	8.3	2.1
TAG	2.2±0.0	2.2±0.0	57.6±0.2	24.0±0.2	4.4±0.0	8.1±0.0	7.8±0.0	-
2-MG	0.9±0.0	1.3±0.0	76.6±0.2	12.8±0.1	1.9±0.0	-	6.3±0.0	-
Proportion in 2-Positition	13.6	19.7	44.4	17.8	14.4	-	26.9	-
Proportion in 1, 3-Position	86.4	80.3	55.6	82.2	85.6	-	73.1	-

*[c]Oboh (1985), Oderinde and Oboh (1988).

Astrocaryum vulgare	Fatty acid composition (Mean±SD mol %)							
Fatty acids	**8:0**	**10:0**	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Whole fat	2.2	2.2	51.1	20.0	4.5	4.5	11.1	4.4
TAG	2.3±0.0	2.3±0.0	54.5±0.2	25.0±0.1	4.5±0.0	6.8±0.0	6.8±0.0	2.3±0.0
2-MG	0.4±0.0	0.4±0.0	66.8±0.4	21.0±0.2	3.4±0.1	0.7±0.0	6.6±0.1	0.7±0.0
Proportion in 2-Position	5.8	5.8	40.9	28.0	25.2	10.2	32.4	10.1
Proportion in 1, 3-Position	94.2	94.8	59.1	72.0	74.8	89.8	67.6	89.9

*[d]Oboh (1985), Oboh and Oderinde (1989)

[a]TG, Triacyl glycerols; 2MAG, 2-Monoacylglycerols; [b]Derived from triacylglycerols by pancreatic lipolysis

[c]Proportion in 2-position of triacylglycerols = $\frac{\text{Mol\% fatty acid in 2-position}}{\text{Mol\% fatty acid in triacylglycerols x 3}}$ x 100

[d]Proportion in 1, 3-position = 100 – proportion in 2- position

Bactris major, *Attalea cohune* (cohune), *Arecastrum romanozoffianum* (pindó) and *Astrocaryum vulgare* (tucum) kernels were characterised by the following:

i. High fat content (>20%)

ii. High 12:0, modest 14:0, and low content of 16:0, 18:0, 18:1, and 18:2 in their fat

iii. A preference of 8:0, 10:0, 16:0, 18:0 and 18:2 for the combined 1, 3-positions

iv. A preference of 12:0 for the 2-position of their triacylglycerols

Litchfield (1972) reported a correlation between the fat content, fatty acid composition and distribution in triacylglycerols characteristic of palm seeds, and the botanical sub-families of the Palmae (Arecaceae) family to which the palm belongs. The characteristics listed above (i, ii, iii and iv) are typical of the seeds of palms belonging to the Cocoideae subfamily, to which belong the oil-bearing palms of commerce. This serves to underscore previous taxonomic evidence placing these palms in this subfamily.

Triacylglycerol composition

Triacylglycerol composition was determined by thin-layer chromatography on silver nitrate-impregnated silica gel. The results are presented in Table 1.23.

Table 1.23. Triglyceride composition of kernel fats from $AgNO_3$ - TLC (% wt)

Kernel oil triacylglycerols	Number of double bonds in triacylglycerols				
	0	**1**	**2**	**3**	**4 or more**
Species					
B. major[a]	88.4	3.8	1.6	3.1	3.4
A. cohune[b]	91.2	3.3	3.6	0.3	1.6
A. romanozoffianum[c]	76.6	7.9	10.2	5.3	-
A. vulgare[d]	84.7	7.1	3.3	2.2	2.7
*E. guineensis**	78.2	12.8	5.2	3.8 (3 or more double bonds)	

Fatty acid composition of the trisaturated triacylglycerols (%wt)

Fatty acid	6:0	8:0	10:0	11.0	12:0	14:0	16:0	18:0
B. major[a]	4.1	T	2.9	-	50.3	23.0	15.0	4.8
A. cohune[b]	-	T	4.2	1.5	52.0	22.0	16.8	3.5
A. romanozoffianum[c]	-	0.6	2.8	-	62.0	25.7	7.2	1.7
A. vulgare[d]	-	0.7	2.3	-	55.1	31.8	7.1	3.0
*E. guineensis**	0.5	6.6	5.7	-	61.9	17.9	5.9	1.5

[a]Oboh (1987). [b]Oboh and Oderinde (1988a). [c]Oderinde and Oboh (1988). [d]Oboh and Oderinde (1989). *Bezard *et al.* (1977)

Bactris major, cohune, pindó and tucum kernel oils were characterised by the following:

i. The trisaturated glycerols were the dominant acylglycerol species in the kernel fats, accounting for 76.6-91.2% of total triacylglycerols.

ii. The fatty acid composition of the trisaturated triacylglycerols indicate that they were composed predominantly of dilauromyristins, with smaller content of other medium chain and long chain triacylglycerols.

iii. In this respect, they are similar to oil palm (*E. guineensis*) kernel oil trisaturated triacylglycerols, but differ from those of coconut oil, which have a higher content of octanoic and decanoic acids.

1.9. Palm kernel fat in edible, personal care, and pharmaceutical applications

1. Lauric/myristic (C12-C14) triacylglycerols have melting points in the region of human body temperature, and are therefore utilised in formulations where a solid form at ambient temperature but a rapid melt at body or mouth temperature is required. In this regard, they find application as cocoa butter substitute (i.e., hard butter) in confectionery and cosmetics. For use as hard butter, a lauric fat can, depending on its physical characteristics, be applied as such, or subjected to fractionation, hydrogenation, and/or interesterification, to provide the required physical properties.
2. Lauric fats are used as replacer for dairy fat in a variety of products, including, ice cream, filled milks, imitation milk, coffee whiteners, imitation sour cream, and whipped toppings (Hamilton, 1968; Oboh, 2012, Oboh, 2022).
3. Due to their euthetic (softening) effect, lauric oils are useful for:

i. Blending with palm oil, prior to interesterification, to produce fat stock for production of refrigerated margarine

ii. Blending with palm oil prior to fractionation to increase the yield of free-flowing oil (palm olein) (Table 1.24)

4. Apart from their use as food fat, lauric hard butters are used in suppository bases, facial creams, lipstick, solid perfumes, stick cosmetics, and as a vehicle for candy-coated laxatives.

5. Palm kernel (or coconut oil)/palm oil (or tallow) blends are saponified to produce toilet and laundry soap.

6. Lauric range (12:0 and 14:0) fatty acids are important materials for the production of basic oleochemicals.

Table 1.24. Fatty acid composition and yields of olein from the fractionation of palm oil/palm kernel oil (PO/PKO) blends (Oboh, 1986, 2006).

Fatty acid[a]	**PO: PKO**										
	100:0	90:10	80:20	70:30	60:40	50:50	40:60	30:70	20:80	10:90	0:100
8:0	-	0.3	0.4	0.9	2.7	1.2	1.1	1.9	2.0	2.4	1.7
10:0	-	0.5	0.8	1.6	3.1	1.7	2.0	2.4	3.7	4.2	3.8
12:0	0.2	5.3	9.6	15.4	4.0	24.9	21.5	35.3	39.6	40.9	44.6
14:0	1.1	3.2	3.8	5.5	13.1	11.0	7.5	11.6	16.3	16.6	19.4
16:0	42.3	38.5	33.5	29.2	31.2	25.7	26.6	19.1	14.9	12.5	9.4
18:0	5.3	4.9	5.0	5.0	5.7	3.8	4.0	2.7	3.7	4.4	3.4
18:1	41.6	38.7	37.7	34.9	33.2	25.2	32.2	22.8	17.3	16.0	13.2
18:2	9.5	8.6	9.1	7.7	6.4	6.4	6.0	4.1	2.5	3.1	4.8
Yield of olein	85.6	89.1	92.1	91.9	93.5	95.8	96.1	97.4	98.3	99.9	100

Table 1.25. Analytical characteristics of tucum kernel fat and its fractions in comparison with values for palm kernel fractions and pindó fat (Oboh and Oderinde 1988c)

Characteristics	**Tucum**			**Palm kernel[a]**		**Pindó**
	First Fraction	**Whole fat**	**Second Fraction**	**Stearins**	**Oleins**	**Whole Fat**
Yield (%)	36.70	-	63.30	-	-	-
Slip point (°C)	34.0	32.0	31.0	29.0-35.0[b]	23-26[b]	27.0
Solidification point (°C)	30.8	27.7	28.8	26.5-32.0	21-24	27.0

Saponification value	251.1	250.7	250.4	249-252	244-246	237.0
Iodine value (Wij's)	8.9	13.5	19.2	4.0-14.5	19-30	13.6
Free Fatty Acids (% as lauric acid)	0.03	0.10	0.48	0.2-6.0	5.20	1.6
Consistency at room temperature	Solid	Solid	Solid	Solid	Liquid	Solid
Effect on palate	Non-sticky, quick melting, cool sensation on melting			-		Non-sticky, quick melting, and cool sensation on melting

[a]Williams (1966). [b]Wiley melting point, complete fusion

Table 1.26. Cooling characteristics of tucum kernel fat, its fractions, and pindó kernel fat in comparison with typical values for palm kernel stearin and coconut stearin (Oboh and Oderinde 1988c).

Fat	Standard Time	Crystallisation time (min)	Minimum temperature (°C)	Solidification point (°C)	Temperature rise (°C)
Tucum fat	33.00	6.0	27.30	27.70	0.40
Fraction 1	9.00	5.0	29.75	30.80	1.05
Fraction 2	23.00	8.0	27.00	28.80	1.80
Pindó fat	30.00	9.0	26.65	27.30	0.90
Coconut stearin[a]	35.00	12.0	25.70	27.00	1.30
Palm kernel stearin[a]	34.00	16.0	27.20	29.80	2.60

[a]Williams (1966).

Table 1.27. Fatty acid composition of tucum kernel fat, its fractions, and pindó kernel fat in comparison with typical values for palm kernel oil, stearin and olein (Oboh and Oderinde, 1988c)

Fat	Fatty acids (wt %)							
	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2
Tucum kernel fat	1.9	3.0	53.7	23.3	5.5	1.9	8.8	1.9
Fraction 1	0.6	1.2	44.8	31.8	7.6	3.8	8.6	1.6
Fraction 2	1.3	1.9	48.5	20.4	6.9	4.1	12.6	4.5
Pindó fat	1.7	2.0	55.5	16.0	6.6	1.7	10.2	1.7
	C_6-C_{10}							
Palm kernel oil[c]	7	-	48.0	16.0	9.0	2.0	15.0	2.0
Palm kernel stearin[a]	6	-	53.0	21.0	9.0	2.0	8.0	1.0
Palm kernel olein[a]	9	-	45.0	13.0	9.0	3.0	19.0	2.0

7. Results from this study (Tables 1.23-1.27) indicate that pindó and tucum kernel fats and fractions derived from tucum fat could be suitable for use as hard butters for confectionery applications. Fractionation improved the characteristics of tucum kernel fat, providing two fractions, one which may be suitable for use as soft confectionery far in temperate, and the other as hard stearins for use in tropical countries in confectionery applications.

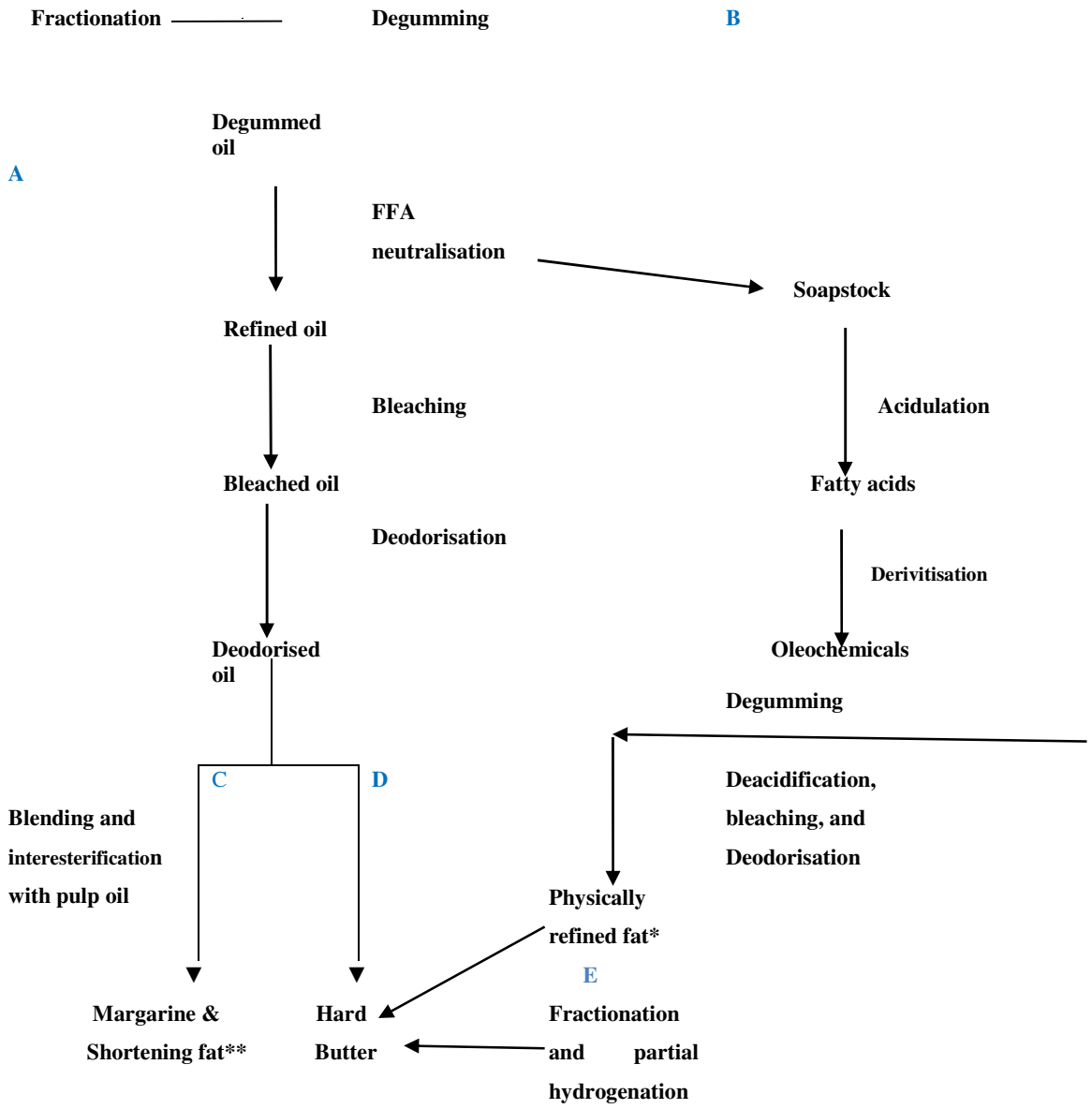


Figure 1.13: Proposed processing routes for kernel oils and food fats derivable from them for edible applications: A: Chemical refining, B: Physical refining, C: Processing route for palm kernel liquid fraction (not applicable to tucum and pindó fats), D: Utilisation of solid fractions (stearins) from cohune and *B. major* oils, both fractions of tucum fat, and pindó fat. E: This step may not be necessary for pindó kernel fat; only refining and fractionation may suffice for tucum kernel fat. *Has co-product, palm fatty acid distillate (PFAD), which is rich in fatty acids and valuable unsaponifiable constituents, and is a raw material for soap and oleochemical production. **Other products derivable from refined, bleached and deodorised lauric fats are dairy fat replacer in a variety of products, including ice cream and filled milks, whip toppings

However:

i. Further studies on a pilot scale are required to adapt tucum fat to the dry fractionation and wet (detergent) fractionation processes which are more feasible on an industrial scale.

ii. Physical characteristics, including differential scanning calorimetric studies of crystallisation. and Nuclear Magnetic Resonance measured solids content at critical temperatures are necessary to ascertain the extent of further modification required to tailor them for specific end-user applications

1.10. *Astrocaryum vulgare* fruit pulp

1.10.1. Fruit analysis

Table 1.28. Pulp: shell: kernel analysis (% fresh wt.)

Component	Oboh and Oderinde (1988b)	Eckey (1954)
Pulp	51.0	34.0
Shell	36.0	46.0
Kernel	13.0	20.0
Fruit weight (g)	30.0-38.0	15.0-20.0

The *A. vulgare* fruits weigh 30.0-38.0 g, half of which is the pulp (mesocarp) (Table 1.28). Based on its wet weight, the oil content makes up 22% of the pulp (40% based on dry weight), second only to its moisture (45%), and higher than its carbohydrate content (Table 1.29).

Table 1.29. Pulp composition (Oboh and Oderinde 1988b)

Constituent	(% fresh wt)
Crude protein	5.9
Crude fibre	5.7
Ash	1.9
Carbohydrate	19.5
Oil[a]	22.0
Moisture	45.0

[a]40.0% based on dry wt. of pulp.

1.10.2. Fruit pulp oil analysis

TABLE 1.30. Fatty acid composition and physico-chemical characteristics of *A. vulgare* pulp oil (Oboh and Oderinde 1988b)

Fatty acid	**(% by wt)**
Palmitic	30.4
Stearic	2.2
Oleic	59.9
Linoleic	2.9
Arachidic	4.6
Physico-chemical Characteristics	
Saponification value	188.6
Iodine value (Wij's)	63.5
Slip melting point (^{o}C)	28.0
Carotenoids (mg/kg)	135.5

Palmitic and oleic are the major fatty acids (Table 1.30), while the triacylglycerols are the dominant lipid species (Table 1.31A). The oil is similar to *E. guineensis* mesocarp oil in its content of diacylglycerols Compared with *Elaeis guineensis* mesocarp oil, tucum pulp oil has a higher content of unsaturated triacylglycerols (Table 1.31B), and gives a high yield of olein of far higher oleic acid content than double fractionated palm olein (palm superolein), with a linoleic acid content similar to that of palm olein, palm superolein, and olive oil (Table 1.32). The low S_3 and S_2O content of the olein (hence its low slip melting point of 7^{o}C) indicate that this oil could make an excellent cooking oil and a good salad oil extender (Table 1.33)

Table 1.31. Lipid classes and triacylglycerol composition of tucum (*Astrocaryum vulgare*) pulp oil.

A. Lipid composition (Oboh and Oderinde, 1988b)

Tucum pulp lipids[a]	TAG	DG[b]	MG	FFA	ST	HC/SE	PL
% by wt (Mean±SD)	86.78±0.05	8.69±0.01	0.58±0.01	1.12±0.01	1.25±0.02	1.25±0.01	0.33±0.01

B. Triacylglycerol composition (mol %) of *Astrocaryum vulgare* pulp oil and palm (*Elaeis guineensis*) mesocarp oil (Oboh, 1984; 2004)

Triacylglycerols	*A. vulgare* oil	Palm (*E. guineensis*) oil[c]
SSS	6.9	10.1
SSU	14.3	6.6
SUS	17.1	46.7
USU	7.4	1.1
UUS	35.7	30.7
UUU	18.6	4.9
SSS	6.9	10.1
SSO	13.7	6.4
SSL	0.6	0.2
SOS	16.6	35.5
SLS	0.5	11.2
OSO	6.8	1.0
LSL	-	-
OOS	33.0	22.4
LOS	1.5	0.8
OLS	1.1	7.1
LSO	0.6	0.1
LLS	0.1	0.2
OOO	16.5	3.5
OOL	1.5	0.2

LOL	-	-
LLL	-	-
OLL	0.1	0.1
OLO	0.5	1.1

[a]TAG=Triacylglycerols, DG=Diacylglycerols, MG=Monoacylglycerols, FFA=Free Fatty Acids, ST=Sterols, HC/SE=Hydrocarbons/Sterol Esters, PL=Polar Lipids, [b]Made up of *sn* 1, -3, = 0.42% and *sn* 1, -2 (2, -3-) = 8.27%; S= Saturated fatty acids; U=Unsaturated fatty acids; O= Oleic acid; L linoleic acid; [c]Oboh (1984; 2004).

Table 1.32: Fatty acid composition (wt %) and analytical characteristics of tucum pulp oil, olein, and stearin, and some other oils and fats (Oboh and Oderinde 1988d)

Fatty acid (wt %)	Tucum stearin	Palm stearin	Tallow	Tucum Oil	Tucum Olein	Single fractionated palm olein	Double fractionated palm olein	Olive oil
12:0	Trace	-	-	-	Trace	-	-	-
14:0	Trace	0.4	3.0	-	Trace	-	-	-
14:1	-	-	0.5	-	-	-	-	-
15.0	-	-	0.5	-	-	-	-	-
16:0	46.5	54.2	25.0	32.0	23.7	39.4	34.9	7-15
16:1	-	-	2.5	-	-	-	-	-
17:0	-	-	1.5	-	-	-	-	-
18:0	2.8	5.0	21.5	1	1.4	4.4	3.7	-
18:1	45.2	31.6	42.0	58.6	61.0	42.3	46.9	70-85
18:2	2.2	7.1	3.0	2.9	10.4	11.3	12.1	4-12
18:3	T	0.2	-	T	T	-	-	-
20:0	3.3	-	0.5	5.5	3.5	-	-	-
Iodine value (Wij's)	43.8	41.9	40-56	57.6	71.4	57.8	62.7	79-88
Saponification value	206.2	200.7	190-202	188.6	204.8	-	-	-
Yield %	14.3	-	-		85.7	-	-	-
Slip melting point ^{o}C	50.0	55.3	47-49.5	28.0	7.0	21.7	15.0	0-7

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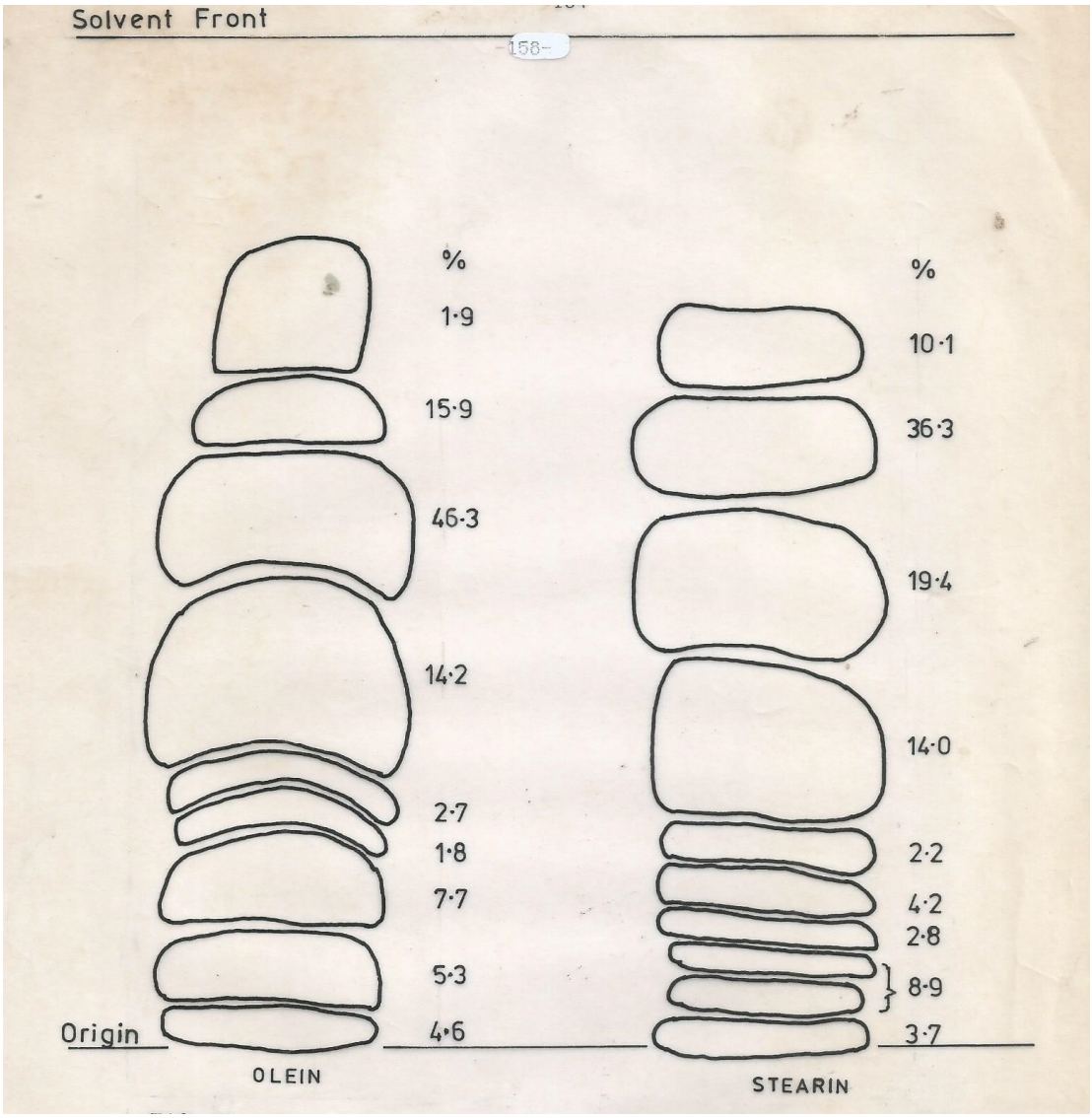


Fig. 1.14. Preparative separation of tucum olein and stearin triacylglycerols by Ag^+ adsorption thin-layer chromatography (TLC).
Operating conditions:
20x20 cm TLC plates coated with a 0.5 mm layer of $AgNO_3$ / Silica gel G, Sample size, 60 mg.
Vertical development with benzene/ petroleum ether (40-60°C)/ diethyl ether, 90/10/3 by volume.
Bands were visualised under uv light, after spraying with 2', 7' dichlorofluorescein solution.

Table 1.33: Major triacylglycerols[a] (wt%) of tucum stearin and olein (Oboh and Oderinde 1988d)

Triglyceride type[b] (%)	Stearin	Olein
SSS	10.1	1.9
SSO	36.6	15.7
SOO	19.4	46.3
OOO	14.0	14.2
LOS	2.2	2.7
OOL	4.2	1.8
SLL	2.8	7.5
LLO	8.0	5.3
LLL	2.7	4.6

[a]Determined by $AgNO_3$ – TLC. [b]S=Saturated fatty acids, O= Oleic acid, L=Linoleic acid

Table 1.34. Fatty acid distribution in tucum pulp olein and stearin (Oboh and Oderinde 1988d)

Fatty acids (mol%)						
	16:0	**18:0**	**18:1**	**18:2**	**18:3**	**20:0**
OLEIN						
Triacylglycerol	32.9	1.9	64.5	0.7	T	-
2- MAG	34.6	T	65.4	T	T	T
Percentage in 2-position	35.1	-	33.8	-	-	-
Mode of esterification	Random	1, 3	Random	-	-	-
STEARIN						
Triacylglycerol	53.8	3.8	42.4	T	T	T
2-MG	53.2	1.2	45.6	T	T	T
Percent in 2-position	33.0	10.2	35.5	-	-	-
Mode of esterification	Random	1, 3	Random		-	

T = trace amount. 2-MAG = 2-Monoacyl glycerol

Tucum stearin has almost equal proportions of palmitic and oleic acids, with low content of stearic and linoleic acids (Table 1.32), making it a rich source of palmitic and oleic acids, and a suitable raw material for basic oleochemicals derived from them; its low linoleic acid content, compared with palm stearin makes tucum stearin more attractive from the standpoint of stability to oxidative deterioration (Oboh, 1994b; 1995; 2009). Its high content of palmitic acid (46.5%), S_3, and S_2O (46.7%), which provide structure, coupled with its multiplicity of triacylglycerols (Table 33, indicating a ß' crystallinity), suggest that tucum stearin would make a useful hard stock for use in margarines and spreads (Wiedermann, 1978; Oboh and Oderinde, 1988d). The palmitic and oleic acids are randomly distributed in the stearin and olein tracylglycerols; the higher content of palmitic acid in the 2- position is suggestive of higher absorption and availability of this acid after digestion, and therefore better utilisation compared with *E. guineensis* pulp oil (Table 34).

1.10.3. Tucum oil refining and bleaching

Background to the study

Pechnick and Luiz (1957, 1962) working on oil from Brazil, and Floch (1958), oil from Guiana, described *A. vulgare* pulp and pulp oil as rich in carotenoids. Wittka (1938) described the oil as difficult to bleach. Oboh and Oderinde (1988b) found a lower level of carotenes in the pulp oil from the Nigeria grown palms than reported by previous authors. However, it was observed that in its crude state, pulp oil from the Nigerian *A. vulgare* palms was less bleachable than crude *E. guineensis* pulp oil, although the latter contains by far more carotenoids and has far more initial colour.

Our findings

In this study, a refining procedure was developed for crude *A. vulgare* pulp oil, which when added to a subsequent bleaching step gave oil of excellent colour (Table 1.35) (Oboh, 1994a).

The effect of refining treatments on the uv-visible spectrum of pulp oil (Fig. 1.15) was characterised by intense absorption in the ultraviolet (uv) region and very low absorption in the visible region.

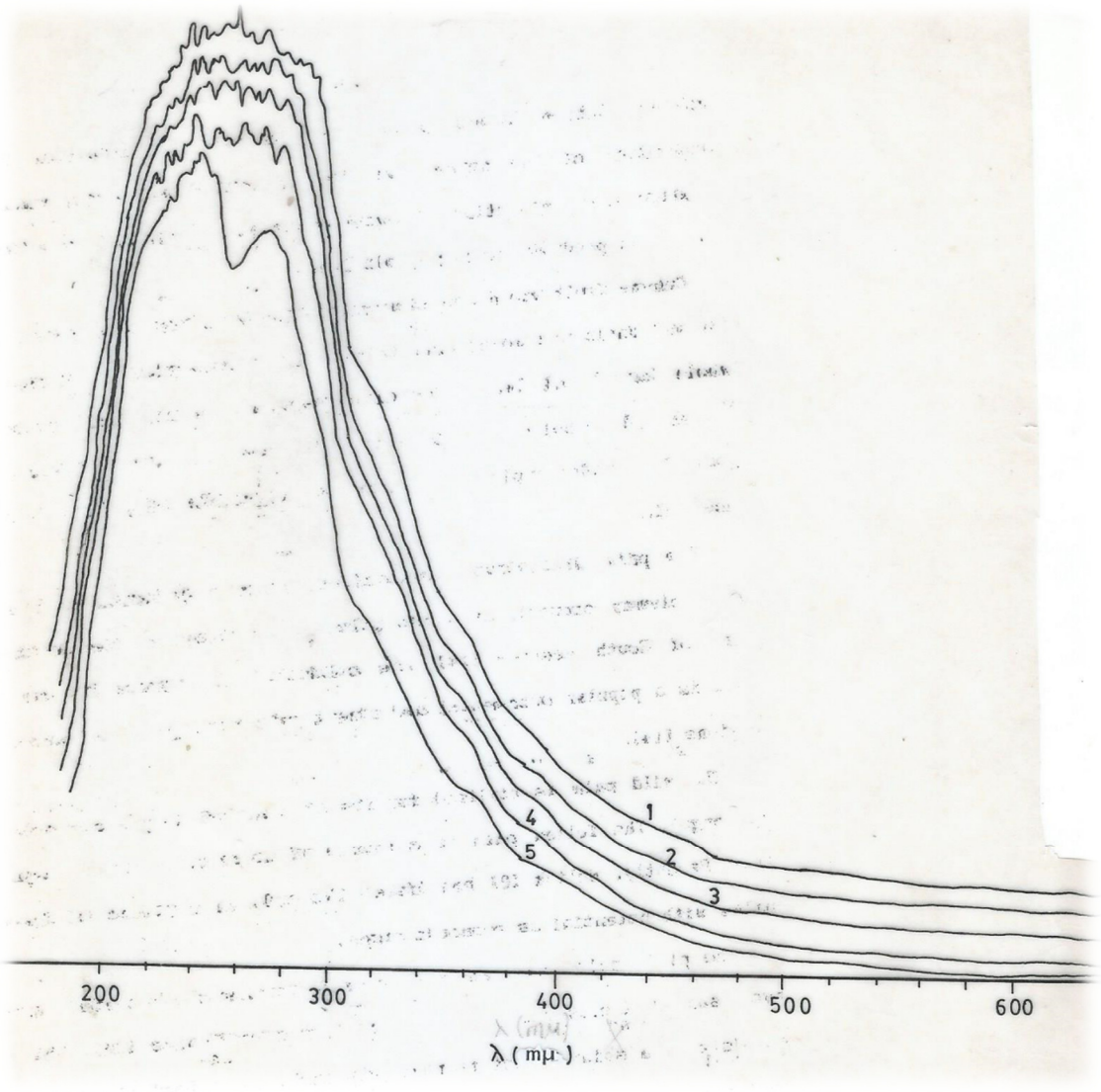


Fig. 1.15. Ultraviolet-visible (uv) spectra of crude and refined tucum pulp oils

(1). Crude oil. (2). Single (12°Be NaOH) refined oil. (3). Single (16°Be NaOH) refined oil. (4). Double refined oil. (5). Triple refined oil

Oxidation of polyunsaturated fatty acids is accompanied by increased absorption in the uv region due to conjugation of double bonds (Holman, 1954). Fatty acids with conjugated unsaturation absorb strongly in the region 230-375 mμ as follows: conjugated diene at 233 mμ, conjugated triene at 268 mμ, and conjugated tetraene at 315 mμ. The intense absorption in the uv region was in agreement with the high peroxide value for tucum pulp oil, and low absorption in the visible region was in keeping with the low level of carotenoids found in the oil.

Of the various refining treatments, only triple refining altered appreciably, the uv spectrum of tucum pulp oil. In all cases refining had little effect on the visible spectrum. Triple refining resulted in the disappearance of the plateau extending from about 230 to 290 mμ. Oxidised linoleate has a principal absorption at 230-236 mμ due to diene conjugation, and a secondary absorption at 260-280 mμ, due probably to a low content of unsaturated ketones (Holman, 1954). The spectral changes in the uv region resulting from triple refining indicate a decrease in the content of products of linoleate oxidation. This is in agreement with the sharp decrease (relative to the crude oil) in peroxide value resulting from triple refining.

Spectral changes due to bleaching of refined oils are shown in Fig. 1.16. Compared with the refined oils, refined and bleached oils gave lower absorption in the visible region, due to removal of carotenoids. Ultraviolet spectra for bleached single and double refined oil were similar to unbleached oil, except for the peak at 315 mμ indicative of tetraene conjugation.

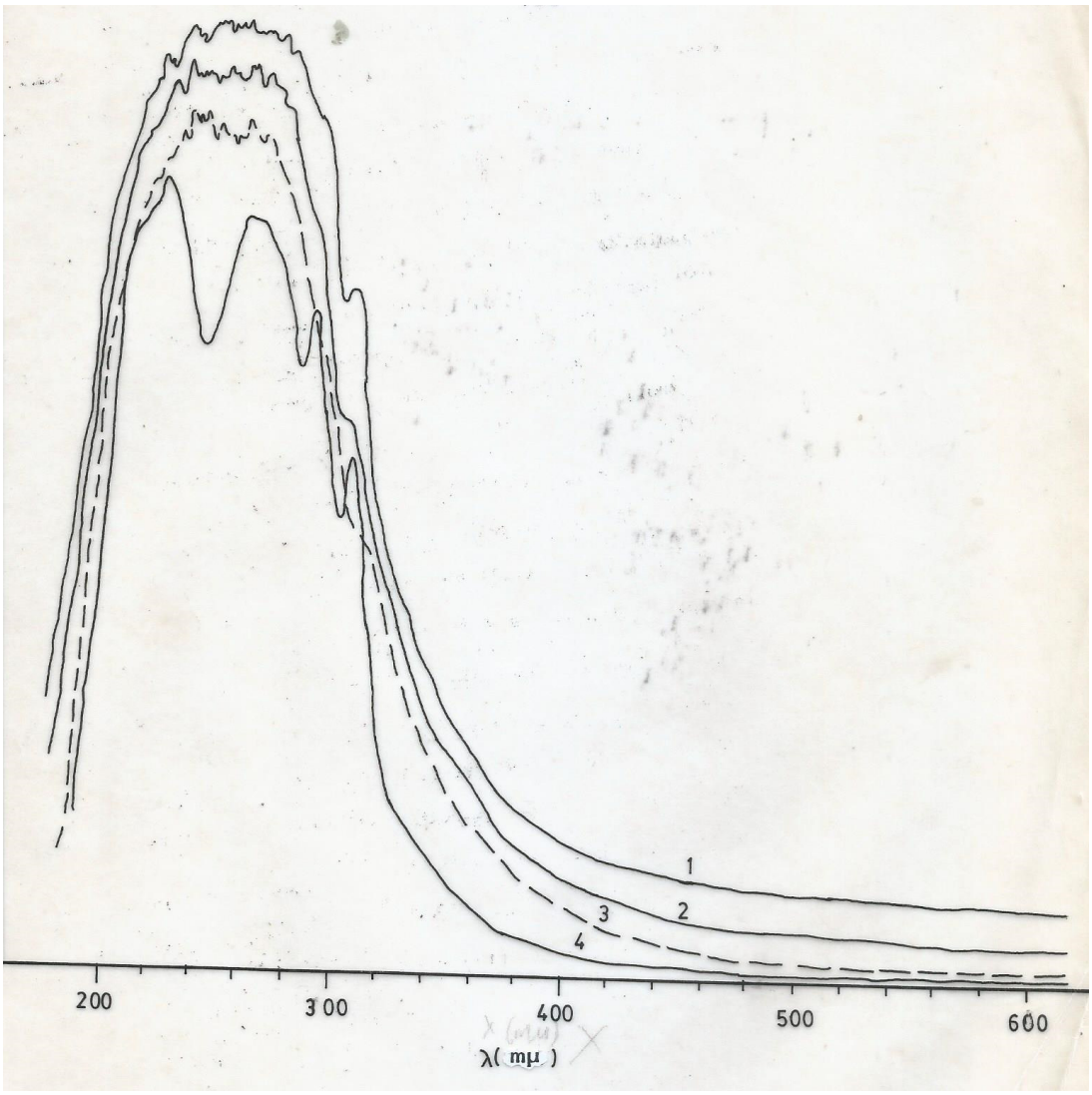


Fig. 1.16: Ultraviolet-visible spectra of refined and bleached tucum pulp oil

(1). Single-refined (12°Be NaOH) oil. (2). Single-refined (16°Be NaOH) oil. (3) Double-refined.

(4). Triple-refined.

Bleaching of triple-refined oil resulted in decrease in absorption in the uv region and the appearance of well-defined peaks at 236, 268, and 315 mμ characteristic of conjugated diene, triene, and tetraene absorption respectively. This is in agreement with Hiscocks and Raymond (1964) who have attributed the residual colour in oils after earth bleaching to the presence of compounds formed by a combination of oxidized fatty acids and oxidized carotenoids. Apparently, only triple refining, of all the refining treatments employed in this study was strong enough to

decompose the oxidized fatty acid-oxidized carotenoid compounds, thereby facilitating the removal of the released peroxides and carotenoids during the bleaching process.

Peroxides already present before refining of oils or formed during that step are known to be extensively destroyed during the bleaching process (Mitchell and Kraybill, 1946). Due to the inability of single and double refining to sufficiently disrupt the oxidized fatty acid-carotenoid complex, oil subjected to these treatments had relatively high carotenoids and peroxides, and high Lovibond colour.

TABLE 1.35. Effects of chemical refining variations on tucum pulp oil and characteristics of bleached[a] oils (Oboh, 1994a).

Refining methods	Carotenoids (mg/100 g)	FFA (%)	PV (meq/kg)	Conjugated fatty acids (%)		Lovibond colour
				Dienoic	Trienoic	
Crude oil	110.3	1.83	43.0	0.41	0.00	3R 20Y
Single-refining						
12° Be NaOH	91.9	0.40	38.0	0.72	0.01	1.2R 7Y
Bleached oil	61.3	0.51	28.0	0.71	0.00	1.3R 9Y
16°Be NaOH	91.9	0.40	34.0	0.80	Trace	2R 20Y
Bleached oil	49.0	0.61	32.0	1.18	0.00	1.4R 9Y
Double-refining						
50.0% max 16°Be NaOH						
66.7% max16° Be NaOH	104.2	0.33	32.0	0.70	0.01	2R 4Y
Bleached oil	55.2	1.81	28.0	0.76	0.01	1.3R 9Y
Triple-refining						
80% max 16°Be NaOH						
80% max 20°Be NaOH						

Max 20 °Be NaOH	85.8	0.12	22.0	1.18	0.00	0.4R 7Y
Bleached oil	14.7	0.28	10.0	0.80	0.01	0R 2Y

[a]Bleached at 105°C for 30 min using 2% fuller's earth + 0.2% activated carbon.

The effects of refining treatments on the uv-visible

TABLE 1.36. Fatty acid composition of triple refined and bleached tucum pulp oil (Oboh 1994a)

Fatty acid	Refined and bleached	Crude
12:0	0.4	Tr[b]
14:0	0.5	Tr
15:1	0.4	Tr
16:0	30.4	30.4
18:0	1.7	2.2
18:1	60.8	59.9
18:2	2.5	2.9
20:0	3.3	4.7

[b]Tr = trace content

Conclusion

A study of various refining methods for the purification of tucum pulp oil, showed that triple refining prior to bleaching of the refined oil at 105°C for 30 min (using a fuller's earth-activated carbon mixture) gave the best oil characteristics (Table 1.35) (Oboh, 1994a), without any significant effect on its fatty acid composition (Table 1.36).

Fig. 1.17 shows various processing routes for tucum pulp oil and potential end-use markets for the products. Potential markets include manufacture margarine and spreads, shortening, cooking oil, salad oil, and as dairy fat replacer in a variety of products, such as filled milk and infant formula. Soapstock from pulp oil refining can also be acidulated to yield fatty acids for the preparation of oleochemicals.

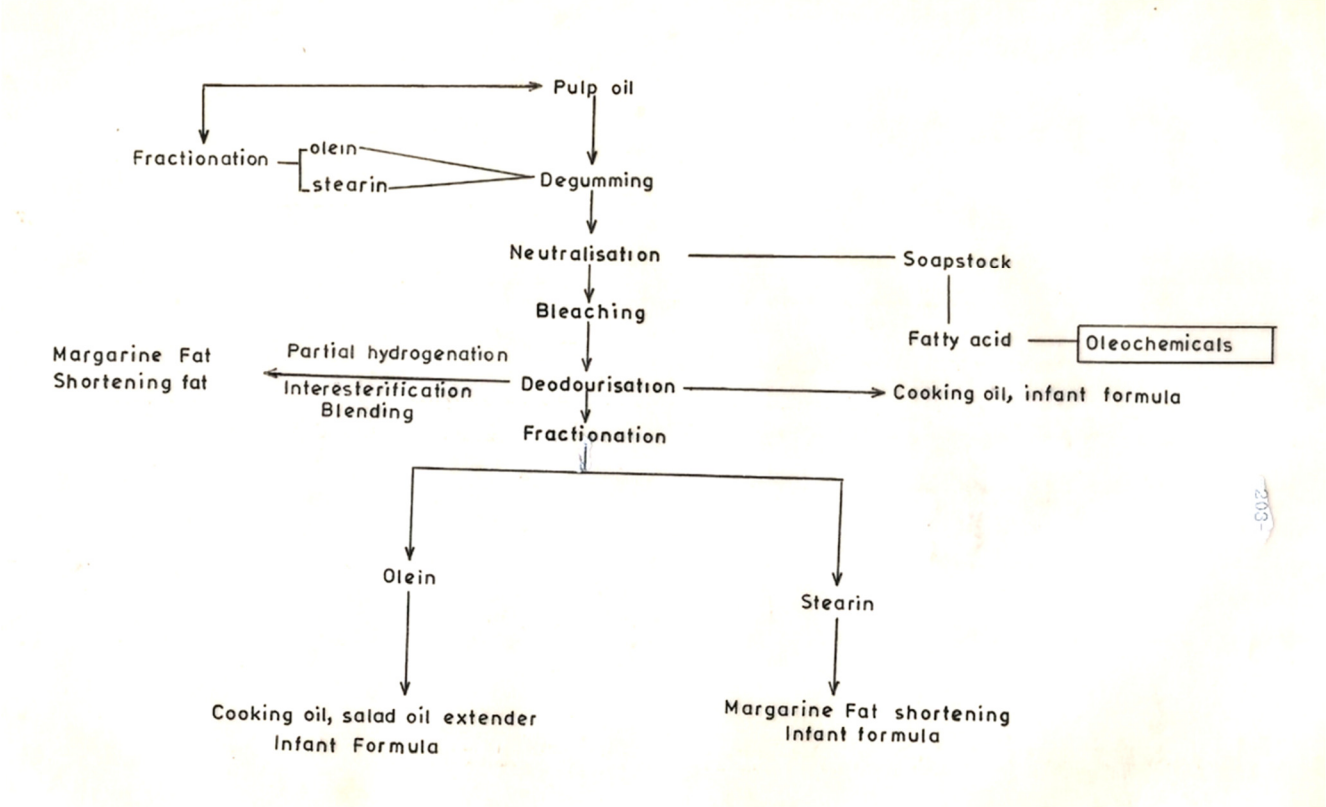


Figure 1.17. Edible use and processing possibilities for tucum pulp oil

1.10.4. Prospects for the commercial exploitation of tucum palm produce

According to Amazon Oil Industry, a Brazilian processor (Amazon Oil Industry, 2010), "there are some isolated oil palm (*Elaeis guineensis*) growers that are beginning to replace the oil palm with *A. vulgare* palms even without receiving support from research institutions to genetically improve this species. Its resistance to diseases and high productivity makes it an alternative for the production of biodiesel, since the operating costs of a plantation is much less than that of the oil palm".

The Brazilian Company also gave the following information: "Average fruit weight of 30 g of which 34% is pulp that has 14% to 16% of oil when it is raw. A mature tree can produce up to 50 kg of fruits per year (25 kg per tree on average), which corresponds to 2.5 kg of pulp oil and 1.5 kg of seed oil. In one hectare, 400 palm clusters can be planted, each cluster with three trunks. In total, this equals 1200 palm trunks and will result in 4.8 tons of fatty material per hectare, more than the oil palm, *Elaeis guineensis*, which produces only 4 tons of oil on average per hectare per year (assuming a harvest of 20 tons of fruits and an extraction of 22% oil). The advantage of

tucumã-do-para is that it forms clusters that do not need to be replanted, which is not the case for *Elaeis guineensis"* (Amazonian Oil Industry, 2010).

1.11. BASIC OLEOCHEMICALS

1.11.1. Introduction

Vice Chancellor sir, so far, I have discussed the composition, characteristics, processing and food applications of fats and oils, and the utilisation of residues from their extraction. Other end use markets for fats and oils are for the manufacture of personal care products (such as soap and cosmetics), and basic oleochemicals, for example, metallic soaps, fatty acids, glycerol, methyl and other esters (derived from their reactions with short chain aliphatic alcohols), and fatty alcohols (Figure 1.18).

OILSEED TREATMENT	OIL & RESIDUE	FURTHER PROCESSING	PROCESSED PRODUCTS
	OIL	Refining	Cooking and salad oils
		Derivitisation	Paints, varnishes, and pharmaceuticals. Other applications
		Fractionation Hydrogenation Interesterification	Margarine/ghee, shortenings, cooking and salad oils
		Soap manufacture	**Household & toilet soap, metallic soaps. Glycerol**
		Methanolysis	**Methyl esters, Glycerol**
		Sodium reduction	**Fatty alcohols**
Seed Processing: Dehulling, Size reduction, expelling, and/or solvent extraction		**Fat Splitting**	**Fatty acids, Glycerol**
	CAKE	Animal feed compounding	Poultry, pigs, cattle, sheep etc.
	MEAL	Human food processing	Protein supplement,

Figure 1.18: Processed oilseed markets

				sauces, meat substitutes
		HUSKS		To plant boiler, soil conditioner.
			Fermentation	Furfural

Basic oleochemicals consist of chemical intermediates fatty acids, glycerol, fatty alcohols, fatty acid methyl esters, and fatty amines, which through various operations are converted to oleochemical derivatives which have many end user applications (Table 1.36). Although only about 15% of the world's production of oil and fats is used for their manufacture, oleochemicals are of major importance as is shown by their many applications. In the past few decades, awareness and concern over the use of petroleum-based products and their impact on the environment have created an opportunity to increase production of these environmentally acceptable materials from agricultural feedstocks. Tallow, coconut oil, palm kernel oil, and palm stearin are the major oleochemical raw materials.

TABLE 1.36. Utilisation of fatty oils including coconut oil, palm oil and palm kernel oil as raw materials in the oleochemical industry[a]

Raw materials	**Oleochemical unit operations**	**Basic oleochemicals**	**Derivative Operations**	**Oleochemical Derivatives**	**End use Markets**
Oleochemical					
Basic					
Derivative					
Oleochemical					
End use					
Tall Oil	Splitting	Fatty acids	Amidation	Fatty Amides	Building auxiliaries
Fatty acids					
Amidation Fatty Amides					

Building auxiliaries					
Tallow	Distillation	Fatty acid Methyl Esters	Dimerization	Dimer and Trimer Acids	Candles
Coconut oil	Fractionation	Fatty Alcohols	Epoxidation	Epoxidized Oils & Esters	Cleaning agents
Palm oil	Separation	Fatty Amines	Ethoxylation	Ethoxylates	Cosmetics
Palm kernel oil	Hydrogenation	Glycerol	Quaternization	Quaternary ammonium compounds	Detergents
Soybean oil	Methylation		Sulphation	Fatty Alcohol Sulphates	Fire extinguishing Agents
Sunflower oil	Deionization		Sulphonation	Fatty Acid Sulphonates	Flotation
Rapeseed oil			Transesterification	Fatty Esters	Food Emulsifier
Canola oil			Esterification	Fatty Esters	Insecticides
Other Vegetable Oils			Saponification	Soaps	Leather
Synthetic					Lubricants
Ethylene					Paints
Propylene					Paper
Other olefins					Pesticides
					Rubber, Soaps
					Textiles
					Biodiesel

[a]**Source: Adapted from Kaufman and Ruebusch, (1990)**

Basic oleochemicals are produced from fats and oils using the following operations (Figs 1.18 and 1.19, Table 1.36):

i. Fat splitting

ii. Fatty acid hydrogenation

iii. Fatty acid methylation

iv. Catalytic hydrogenolysis or sodium reduction of methyl esters

Further processing involves the following operations:

i. Glycerol distillation and/or deionisation

ii. Fatty acid separation by fractional distillation and/or fractional crystallisation (fractionation)

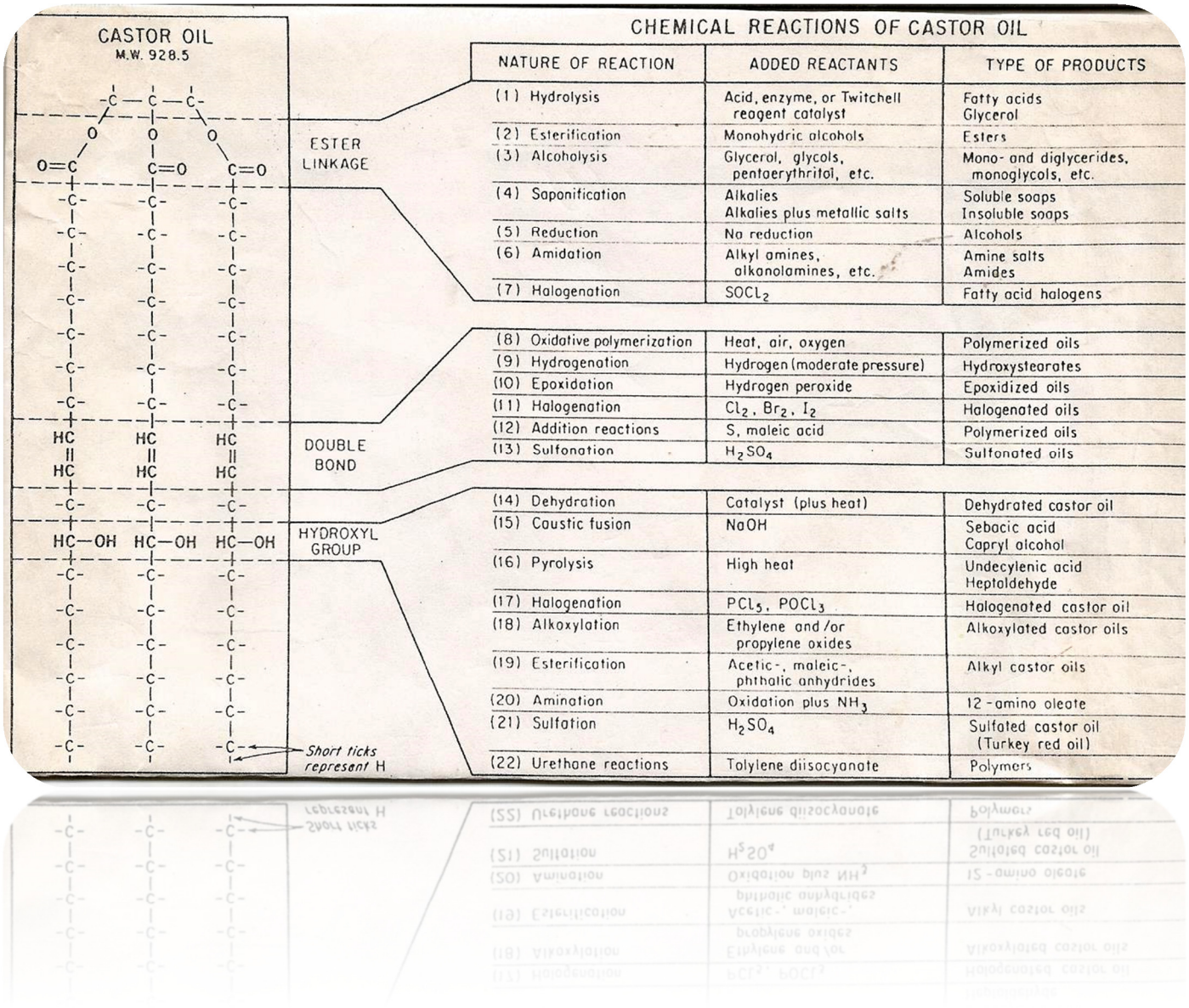


Figure 1.19: Chemical reactions of castor oil, a highly functional vegetable oil.

They can also, alternatively and competitively, be produced from petrochemicals via olefin chemistry (Kaufman and Ruebusch, 1990).

1.11.2. Fatty acids

The use of tallow as raw material in the production of oleochemicals, and the potentials of palm stearin, tucum oil, and tucum stearin as its replacer.

In addition to their use as food fats and oils, fats including palm and palm stearin, palm kernel oil, tucum oil and stearin may also be split (i.e., hydrolysed) to yield fatty acids and glycerol, which

are suitable materials for the production of fat-based chemicals (oleochemicals). In this section, oleochemicals that are available, or are potentially derivable from the fatty acids of these materials (Table 1.37) are enumerated and their production processes and utilisation are discussed.

Table 1.37. Characteristics of tucum pulp oil, its stearin, palm oil, palm stearin and tallow

Fatty acid (%)	Tucum pulp oil[a]	Tucum stearin[b]	Palm oil[c]	Palm stearin[c]	Bleachable fancy tallow[c]
12:0	-	-	0.1	0.1-0.6	-
14:0	-	-	1.0	1.1-1.9	3.0
14:1	-	-	-	-	0.5
15:0	-	-	-	-	0.5
16:0	30.4	46.5	43.7	47.2-73.8	25.5
16:1	-	-	0.1	0.05-0.2	2.5
17:0	-	-	-	-	1.5
18:0	2.2	2.8	4.4	4.4-5.6	21.5
18:1	59.9	45.2	39.0	15.6-37.0	42.0
18:2	2.9	2.2	10.3	3.2-9.8	3.0
18:3	-	-	T	0.1-0.6	-
20:0	4.6	3.3	0.5	0.1-0.6	0.5
Iodine value (Wij's)	63.5	43.8	51-55	32-36	40-56
Saponification value (mg KOH/g)	188.6	206.2	190-202	-	-
Unsaponifiable matter (%)	1.0[d]	-	0.5 max.	0.8 max.	1.0 max.
Slip point °C	28.0.	50.0	-	44°C min.	Semi-solid
Consistency at ambient temp.	Liquid	Plastic solid	Semi-solid	Plastic solid	

[a]Oboh & Oderinde (1988a). [b] Oboh & Oderinde (1988b). [c] Ooi and Pee (1985). [d] Lubrano *et al.* (1994).

Purified oils and fats are either hydrolysed to yield fatty acids and glycerol, or subjected to methanolysis to give fatty acid methyl esters and glycerol. The final products desired determine the choice of process.

1.11.2. Fat splitting

The aim of fat splitting is primarily to release fatty and glycerol from the triacylglycerol molecules in which they are bound. This, when accomplished, makes them these products available for the various processes involving their purification and derivation. Purified fatty acids, glycerol and

derivatives prepared from them, are suitable for various edible, e.g., docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA) and non-edible applications (e.g., toilet soap, cosmetics, and oleochemicals). Fatty acids and glycerol from various lipid sources (plant animal, marine, microbial) are referred to as natural, to distinguish them from those derived from petrochemical raw materials, which are referred to as synthetic. Other sources of natural fatty acids are refining residues - the distillates from deodorisation and physical refining, soapstock from chemical refining of fats and oils, and tall oil, a by-product of the pulp and paper industry.

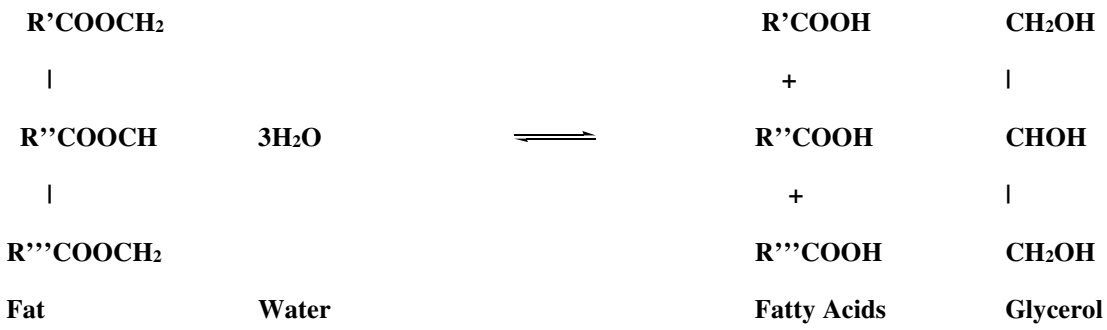


Figure 1.20: Fat splitting

1.11.3. Fat splitting processes

The method of choice for fat splitting is the single-stage continuous high pressure, uncatalyzed counter-current splitting, also known as the Colgate-Emery process (Fig. 1.21). This process utilises high temperature and pressure (260°C and 65 bar, respectively) to effect splitting. Liberated glycerol is removed with the water stream. Splitting efficiencies of 98-99% in only 2-3 hr are achieved, with little or no discolouration of the fatty acids.

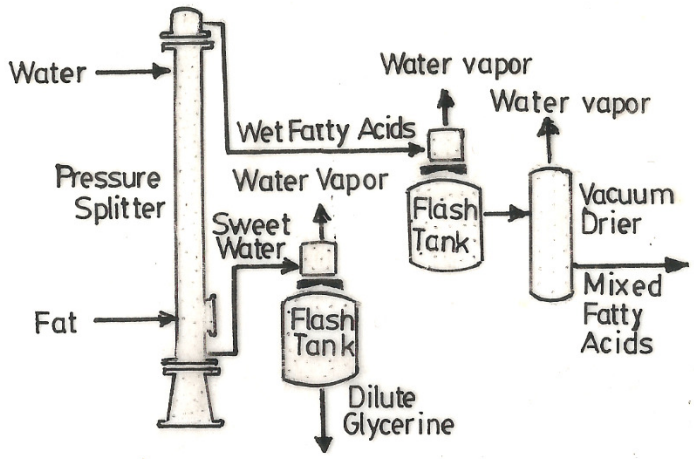


Fig.1.21: The Colgate-Emery Process (Combs, 1985).

Small capacity batch processes.

Practical hydrolysis methods require consideration of both capital cost and operating expenses. When a large number of different fat stocks are processed, and the total volume of each one is fairly small, a batch process is indicated. Two processes which meet these requirements are the Twitchell Process and the enzymatic hydrolysis process.

The enzymatic process

Lipolytic enzymes such as those obtained from castor beans have been used to split fats (Lawrence, 1954; Combs, 1985), but this technique was generally regarded as inefficient, with best conversions of only around 90%. It was sluggish and not easy to handle as a unit operation, and required from 24 to 48 hr for completion. Another limitation of this method was that process temperature was limited to 40°C.

However, Akaike (1985) reported a new lipase hydrolysis process, known as the Solid Phase Hydrolysis Process, which is claimed to operate at ambient temperature (30-35°C) and proceeds without agitation (Fig. 1.22). Almost complete hydrolysis (98-99%) is claimed, using the method, with the advantage that it can be used for splitting highly unsaturated oils.

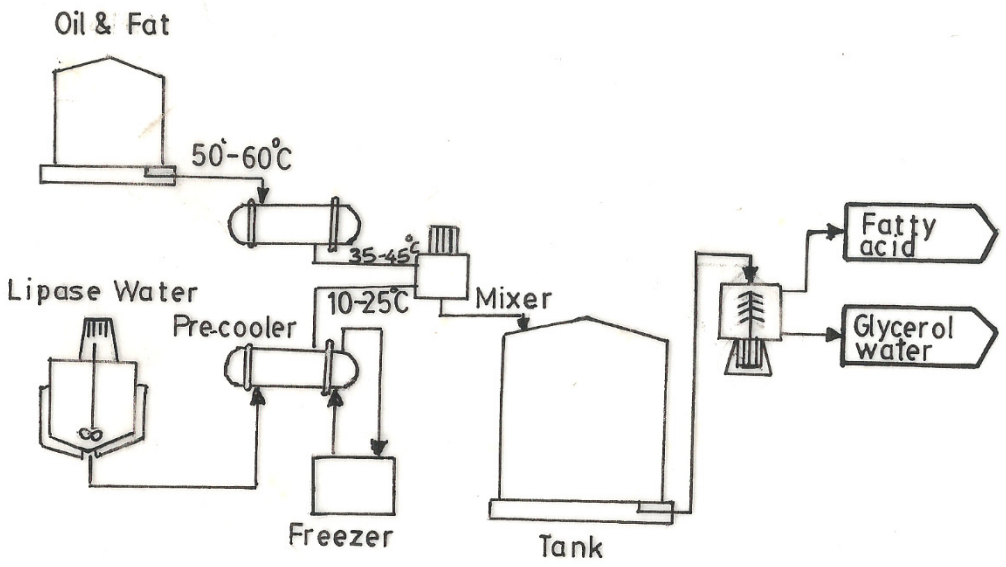


Fig. 1.22: The Enzymatic Process for Fat Spitting (Akaike, 1985)

1.11.4. The Twitchell Process and Panning and Pressing; appropriate technologies for artisanal and small-scale fatty acid production

The Twitchell Process

Ernst Twitchell (1863-1929) was a pioneer in the oleochemical industry. He attended the University of Cincinnati, where he earned a BS degree in chemistry in 1886. In 1886, Twitchell accepted a position with the Emery Candle Company as a chemist and general manager. While there, he developed and perfected the Twitchell Process for fat splitting. Five patents were issued for this method between 1898 and 1915. The fatty acids produced were suitable for the manufacture soap and candles.

The success of the process led to the formation of a company named "The Twitchell Process Company" of which he was the chairman of the board and remained so till 1925. By 1910, Twitchell had endowed the Twitchell Fellowship in the Department of Chemistry of his alma mater. The University responded by conferring a Doctor of Science (honoris causa) in 1915 (List, 2017).

The Twitchell Process is by far the simplest fat splitting process and provides a good entry point into the oleochemical industry for artisanal and small-scale operators. Wigner (1952) and Lawrence (1954) have provided excellent description of this process.

Before splitting, the fat is usually washed with sulphuric acid to remove impurities. With fats that have previously undergone purification, acid washing is not necessary. It is however necessary to add acid to the water used for the splitting of such fats. For the splitting operation, a certain amount of water, usually about 25 to 50%, based on the weight of the fat is added to the acid-washed or refined fat in the first instance. A little Twitchell catalyst (0.25 to 1.0% based on the weight of the fat) is then added to the water. This mixture is boiled for 36-48 hours, usually in 2 to 4 stages, with replacement of water after each stage.

The tanks are provided with covers to minimise contact of the charge with air, which can cause darkening of the product. The operation is finished by adding fresh water to the fatty acids and boiling to remove mineral acid present. Before removing the acids from the treatment tank, the residual mineral acid is neutralised with barium carbonate. This treatment increases the stability of the fatty acids to air. The degree of split obtained depends upon the number of stages.

In order to obtain high yields of fatty acids, free glycerol concentration must be kept as low as possible. This will however result in a glycerol solution (sweet water) that is too dilute for economic recovery. By ensuring a high degree of split at the first stage (about 85%), the dilute sweet water from a second split is contacted with fresh fat. In this manner it is possible to obtain a 10-12% glycerol sweet water. A 4-stage process appears to be the practical maximum for economic glycerol recovery (Wigner, 1952). The practical limit of splitting is about 92-95%. A higher degree of splitting would take too much time and produce very weak glycerol solutions (Wigner, 1952). Oboh (2006) achieved good results in a preliminary investigation using a locally produced modified catalyst prepared from palm oil fatty acids, naphthalene and conc. H_2SO_4 (Table 1.38).

The author found catalyst application at 0.25 to 0.5% suitable for production of palm oil fatty acid mixtures.

Table 1.38. Palm oil splitting* at atmospheric pressure (Oboh, 2006)

Twelve-hr boiling periods	Total duration of boiling (hr)	Free fatty acid (% as palmitic acid) at various catalyst levels		
		1.0%	**0.5%**	**0.25%**
0	0	9.80	9.80	9.80
1	12	71.68	58.14	46.13
2	24	-	73.18	52.48
3	36	81.42	78.18	58.75
4	48	85.20	86.61	71.17
5	60	-	88.55	-
6	72	-	95.50	83.28
7	84	-	-	95.01
Colour	-	Dark brown/ caramel	Light brown	Ivory/cream

***Fat: water = 1:2**

The fatty acid mixture produced can be bleached to acceptable colour using a mixture of fuller's earth and activated charcoal (Oboh, 2006), or distilled under vacuum to yield light coloured fatty acids. In the case of tallow, the fatty acid mixture is then separated into a hard fraction, industrial stearic acid (should not be confused with octadecanoic acid, 18:0) and a liquid fraction, industrial oleic acid (should not be confused with 9-octadecenoic, 18:1), using the panning and pressing method.

Panning and pressing

Panning and pressing is the oldest method employed in industry for the separation of fatty acids. In the method, the crystallised fatty acid mixture is poured into burlap bags, which are loaded unto the press (Fig. 1.23). Pressure is applied and the liquid phase is squeezed out. The solid phase left in the bag is known as the single-press stearin. The liquid phase "oleic acid" is run into its storage tank.

Panning and pressing may be used for the separation of fatty acids of which the solid acids, on cooling, can produce a suitable crystalline structure for easy separation from the liquid acids by pressing. The cold press stearic acid (referred to as "single-press stearic acid") may be re-panned, loaded unto air-cooled racks and pressed in the hot press to provide double-press stearic acid (Fig. 1.23).

At the artisanal level, preparation of mixed fatty acids (without separation into industrial stearic and oleic acids) can be done by a simple saponification using sodium or potassium hydroxide, followed by acidulation with dilute sulphuric acid.

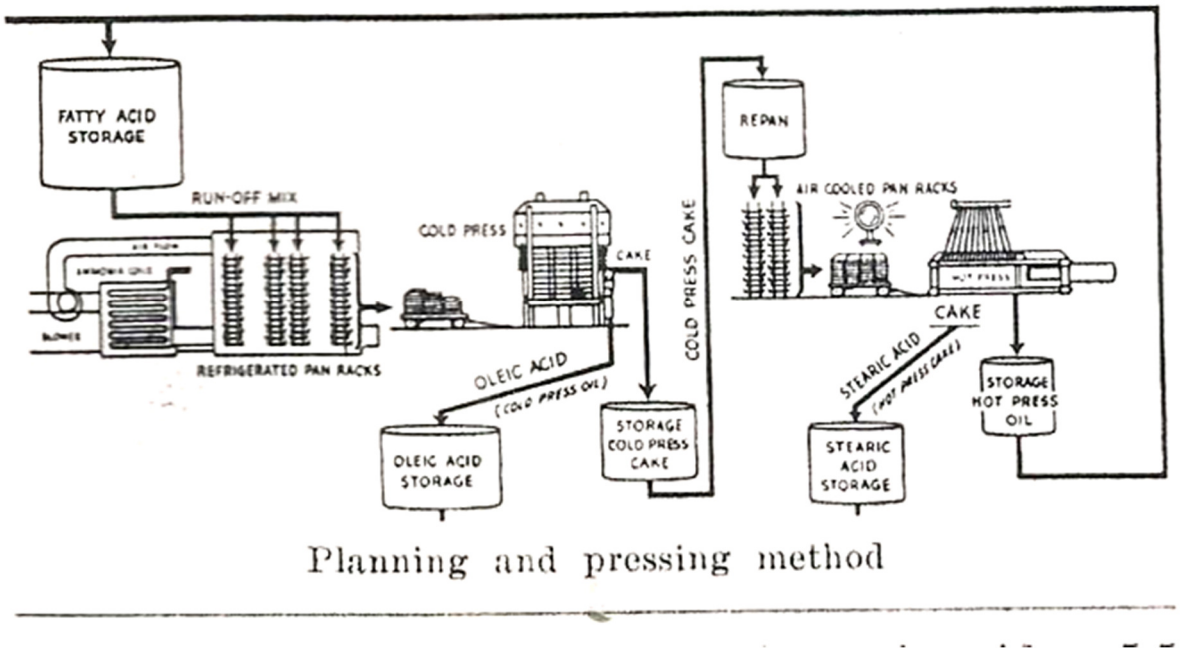


Fig. 1.23: The panning and pressing method of fatty acid fractionation (Muckerheide, 1954)

Patents awarded to Ralph Potts (1900-1981) in the 1940s and 1950s dealt with the flash and fractional distillation of fatty acids (List, 2017). It became possible to purify fatty acids by separating them from undesirable colour bodies, resulting in product of very good colour (Fig. 1. 24). Also, flash distilled fatty acids could be separated into several fractions based on chain length (Fig. 1.24). Further separation of fatty acids of same chain length, but different degrees of unsaturation is possible using solvent fractionation (Fig. 1.25).

Fatty acids from fat splitting may be bleached or distilled to yield product of acceptable colour, the latter being the common practice. A simple distillation removes odour and low boiling unsaponifiable matter (low boilers) and triacylglycerols, polymerised products, colour bodies, hydrocarbons, and other breakdown products (high boilers). Distilled fatty acids normally retain the fatty acid chain length distribution found in the original oil.

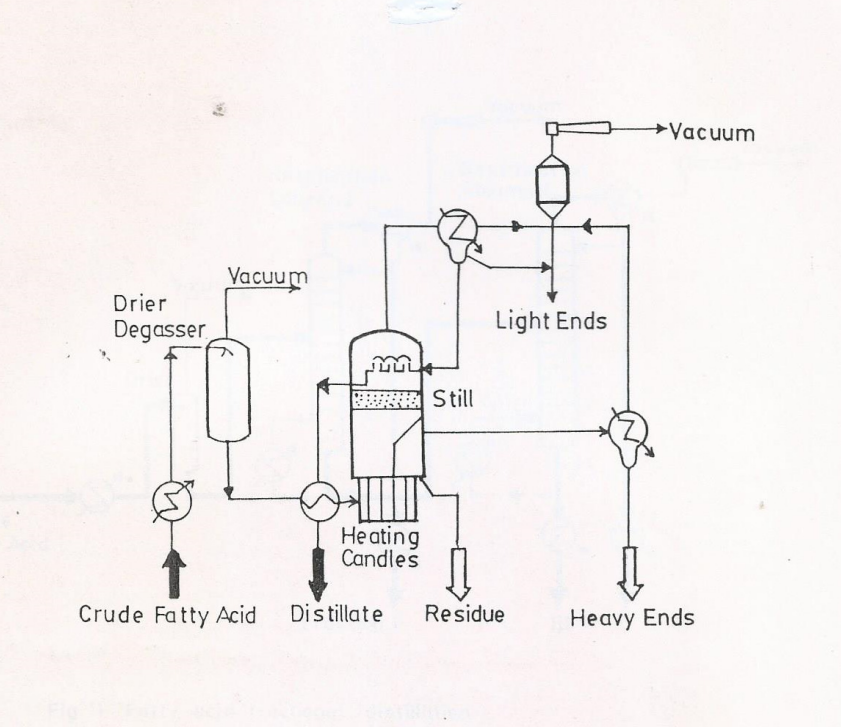


Fig. 1. 24: Flash distillation for purification of fatty acid mixtures (Lurgi GmbH, 1987b)

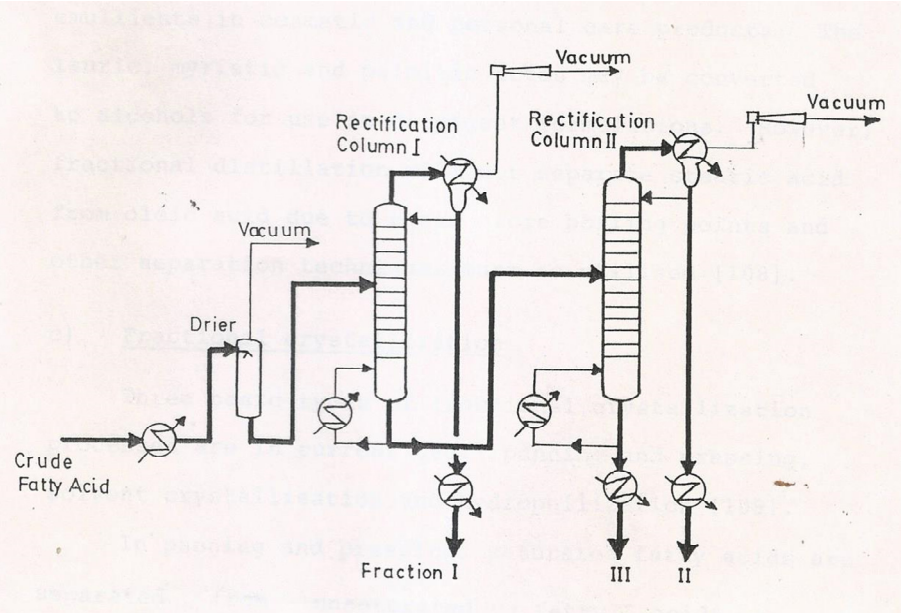


Fig. 1.25. Fractional distillation of fatty acids (Lurgi GmbH, 1987b)

1.11.5.Properties, purification, and utilisation of fatty acids derived from tucum pulp stearin

C16- C18 range fatty acids

Table 1.33 shows the fatty acid composition of tucum pulp oil, its hard fraction (stearin) and the accepted typical specifications for tallow, palm oil and palm stearin, three principal fats that are used for the production of oleochemicals. Tucum pulp oil and stearin derived from it, and these fats share one feature in common- they are composed mainly of fatty acids of carbon chain length 16-18.

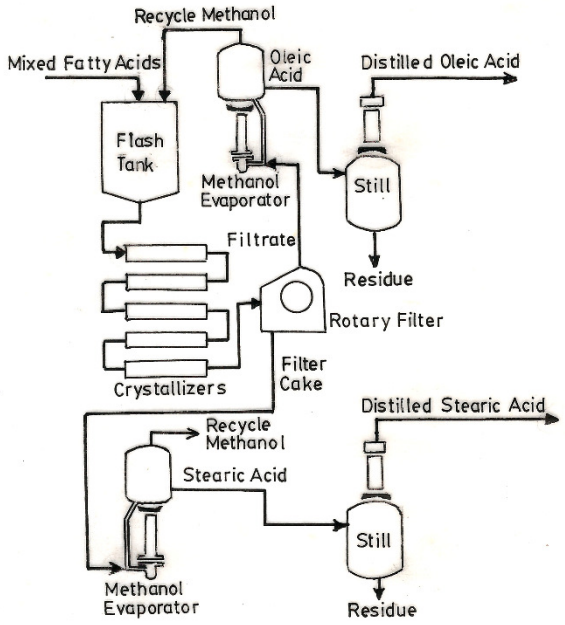
The proportions of the C16 and C18 acids differ, however in the various fats and oils. Tallow, the benchmark natural oleochemical raw material has as dominant fatty acids, palmitic (25.0%), stearic (21.5%) and oleic (42.0%). Other fatty acids found in tallow are 14:0 (3%), 14:1 (0.5), 15:0 (0.5%), 16:1 (2.5%), 17:0 (1.5%) and 20:0 (0.5%). Linoleic represents 3.0%. Palm oil and its stearin have as their major fatty acids, palmitic and oleic, with considerable linoleic acid content, which constitutes about 10% of palm oil fatty acids, but less in palm stearin. Palm oil and stearin in addition, contain minor quantities of lauric, myristic, palmitoleic, stearic, linolenic, and arachidic acids. The implication of the higher polyunsaturation of palm oil relative to tallow is a higher susceptibility of the former to oxidative deterioration.

Compared with tallow, which has both palmitic and stearic acid as dominant saturated fatty acids, palm oil, palm stearin, tucum pulp oil and tucum stearin contain only minor quantities of stearic acids, the only major saturated fatty acid being palmitic. The dominant fatty acids of tucum pulp oil are palmitic and oleic acids, which constitute about 30% and 60% respectively. Arachidic acid (20:0) content at a 4.6% is a minor constituent. Linoleic acid constitutes only 2.9% of tucum pulp oil (similar to the 3.0% found in tallow), while linolenic acid is absent.

Tucum pulp stearin has similar proportions of palmitic and oleic acids (46.5 and 45.2% respectively) and minor quantities of linoleic (2.2%) and arachidic (3.3%). Tucum pulp oil and stearin could be good sources of palmitic and oleic acids, having an advantage over tallow; palm oil and palm stearin (unlike tallow) contain only traces of fatty acids of chain length less than 16C, and do not contain any 17:0; unlike palm stearin they have low linoleic acid content similar to that of tallow.

One of the main uses of this "whole" fatty acid product is in the manufacture of soaps and shampoos, where the wide range of chain length distribution is considered desirable for certain functional properties, such as flash foaming and bubble size. Tucum oil-based soap would exhibit the excellent cold-water solubility, foaming and mildness of oleate and the greater (relative to laurate) foam stability and detergency characteristics of palmitate (Reinish, 1953, Oboh, 2009).

Current technologies for fatty acid separation on a commercial scale include fractional distillation and the various fractional crystallisation processes. Dry fractionation involves cooling mixed fatty acids in shallow pans in order to crystallise the saturated fatty acids, followed by pressing to effect liquid–solid separation (Muckerheide, 1954; Zilch, 1979) (Figure 1.23). In solvent fractionation processes, mainly the Emersol Process, which uses methanol (Fig, 1. 26) and the Solexol Process (furfural) the solution of mixed fatty acids is subjected to controlled cooling in order to crystallise the saturated fatty acids, followed by filtration using a rotary filter (Zilch, 1979; Combs, 1985).



Fig, 1.26: The Emersol Process for solvent crystallisation of fatty acids (Combs, 1985).

In the Hydrophilisation Process, a cooled fatty acid mixture is mixed with an aqueous solution of a detergent (e.g., sodium lauryl sulphate) and an inorganic salt (e.g., magnesium sulphate), followed by centrifugation to separate liquid from solid fatty acids (Stein, 1968). Separated fatty acids from these processes can be further separated from impurities by distillation.

Starting from crude tucum fatty acids, distillation for purification of the whole fatty acid mixture, followed by fractional distillation and/or any of the fractional crystallisation processes would yield two major fractions- oleic and palmitic acids. Distillation of crude fatty acids from tucum oil splitting, followed by hydrogenation (Fig. 1.27) would convert oleic and linoleic acids to stearic acid, thus giving a mixture of saturated fatty acids (16:0, 18:0, and 20:0) referred to in the industry as "technical stearic acid". Technical stearic acid bears this name because of its hard consistency and is not to be confused with the pure stearic acid (octadecanoic acid, 18:0).

Palmitic, oleic and 'stearic' acids recovered from tucum pulp oil by splitting and fatty acid separation and hydrogenation could be the starting materials for the synthesis of some useful derivatives. Fatty acids and the esters derived from them are used as oily components in a large variety of formulations of

cosmetics, where their lipophilic nature makes them valuable as emollients for creams, lotions, moisturising agents, etc. Palmitic acid may be reacted with isopropyl alcohol to produce isopropyl palmitate for use in cosmetics and personal care products. One of the more common uses of oleic acid is for the manufacture of various soaps and detergents. Since water solubility increases with the degree of unsaturation, liquid sodium, potassium and triethanolamine soaps may be prepared from oleic acid (Valance, 1949; Reinish, 1953). Usually, oleic acid is combined with coconut or palm kernel fatty acids to provide the desired foam structure and stabilities (Reinish, 1953).

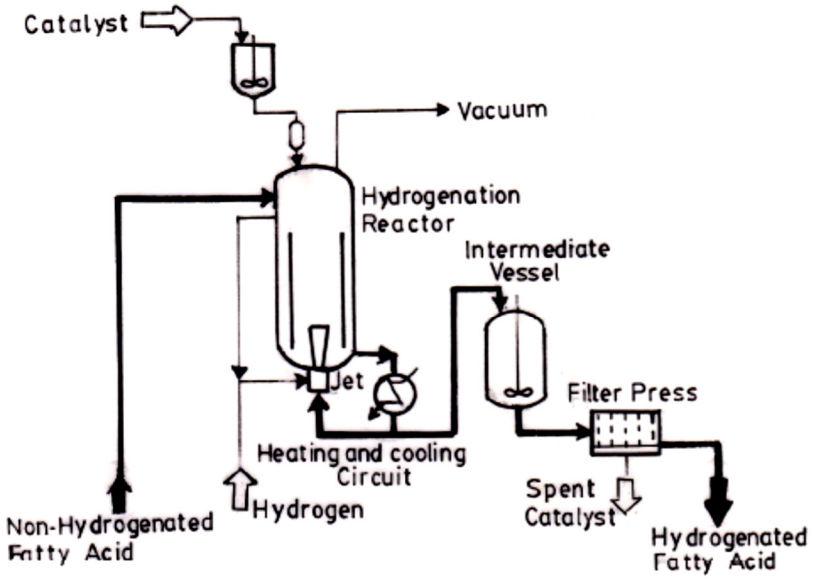


Fig. 1.27. Fatty acid hydrogenation (Lurgi GmbH, 1987)

The markets for technical (industrial) stearic acid include, manufacture of rubber goods and tyres, buffing compounds, greases, metallic stearates, industrial soap and textile specialties as well as candles, coated fillers, paper, plastics and personal care products including toilet soap, shaving creams, shampoos and cosmetics. Frequently, the soap or surfactant esters will provide emulsifying properties to the cosmetic formulation. The following is a list of applications where fatty acids and /or derivatives are used in various personal care products and cosmetics (Reck, 1985):

- Hand creams and lotions

- Emollient creams and lotions
- Liquid and cream shampoos
- Shaving soaps and creams
- Face powders and bath powders
- Rouges
- Hair dressings
- Hair conditioners
- Hair colorants and tints
- Aromatic products
- Deodorants and antiperspirants
- Eye creams and mascara
- Baby toiletries

Metallic soaps constitute another class of fatty acid derivatives, which are used extensively. The combination of acids and metal (inorganic) compounds to produce specialty soaps is almost limitless and methods of preparation are many and varied (Pilper, 1963). An industrial process for the production of metallic soaps is illustrated in Fig. 1.28. Following is a list of applications for metallic soaps (Pilper, 1963; Carmichael, 1954; Reck, 1985):

- Driers for paints, varnishes and printing inks
- Catalysts in condensation reactions
- Stabilisers for polyvinyl chloride resins
- Fungicides
- Mould release agents
- Lubricants in paper coating
- Lubricants for drawing ferrous metals
- Antiblocking and anticaking agents
- Water repellents
- Cosmetic formulations

• Lubricating greases

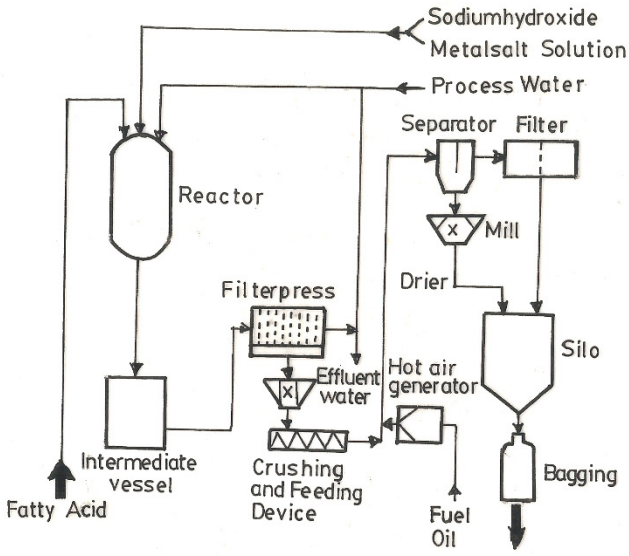
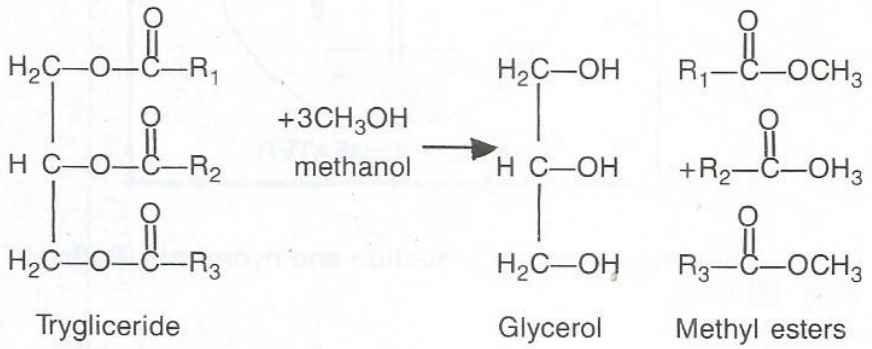


Fig. 1.28: Metallic soap production process (Lurgi GmbH, 1987)

1.11.6. Fatty acid methyl esters and fatty alcohols

1.11.7. Fatty acid methyl esters and their derivatives

Fatty acid methyl esters, derived from natural fats and oils (Fig. 1.29) can be used as alternatives to fatty acids in the production of a number of derivatives. These include ester sulphonates, fatty alkanolamides, fatty alcohols, isopropyl esters and sucrose polyesters. By using methyl esters as raw materials several benefits may be realised such as the ability to use milder conditions during synthesis, and the need for less expensive materials of construction. In addition, methyl esters are preferable to fatty acids for distillation because they have lower boiling points and are less corrosive (Ogoshi and Miyawaki, 1985).



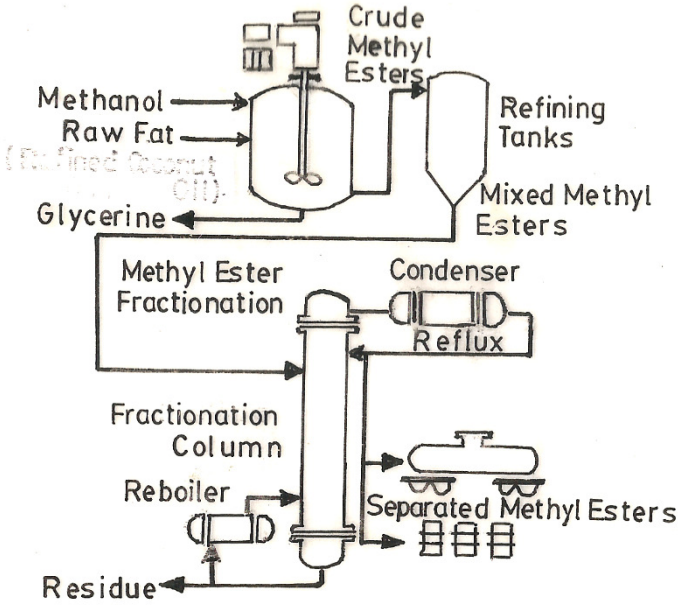


Fig. 1.29. Methanolysis and fractionation of methyl esters (Combs, 1985)

1.11.8. Ester sulphonates and their applications

Polymerisation emulsifiers

Fatty acid methyl esters are processed into ester sulphonates (α-sulpho-methyl esters, α-SFMe). Methyl esters are hydrogenated and sulphonated by gaseous sulphur trioxide to produce α-SFMe. Bleaching of the product with hydrogen peroxide is followed by neutralisation with aqueous NaOH. Long-chain ester sulphates of the palm/tallow range (C16- C18, a range that includes the potential tucum

oil and stearin-based products) perform well as polymerisation emulsifiers for PVC. Compared with lauryl alcohol sulphates, they give improved stabilisation and better gelation properties in the manufacture of PVC plastisols.

In ethyl acrylate/acrylic acid copolymers, these fatty acid ester sulphonates achieve almost the fine dispersion given by lauryl alcohol sulphate (Knaut and Richtler, 1985).

Detergents

The potential tucum sulphonates, like palm/tallow sulphonates, could exhibit good hard water detergency performance, sufficient biodegradability, good foam control and excellent detergency performance in heavy duty detergents. Particularly in foam controlled heavy-duty detergent powders, linear alkyl benzene sulphonate can be substituted by these long-chain (C16-C18) α-sulpho- fatty acid methyl esters to a proportion of up to 50% when traditional foam depressants (long chain soaps) are used (Knaut and Richtler, 1985). Sulphonated methyl esters of vegetable origin are important in the personal care industry, where they provide a milder irritation profile than fatty acid soaps and fatty ether sulphates which are the commonly used materials (Crandall, 2003).

Edible surfactant, food additives and preservative

Sucrose esterified with 1-3 fatty acids known as sucrose fatty acid esters (SFE), and sucrose fatty acid polyesters (SPE, sucrose esterified with six to eight fatty acids) are products of the reaction between sucrose and methyl esters (Akoh, 2002; Rizzi and Taylor, 1978). SFEs are highly hydrophilic surfactants, which are highly digestible and absorbable, and may be used as solubilisation, wetting, dispersion, emulsifying (especially in oil-in-water [O/W] and some water-in-oil [W/O] emulsions) and stabilisation agents. They may also be applied as antimicrobial protective coating for fruits (Harrigan and Breen, 1989; Drake *et al*., 1989).

These surfactants have a wide range of lipophilic-hydrophilic balance (HLB, 1-16), are tasteless, odourless, non-toxic and biodegradable, and may be used in food, cosmetics and pharmaceuticals. Sucrose polyester (SPE) is a non-digestible and non-absorbable fat-like substance which has the potential to lower cholesterol levels in certain lipid disorders (Mellies *et al.*, 1985; Grundy *et al.*, 1986).

Isopropyl esters

The reaction of methyl esters with isopropyl alcohol is the preferred method for the production of isopropyl esters, which are emollients (Johnson, 1978).

Soap manufacture

Saponification of methyl esters is one of the processes for soap making (Ogoshi and Miyawaki, 1985).

As diesel substitute (biodiesel)

A direct application of methyl esters is as diesel substitute. Here methyl esters produced from palm oil have been the dominant material. Biodiesel is required to constitute a certain percentage of in conformity with the Kyoto protocol targets for reducing greenhouse gas emissions. The rise in demand for green energy has led to increased demand for other vegetable oils. A consequence of this has been an expansion in the production of these commodities, with the risk of damage on a large scale, to tropical rain forests due to clearing of trees to establish new plantations. Here, increased exploitation of oils and fats from currently under-utilised palms, such as the tucum palm, could come to the rescue by providing oil from vast hectarages of natural stands. This in addition to exploiting their habitats in a sustainable manner could improve local economies in the areas in which they are found.

1.11.9. Fatty alcohols

Specific technologies have been developed for the reduction of natural and synthetic esters and fatty acids to the corresponding alcohols. The Bouveault-Blanc reaction for reducing esters to alcohols by the action of metallic sodium in the presence of an added alcohol is applied on an industrial scale to the production of fatty alcohols (Figs. 1.29 and 1.30). A major feature of this reaction is that it has as a product, fatty alcohols that retain the unsaturated carbon chain. Also, it is suitable for small-scale production, and operates at atmospheric pressure thereby allowing the use of relatively inexpensive equipment (Hansley, 1947; Kastens and Peddicord, 1949).

Another route to unsaturated fatty alcohols is by the selective hydrogenation (referred to hydrogenolysis) of fatty acids or their esters. Zinc chromite and cadmium modified copper chromite are the catalysts of choice for the process, which selectively hydrogenates the functional group while maintaining the double bonds in the alkyl chain. Using methyl ester as the starting material, the reaction is carried out at high pressure (205-275 atm) and high temperature (300-350°C). Oleyl alcohol may be produced from oleic acid, in which case the intermediate ester (oleyl oleate) is formed and is subsequently reduced to the alcohol. Natural fats and oils are composed of both saturated and unsaturated fatty acids in various proportions, and their sodium reduction or selective hydrogenolysis leads to the production of mixed fatty alcohols.

Palmitic acid from fat splitting and fatty acid separation may be converted to cetyl alcohol for use in cosmetics or for sulphation followed by neutralisation with sodium hydroxide to produce sodium palmitoyl sulphate. The latter is an anionic surfactant, which is included in several formulations including detergents, toothpaste, and shampoos, and is used in emulsion polymerisation.

Oleyl alcohol (9,10-octadecen-1-ol) is the most important fatty alcohol produced, and a variety of grades are available ranging in iodine value from around 45 to about 95 (Harshaw/Filtrol Partnership, 1986). In particular oleyl alcohol is an intermediate for biodegradable detergents. Sodium oleyl sulphate unlike its saturated counterpart sodium octadecyl sulphate is highly soluble and therefore generally more useful in different types of surface-active and detergent formulations for household or industrial applications.

Polyoxyethylene derivatives prepared by the addition of ethylene oxide to fatty alcohols are important non-ionic detergents. Their sulphates are anionic surfactants, which feature in several surfactant formulations. The emollient properties of cetyl and oleyl alcohols are utilised in the formulation of shaving creams, ointments and cosmetics. The ability of fatty alcohols to reduce stickiness and tackiness in many oily and waxy formulations necessary for the preparation of carbon papers, cutting oils, hydraulic fluids and lubricating oils provide other markets. Fatty alcohols are used as flotation and antifoaming agents (Knaut and Richtler, 1985).

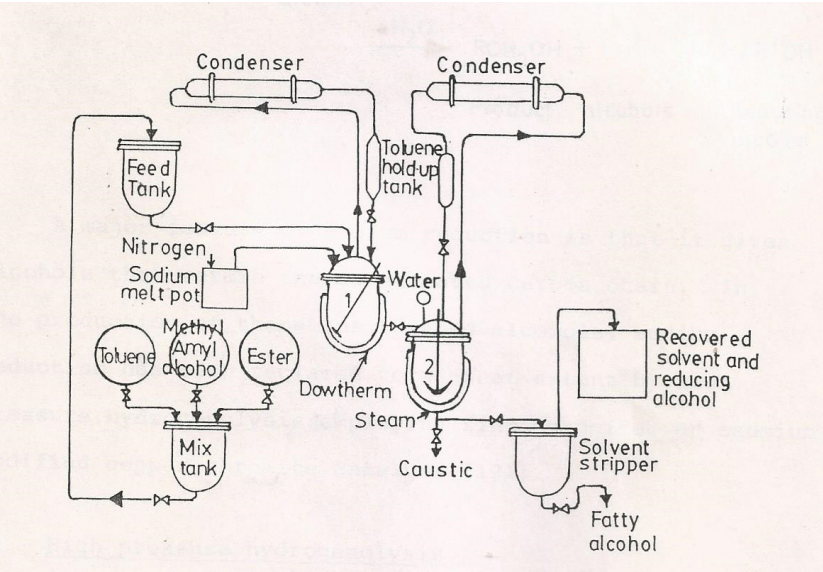


Fig. 1.30: Process flow sheet, sodium reduction unit (Wilson, 1954): 1. Reduction kettle. 2. Hydrolysis kettle1.11.7.

1.11.10. Synthesis and characterization of fatty acid methyl esters and fatty alcohols and their characterization.

Mr. Vice Chancellor Sir, I have enumerated the potential products which can be made from tucum pulp and kernel oils due to their fatty acid composition. In this study, I went further to prepare from these oils (and palm oil and palm kernel oil for comparison), fatty acid methyl esters and fatty alcohols, and characterized them, using a variety of chemical and physical, methods. The fatty acid methyl esters were synthesized by methanolysis, and the fatty alcohols by the sodium reduction method (Figure 1.30). The following are my findings.

Findings

The palm and tucum pulp and kernel oils used for fatty acid methyl ester synthesis had the fatty acid composition and physico-chemical characteristics shown in Table 1.39.

The fatty acid composition, iodine values, saponification values, and consistency at ambient temperature were in agreement with previously stated values for these oils and fats. They exhibited five prominent IR bands characteristic of glyceride oils (Figure 1.31): A weak band with a maximum at 3 μ, arising from O-H stretching due to the presence in the oil of partial glycerides, the characteristic strong C-H stretching band at 3.3-3.6 μ, the very strong band at 5.8 μ arising from the C=O stretching of the ester carbonyl group, and the weak bands at 8.5-8.9 and 14 μ caused respectively by C=O stretching of the ester moiety and the CH_2 rocking of the (CH_2) chain (Table 1.39).

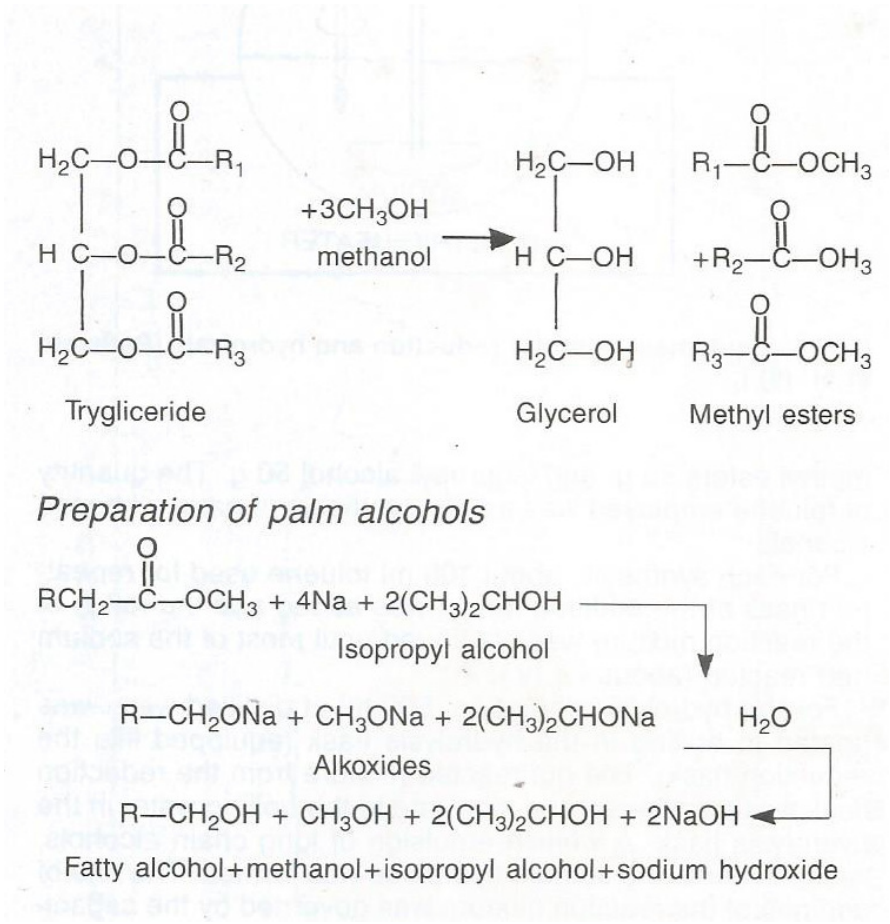


Fig. 1.30: Preparation of fatty acid methyl esters and fatty alcohols (Oboh and Lori, 1992; Oboh, 1995)

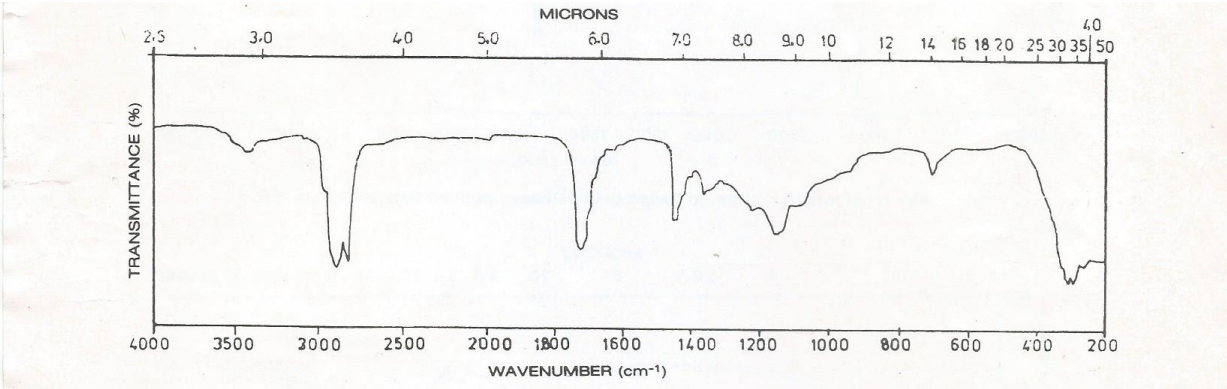


Fig. 1.31. Infrared spectrum of refined and bleached palm oils and tucum oils (Oboh, 1995)

Table 1.39. Characteristics of oils

Fatty acid	Palm oil	Tucum pulp oil	Palm kernel oil	Tucum kernel oils
8:0	-	-	1.7	2.0
10:0	-	-	3.8	2.4
12:0	0.2	-	44.6	45.5
14:0	1.1	-	19.4	20.2
16:0	42.3	30.4	9.4	5.6
18:0	5.3	2.2	3.4	5.6
18:1	41.6	59.9	13.2	12.6
18:2	9.5	2.9	4.8	6.0
20:0	-	4.6	-	-
Saponification value	207.3	188.6	243.2	232.1
Iodine value (Wij's)	54.2	63.5	18.2	16.5
Consistency at ambient temperature (27°C).	Semi-solid	Liquid	Liquid	Solid
IR bands (cm^{-1})	Five prominent bands characteristic of glyceride oils: 1. A weak band with a maximum at 3 μ, arising from O-H stretching due to the presence in the oil of partial glycerides. 2. The characteristic strong C-H stretching band at 3.3-3.6 μ. 3. The very strong band at 5.8 μ arising from the C=O stretching of the ester carbonyl group. 4. The weak band at 8.5-8.9 caused by C=O stretching of the ester moiety. 5. The band at 14 μ caused by the CH_2 rocking of the (CH_2) chain.			

The yield and characteristics of fatty acid methyl esters produced from a single-stage methanolysis of palm and tucum oils are shown in Table 1.40. The reaction gave reasonable yields (58.2 – 74.8%) of liquid free flowing, non-sticky products.

Table 1.40. Yield and characteristics of fatty acid methyl esters (FAMES)[a]

Characteristics	Palm oil FAMES[b] (Oboh and Lori, 1992)	Tucum pulp oil FAMES (Oboh, 1995)	Palm kernel oil FAMES Oboh and Lori, 1992)	Tucum kernel oil FAMES (Oboh, 1995)
Crude product yield (%)	96.5	95.6	95.6	95.0
Crude product purity (%)	78.9	67.0	70.0	62.3
Yield of FAMES (%)	74.8[c]	63.8[d]	70.1[e]	58.2
Free fatty acid content	0.2[f]	0.3[g]	0.1[h]	0.3
Iodine value (Wij's)	53.8	63.5	18.3	16.7
Saponification value	207.6	118.7	242.5	241.0
Consistency at ambient temperature (27°C)	Liquid	Liquid	Liquid	Liquid

[a]From single-stage methanolysis using 0.5% KOH as catalyst, [b]analytical values are the average of 3 determinations, [c]based on an average molecular wt of 256 for palm oil fatty acids and a theorectical yield of 105.5%, [d]based ion an average molecular wt of 282 and a theorectical yield of 105.0, [e]based on an average molecular wt of 200 for kernel oil fatty acids, and a theorectical yield of 107.0%, [f]as palmitic acid, [g]as oleic acid, [h]as lauric acid.

Table 1.41. Yields and characteristics of crude fatty alcohols[a] derived from palm oil and palm kernel oil (Oboh and Lori, 1992)

Characteristics	Palm oil-based product	Palm kernel oil-based product
Product yield (%)	99.4	98.8
Product purity (%)	76.4	75.9
Yield of alcohol (%)	85.9[b]	88.3[c]
Free fatty acid (%)	0.5[d]	0.4[e]
Iodine value (Wij's)	53.4	18.5
Melting range (°C)	85-101	-
Consistency at ambient temperature (27°C)	Soft waxy solid	Semi-solid
Characteristic IR bands (cm^{-1})	1. The band at 3.0 μ (from intermolecular H-bonding of OH) 2. The band at 3.3-3.6 μ (the C-H stretching band) 3. The weak band at 5.8-5.9 μ (from C-O stretching of the carbonyl) gp. 4. The strong band at 6.4 μ (from the antisymmetric and symmetric stretching of the carboxylate ion of soap). 5. The C-H bending band at 6.9 μ. 6. The alkyl band at 7.3 μ. 7. The C – O band at 9.6 μ due to the C- O – H of alcohol. 8. In the spectrum of the palm kernel-based product there is an additional band at 5.8 μ arising from the C=O stretching of the ester carbonyl, indicating incomplete conversion of the ester to alcohol.	

[a]Mean of 3 determinations, [b]based on average molecular wt of 270 and 240 of FAMES and fatty alcohols respectively, and a theorectical yield of 88.9% alcohols, [c]based on average molecular weights of 214 and 184 for FAMES and fatty alcohols respectively, and a theorectical yield of 86.0% for alcohols, [d]as palmitic acid, [e]as lauric acid.

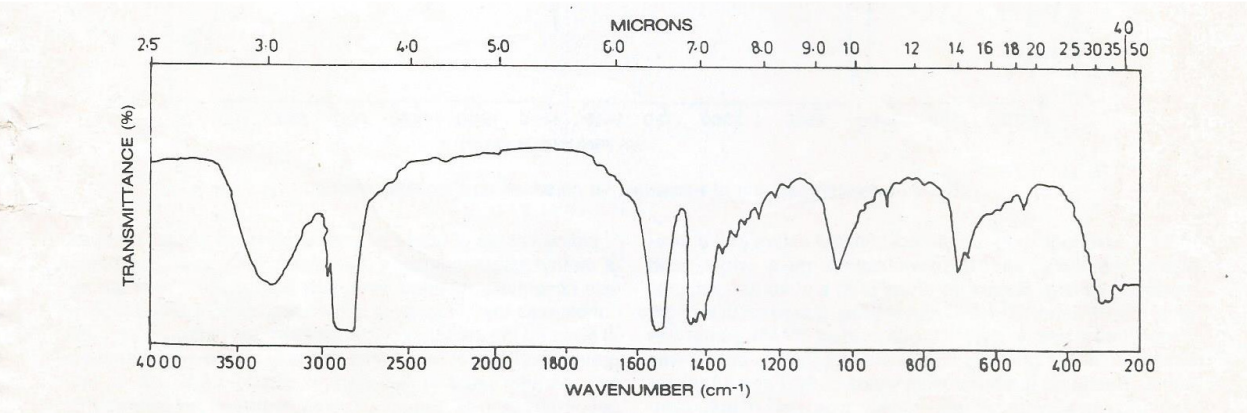


Fig. 1.32. Infrared spectrum of crude fatty alcohols

The yields and characteristics of the crude fatty alcohol preparations derived from pulp and kernel oils are shown in Tables 1.41 and 1.42. Thin layer chromatography (Fig. 1.33) showed the presence of considerable content of unreacted FAMES and co-product wax esters, with low free fatty content (less than 1%, except for the product derived from tucum pulp oil) and trace content of soap. The crude alcohol was purified by saponification with 2N ethanolic KOH and extraction with hexane. The hexane extract was washed with distilled water and dried over anhydrous sodium sulphate. The hexane was removed under vacuum in a rotary evaporator.

Table 1.42. Yield and characteristics of crude fatty alcohols derived from tucum fats (Oboh, 1995) [a]

Characteristics	**Tucum pulp oil-based product**	**Tucum kernel fat-based product**
Product yield (%)	99.6	98.8
Product purity (%)	77.4	68.8
Yield of alcohol (%)	86.6[b]	80.0[c]
Free fatty acid (%)	1.1[d]	0.4[e]
Iodine value	60.9	16.0
Melting range (°C)	108-110	106-110
Consistency at ambient temperature (27°C)	Semi-solid gel	Waxy solid
Characteristic IR bands (cm^{-1})	1. 3.0 μ (OH) 2. 9.6 μ (-C-O-H) 3. 3.3-3.6 μ (C-H) 4. 6.9 μ (-CH-) 5. 7.3 μ (CH_3) 6. 5.8-5.9 μ (-C=O) 7. 8.6 μ (-$COOCH_3$) 8. 6.4 μ (-COO^-) 9. 14.0 μ (-$(CH_2)_n$-)	1. 3.0 μ (OH) 2. 9.6 μ (-C-O-H) 3. 3.3-3.6 μ (C-H) 4. 6.9 μ (-CH-) 5. 7.3 μ (CH_3) 6. 5.8-5.9 μ (-C=O) 7. 8.6 μ (-$COOCH_3$) 8. 6.4 μ (-$C00^-$) 9. 14μ (-$(CH_2)_n$-)

[a]Mean of three determinations, [b]Based on average molecular wt of 296 and 266 respectively for FAME and fatty alcohols respectively, and a theorectical yield of 89.9% for fatty alcohols, [c]Based on average molecular weights of 214 and 184 for FAME and fatty alcohols respectively, and a theorectical yield of 86.0% for fatty alcohols. [d]As oleic acid, [e]As lauric acid

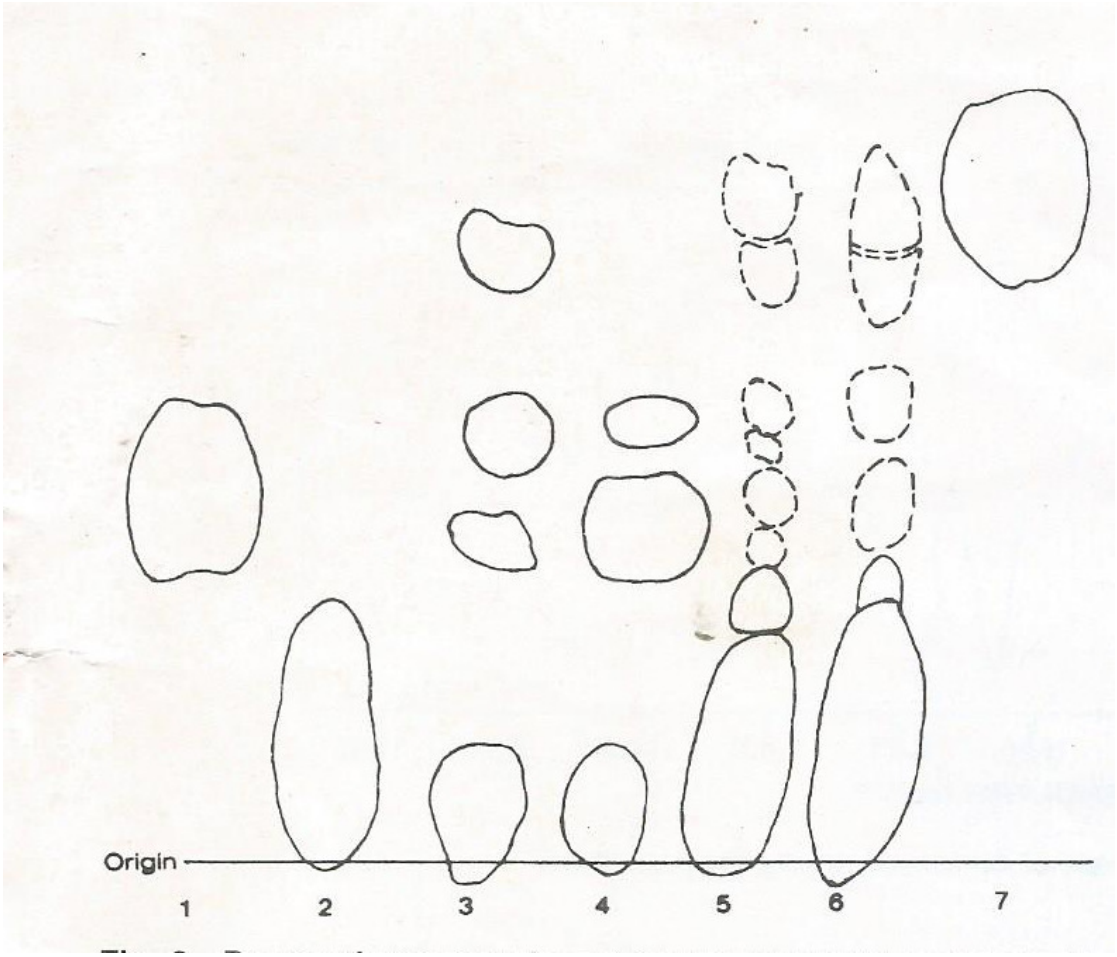


Fig. 1.33: Separation of tucum kernel fat and pulp oil based fatty alcohol by adsorption thin-layer chromatography (1). Methyl ester standard; (2) 1-octanol standard; (3) pulp oil based crude alcohol; (4) kernel fat based crude alcohol (5) pulp oil based purified alcohol; (6) kernel oil based purified alcohol (7) hydrocarbon standard

***Operating conditions*: 20 x 20 cm TLC plates coated with a 0.75 mm layer of silica gel G, sample size 50 mg, vertical development with methanol/benzene/hexane, 1/29/70 by volume**

The characteristics of the purified fatty alcohols from the sodium reduction of palm oil and tucum fatty acid methyl esters are given in Table 1.43. The purified alcohols gave the distinct infra-red bands at 3.0 μ, 3.3-3.6 μ, 6.9 μ, and 9.5 μ (Fig. 1.34) characteristic of long chain alcohols, and refractive indices n_D 27.5 ^oC of 1.4590 and 1.4505 for the palm oil and palm kernel oil-based alcohols, and 1.460 and 1.448 for the tucum pulp and kernel oil-based products respectively. There was similarity between the iodine values of 53.4 and 18.5 for the palm oil and palm kernel-based products, and 60.9 and 16.0 for the tucum pulp oil and kernel oil-based products respectively and the iodine values of the oils from which they were derived (Table 1.29). This indicates that the fatty alcohol composition

is similar to the fatty acid composition of the oils from which they were derived because unsaturated sites on the carbon chain are retained, and with the purified kernel oil-based product consisting mainly of n-lauryl and n-myristyl alcohols, and lesser amounts of n-octyl, n-decanoyl, n-oleyl, n-palmityl, n-stearyl and n-linoleyl alcohols. The mesocarp oil-based products would be composed mainly of palmityl (cetyl) alcohol, constituting 30% and 42.3% of tucum pulp oil and palm oil-based alcohols respectively. Cetyl alcohol is easily separable from oleyl alcohol, and finds application in surfactant manufacture and as an emollient in cosmetics. Also, the palm oil-based product would contain 41.6% oleyl alcohol.

Purified fatty alcohols from sodium reduction of tucum pulp oil and palm oil FAMES exhibited characteristics (Table 1.43) similar to those of n-oleyl alcohol. N-oleyl is a unique long chain monounsaturated alcohol, which is available only from natural sources (Wilson, 1954; Monick, 1979). A variety of grades of this alcohol are available ranging in iodine value from 45-95 (Harshaw/Filtrol, 1986). N-oleyl alcohol is an intermediate for biodegradable detergents. Sodium oleyl sulphate, unlike the saturated product sodium octadecanoyl sulphate is easily soluble, and therefore generally more useful in different types of surface-active and detergent applications for household and industrial use (Klonowsky *et al*., 1970).

Due to their high content of medium chain fatty alcohols, the kernel oil-based products would be good starting materials for the manufacture of surfactants with good cold-water stability and emulsification power (Knaut and Richtler, 1985).

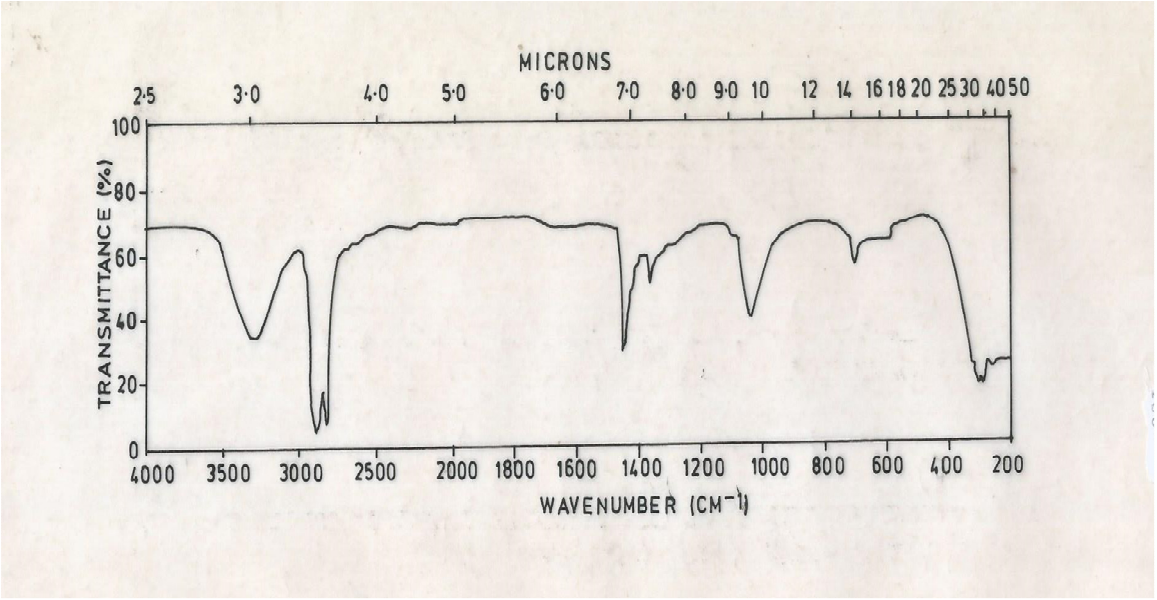
Table 1.43. Characteristics of the purified alcohols (Oboh and Lori, 1992, Oboh, 1995).

Characteristics	**Palm oil-based alcohol**	**Palm kernel oil-based alcohol**	**Tucum pulp oil-based alcohol**	**Tucum kernel oil-based alcohol**
Refractive index, n_D (27.5^{o}C)	1.4590	1.4505	1.460	1.448
Iodine value (Wij's)	53.4	18.5	60.9	16.0
Consistency at ambient temperature (27.5^{o}C)	Semi-solid	Viscous Liquid	Viscous Liquid	Viscous Liquid

Colour	Dark yellow	Light yellow	Light gray	Light yellow
IR bands	3.0 μ (OH), 3.3-3.6 μ (C-H), 6.9 μ (-CH-), and 9.6 μ (-C-O-H)			

Fig. 1.34: Infrared spectrum of purified fatty alcohols

The high oleyl alcohol content of tucum pulp oil-based alcohols (IV= 60.9) represents a valuable and abundant source of this material for the chemical industry. Tucum stearin (IV= 43.8) also contains a high



proportion of oleic acid (Table 1.31), and on its sodium reduction or selective hydrogenolysis would yield industrial oleyl alcohol. Due to its low linoleic acid content, tucum pulp stearin would possess oxidative stability comparable to that of tallow, the principal raw material for industrial oleyl alcohol production, and superior to the palm oil-based product of much higher linoleic acid content. The bi-functional nature of unsaturated alcohols provides a basis for their use as intermediates in the synthesis of polyfunctional oleochemicals. Reaction of oleyl alcohol with oleic acid using chemical or biocatalysts yields wax esters, which can be used as an oily component of cosmetics (Thum, 2005). Other applications of oleic acid based wax esters are in pharmaceuticals, and polish. They can also be sulphurised for use as extreme pressure lubricant additive (Bell *et al*, 1977), where their resistance to autoxidation is desired. Synthesis of wax esters from tucum pulp fatty acids and fatty alcohols using a calcium acetate/barium acetate 3:1 catalyst and xylene as solvent gave a crude product with a saponification value of 127.4, an iodine value of 69.4 and a free fatty acid content of 29.2% (Oboh, 1987a; 2009).

The potential for the utilisation of tucum pulp and stearin, and kernel oil in basic oleochemical production is illustrated in Figures 1.35 and 1.36.

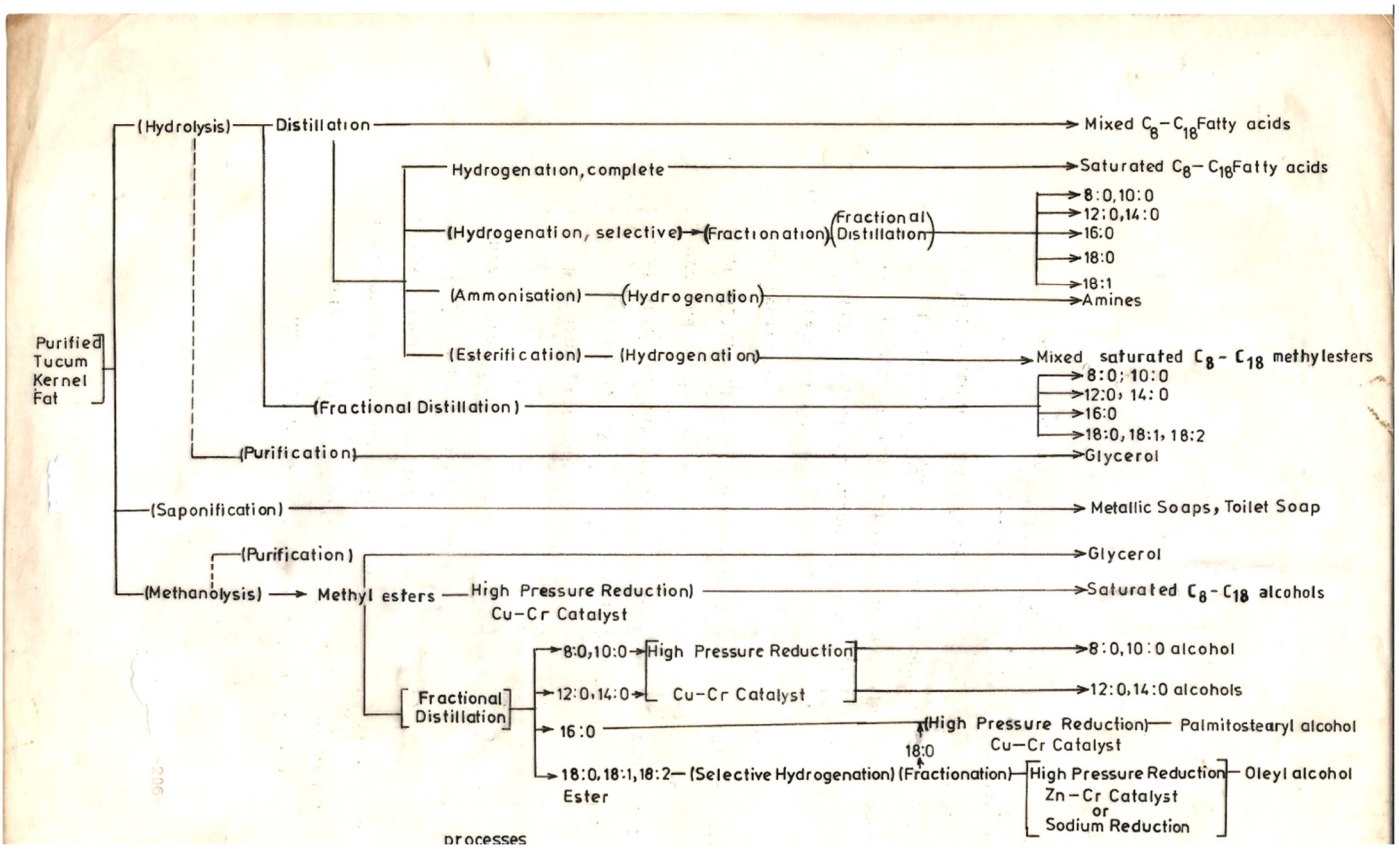


Figure 1.35: Basic oleochemical processes and some oleochemicals from palm kernel oils (1994b)

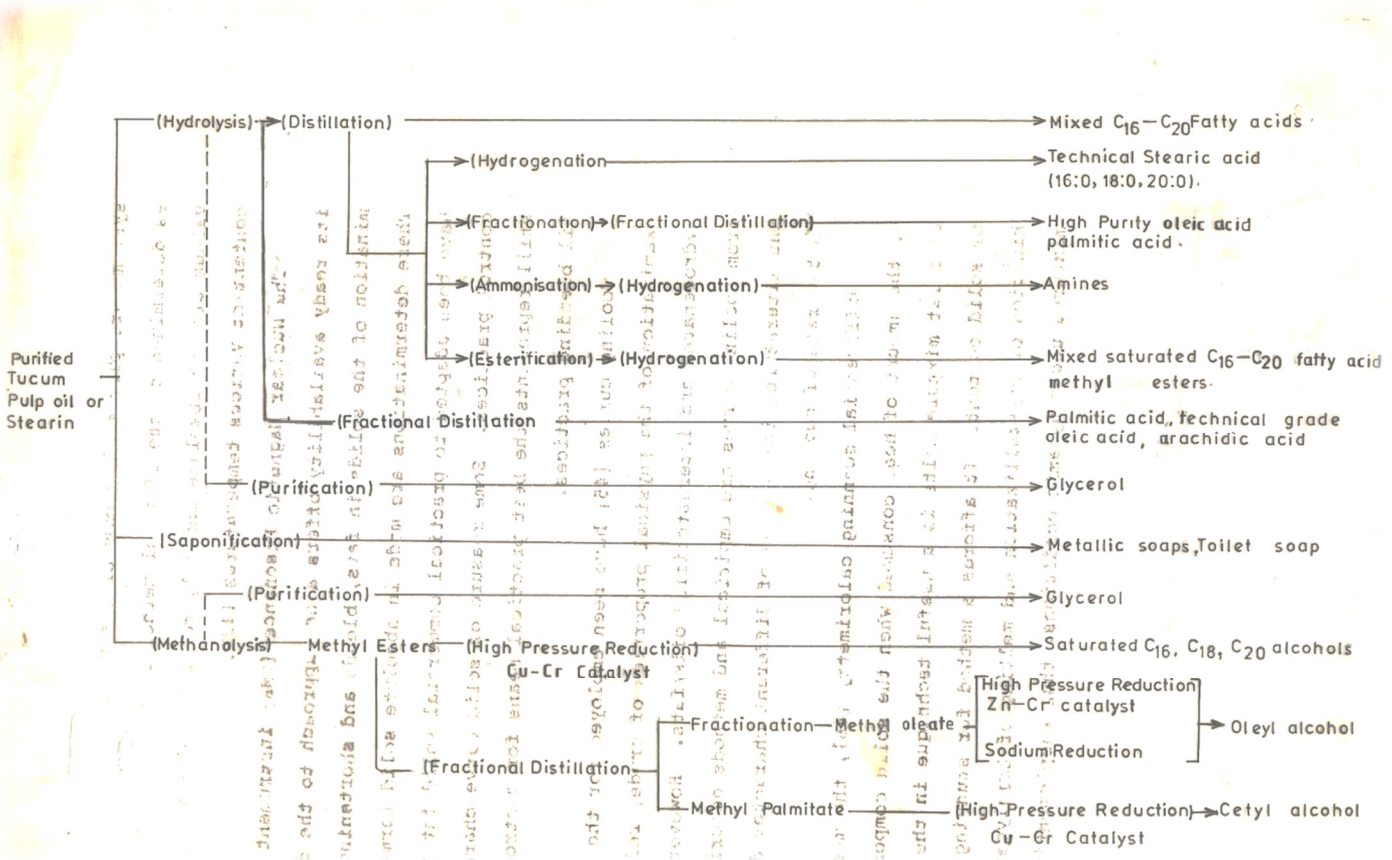


Figure 1.36: Basic oleochemical processes and some oleochemicals from purified tucum oil and stearin (1994b).

2.0. STUDIES ON GREEN LEAFY VEGETABLES

2.1. Some aspects of their composition and biological activity

Green leafy vegetables are a good source of dietary fibre, carotenoids, vitamin C, foliate, other phytochemicals that exhibit biological effects, and minerals. They present an inexpensive and readily available approach to combating certain micronutrient deficiencies. Due to their high moisture and adequate fibre content, they provide bulk in the diet and a feeling of satiety at the expense of energy dense dietary components. Thus, they are helpful in the prevention or management of some chronic conditions, which arise partly as a result of excessive energy and inadequate fibre intake. Their phytochemicals also offer protection against disease (Wardlaw and Kessel, 2002).

In this study, the moisture, protein, and mineral content of leafy vegetables from five tropical plant species, namely *Vernonia amygdalina* (bitter leaf, oriwo in Edo), *Telfairia occidentalis* (ugu in Ibo, eb'umenkhen in Esan), *Jatropha tanjorensis* (hospital too far), *Ocimum gratissimum* (scent leaf in English Nigeria, eb'alubhonkho in Esan), and *Gnetum africanum* (okazi in Ibo) were examined. Following are the results (Table 2.1). Included for comparison are literature values for cassava, potato and cowpea leaves.

2.1.1. Proximate composition and antimicrobial activity of the leafy vegetables

Water (72.06-82.07%) was the major constituent of the vegetables. Protein (1.12-2.33%) and ash (0.27-1.33%) were minor constituents. Phosphorus content (5.24-11.35%) was low, its content in the leaves constituting less than 1% of RDA. The contribution of the leaves to the RDA for selenium (0.98-1.64%) and zinc (0.75 to 4.07%) respectively were modest. For Fe, the contribution of the vegetables to its RDA varied from modest to high: *V. amygdalina* (3.13 to 4.70%), *J. tanjorensis* (6.27-9.40%), *T. occidentalis* (6.33 to 9.50%), and *O. gratissimum* (5.27 to 7.9%). These were comparable to literature values for cabbage (4.0 to 6.0%), but far lower than the values for cowpea leaves (12.67 to 19.0%); the contribution of *G. africanum* (26.73 to 40.10%) was the highest by far.

Leafy vegetables are high moisture, low acid produce, which support the growth of a wide range of microorganisms, which cause food poisoning, especially those, for example *S. aureus* and *E. coli*., which produce heat-stable toxins that may not be destroyed by heat treatment such as cooking (James and Kuipers, 2003; Eyabi, 2001; Schmidt, 1985). Some leafy vegetables, for example, *G. africanum* and *T. occidentalis*, may be eaten uncooked, in combination with palm oil in salads

(Oboh *et al.*, 2009). It was of interest therefore, to find out whether the vegetable had any antimicrobial effect on some common food poisoning organisms. The effect of an aqueous extract of the leaves on the gram-positive bacterium *Staphylococcus aureus* and the gram-negative bacterium *Escherichia coli* is presented in Table 2.1. All the leaves displayed activity against the organisms except *T. occidentalis* which exhibited activity against *E. coli* only, and *G. africanum* which had no activity against both organisms.

TABLE 2.1. Moisture, protein, mineral content, and antimicrobial activity of the leafy vegetables studied, in comparison with literature values for cassava, cabbage and sweet potato leaves

Leaves	Moisture (% by wt)	Protein (% by wt)	Ash (% by wt)	Colour	MINERALS (mg/100 g)				ANTIMICROBIAL ACTIVITY	
					P (RDA*= 1300 mg)	Se (RDA= 0.055 mg	Fe (RDA=10-15 mg)	Zn (RDA= 15 mg)	Zone of inhibition (cm)	
									Escherichia coli	*Staphylococcus aureus*
Vernonia amygdalina[a]	82.0	1.3	0.5	Dark green	6.16 (0.47%) **	8.2×10^{-4} (1.49%)	0.47 (3.13-4.7%)	0.113 (0.75%)	0.8	0.8
Jatropha tanjorensis[b]	78.77	2.01	0.51	Dark green	7.70 (0.59%)	5.4×10^{-4} (0.98%)	0.94 (6.27-9.4%)	0.61 (4.07%)	1.13	1.60
Telfaria occidentalis[c]	77.43	1.70	0.27	Dark green	8.48 (0.65%)	9.0×10^{-4} (1.64%)	0.95 (6.33-9.5%)	0.36 (2.4%)	1.7	0.0
Ocimum gratissimum[d]	81.35	1.21	0.57	Dark green	5.24 (0.40%)	7.0×10^{-4} (1.27%)	0.79 (5.27-7.9%)	0.15 (1.0%)	1.2	1.0
Gnetum africana[e]	72.06	2.23	1.33	Dark green	11.35 (0.87%)	6.4×10^{-4} (1.15%)	4.01 (26.73-40.10%)	0.41 (2.73%)	0.0	0.0
Cassava[f]	80.0	6.0	-	Dark green	-	-	-	-	-	-
Cabbage[f]	79.0	1.4	-	Dark green	54.0 (4.15%)	-	0.6 (4.0-6.0%)	-		
Cowpea[g]	85.0	4.7	-	Dark green	9.0 (0.69%)	-	1.9 (12.67-19.0%)	-		
Sweet potato[f]	83.0	4.6	-	Dark green	-	-	-	-		

*RDA=Recommended Dietary Allowance. **() in parentheses: Proportion of the RDA, which is provided by 100 g of the vegetable. [a]Oboh and Masodje (2009a); [b]Oboh and Masodje (2009b); [c]Oboh *et al.* (2009), [d]Oboh *et al*. (2009); [e]Oboh and Masodje (Unpublished), [f]Van Gastel and van den Wijingaart (1997); [g]Madamba *et al*. (2006)

2.2. Effects of Drying and Salting on Leafy Vegetables

2.2.1. Vernonia amygdalina leaves (Oboh and Madojemu, 2010; Oboh *et al.*, 2013; Oboh *et* 2019)

Tables 2.3-2.7 show the effects of the various treatments on the characteristics of *V amygdalina* leaves

TABLE 2.3. Sensory characteristics of fresh and fermented *V. amygdalina* leaves

	Treatments				
Characteristics	**Fresh**	**Light brine**	**Light salting (dry salt)**	**Light salting + Vinegar**	**Heavy s**
Colour	Dark Green	Dull dark green	Dark dull dark green	Lighter shade of dirty dark green	Dark gr
Taste	Very bitter	Harsh bitterness gone. Tastes like *eru* a Nigerian condiment.	Harsh bitterness gone. Tastes like *eru.*	Harsh bitterness gone. Tastes slightly different from the product from salt treatment alone.	Very bit salty.
Odour	Fresh green leafy smell	Slight but not offensive. Smells like *eru.*	Slight but not offensive. Smells like *eru.*	Slight but not offensive. Smells like *eru.*	Fresh leafy sm
Appearance and texture	Firm and slightly coarse	Slightly less firm than fresh leaves. Slightly more coarse than fresh leaves.	Slightly firmer than product of light brining. Less coarse than fresh leaves.	Retained more of the original structure of the fresh leaves than products from salt treatment alone. Smooth feel.	Similar leaves. S coarse.

The organoleptic characteristics of *V. amigdalina* leaves are shown in Table 2.3. Heavy salting resu in the best-preserved leaves, followed by light salt and vinegar treatment. Light brining and light sal

produce dull dark coloured largely debittered leaves, which had a pleasant smell, indicating the possibility of culinary application as condiment.

TABLE 2.4. pH values for fresh and treated *V. amygdalina*

Leaves	***Vernonia amygdalina***
Treatments	**pH**
Fresh (untreated)	6.89
Heavy salting	4.30
Light brining	5.00
Light salting	5.36
Light salt + vinegar	4.50

All treatments gave products with reduced pH (Table 2.4), the lowest being the heavy salted (i.e., the most acidic), closely followed by leaves from light salt and vinegar treatment. These treatments also produced leaves with the closest characteristics to the fresh (untreated) leaves.

TABLE 2.5. Carotene, vitamin C, moisture and fibre content of *V. amygdalina* leaves subjected to different preservation treatments.

Bitter leaf	**ß- carotene (mg/ g DM*)**	**Total carotene (mg/ 100 g DM)**	**Vitamin C (mg/100 g DM)**	**Moisture (% fresh wt)**	**Crude fibre (mg/g)**
Fresh	0.326 ± 0.037^{c}	1.403 ± 0.050^{b}	2131.4 ± 8.370	81.00 ± 1.00^{c}	6.44 ± 0.04^{b}
Oven Dried	$0.071 \pm 0.006^{a, b}$	$1.077 \pm 0.017^{a, c}$	$1604.9\pm 72.610^{a, c}$	-	-
Blanched and oven dried	0.334 ± 0.036^{c}	1.384 ± 0.110^{c}	$1551.9 \pm31.400^{a, c}$	-	-
High Salt	$0.014 \pm 0.009^{a, b}$	0.039 ± 0.010^{a}	$15.495 \pm 2.247^{a, b}$	$36.90 \pm 1.94^{a, d}$	$3.23\pm 0.29^{a, d}$
Light brine	$0.031 \pm 0.007^{a, d}$	$0.058 \pm 0.014^{a, d}$	$56.216 \pm 1.079^{a, d}$	$46.00 \pm 3.97^{a, d}$	$3.04 \pm 0.11^{a, d}$

Light salt	0.037 ± 0.046[a, d]	0.058 ± 0.008[a, d]	43.603 ±2.250	48.40 ± 3.50[a, d]	3.35 ± 0.44[a, d]
Light salt+ vinegar	0.007 ± 0.001[a, b]	0.017 ± 0.003[a, b]	5.405 ± 1.081	43.80 ± 7.44[a, b]	2.98 ± 0.15[a, d]

*DM = Dry Matter; **Mean ± Standard Deviation; t-test: [a]values differ significantly compared with the fresh sample mean ($p < 0.05$). ANOVA: [b]mean values differ significantly from other means within the same group ($p < 0.05$). [cd]values are not significantly different ($p < 0.05$) within the same group.

TABLE 2.6. Ash, iron, calcium and sodium content (dry wt) of fresh and preserved *V. amygdalina* leaves.

Bitter leaf	**Ash (g/100 g)**	**Fe (µg g^{-1})**	**Ca (µg g^{-1})**	**Na (µg g^{-1})**
Fresh	3.03 ± 0.07[c]	6.76 ± 0.57[c]	2.79 ± 0.72	5.21 ± 0.73b
Oven dried	2.28 ± 0.03[a]	5.19 ± 1.30[c]	1.99 ± 0.31[a, c]	3.06 ± 1.15[a]
Blanched and oven dried	3.43 ± 0.03[c]	4.54 ± 0.74[c]	1.21 ± 0.37[a, c]	2.39 ± 0.38[a]
Heavy salt	2.64 ± 0.04[c]	0.46 ± 0.45[a, d]	4.55 ± 1.72[a]	318.00 ± 2.65[a]
Light brine	1.47 ± 0.06[a]	0.22 ± 0.07[a]	2.30 ± 0.81[b]	209.00 ± 12.29[a, c]
Light salt	1.96 ± 0.40[a, d]	0.60 ± 0.33[a]	3.13 ± 0.93[ac]	295.30± 7.38[a]
Light brine + vinegar	1.90 ± 0.27[a, d]	0.46 ± 0.15[a, d]	3.17 ± 2.25[a, c]	181.3 ± 41.48[a, c]

t-test: [a]values differ significantly compared with the fresh sample mean ($p < 0.05$). ANOVA: [b]mean values differ significantly from other means within the same group ($p < 0.05$). [c, d] values are not significantly different ($p < 0.05$) within the same group.

TABLE 2.7. Percentage retention (or increase) of nutrients after treatments

	β-carotene	**Total carotene**	**Vitamin C**	**Moisture**	**Crude fibre**	**Ash**	**Fe**	**Ca**	**Na**
Fresh	100	100	100	100	100	100	100	100	100
Oven dried	21.78	76.76	75.30	-	-	75.25	76.78	71.33	58.73
Blanched and oven dried	100.00	98.65	72.81	-	-	(113.15) *	67.16	43.37	45.87
Heavy salt	4.29	26.78	0.73	36.90	50.16	87.13	6.81	(163.08)	(6103.65)
Light brine	9.51	4.13	2.64	46.00	47.21	48.52	3.25	82.44	(4011.52)
Light salt	11.35	4.13	2.04	48.40	52.12	69.69	8.86	(112.19)	(5667.95)
Light brine + vinegar	2.15	1.21	0.25	43.80	46.27	62.71	6.81	(113.62)	(3479.85)

*() In parenthesis: Increase in nutrients levels after treatment

Table 2.7 shows nutrient retention (or increase) after the various treatments. Blanching prior to oven-drying, gave higher retention of β-carotene and total carotene, with similar values for vitamin C after oven drying with or without prior blanching. Total mineral matter had a high retention.

However, higher content of Fe, Ca, and Na were found after oven-drying alone than after prior blanching, due to leaching of these minerals during the blanching process.

Salting, in its various modifications, resulted in high loss of nutrients. It resulted in dehydration of the leaves, with heavy salting resulting the highest moisture loss, followed by light brine and vinegar treatment, light brine, and light salt treatment, which had the least moisture loss. This followed the patterns displayed by pH and organoleptic tests, the best preserved having both the lowest moisture content, and the lowest pH and the best protection of the organoleptic characteristics of the leaves. This indicates that the combination of three factors aided the preservation of the organoleptic characteristics of the leaves as follows:

i. The salinity of the medium, which provided an environment hostile to most microorganisms, except for the halophiles. In the process, the salt exerts a selective action on the naturally occurring organisms to promote a desirable fermentation.
ii. Production of short chain organic acids, resulting in pH values hostile to the survival spoilage bacteria; salt tolerant microorganisms use as their nutritive material, the soluble constituents that diffuse out of the vegetable as a result of the action of the salt on vegetable tissue.
iii. The dehydration of the leaves.

The results of tests for phytochemicals and the total phenolic content of the fresh and preserved leaves are presented in Table 2.8. These compounds when present in the diet could provide biological and pharmacological benefits.

TABLE 2.8. Phytochemicals of fresh and salted *Vernonia amygdalina* leaves.

Samples	Saponins	Tannins	Flavonoids	Alkaloids	Steroids	Glycosides
Fresh	+	+	_	_	+	+
Light brine	+	+	_	_	_	+
Light salt	+	+	_	_	+	+

Light brine + vinegar	**+**	**+**	_	_	_	**+**
Heavy salt	**+**	**+**	_	_	_	**+**
No salt	**+**	_	_	_	**+**	**+**

+: Present. -: Absent.

.

Saponins and glycosides were found in all the leaves (fresh, salted and unsalted) and tannins were present in all except the unsalted. Steroids were detected in the fresh, light salted and water treated (unsalted) leaves. Flavonoids and alkaloids were not detected in any of the samples.

TABLE 2.9. Total phenolic content (TPC) of fresh and salted *Vernonia amygdalina* leaves

Samples	**Total phenolic content (mg GAE[1]/L)**	**% Loss relative to the fresh[2]**
Fresh	799.00	-
Light brine	432.00	45.93
Light salt	532.00	33.42
Light brine + vinegar	386.00	51.69
Heavy salt	511.00	36.05
No salt	581.00	27.28

[1]Gallic Acid Equivalent. [2]Percentage loss relative to the fresh = 799.0 – TPC/ 799.0 x 100

The fresh sample gave the highest total phenolic content (TPC) (Table 2.9). The highest loss of TPC was for the light brine + vinegar preserved leaves (51.69%). The lowest loss was for the badly preserved water treated leaves (27.28%). Of the salted leaves, the heavy-salted and light-salted lost about a third of their TPC (36.05 and 33.42% respectively), and light brining resulted in the loss of 45.93%. Thus, the best-preserved leaves in terms of organoleptic properties (i.e., the heavy-salted) lost only about a third of their TPC.

TABLE 2.10. Fungal counts of fresh and fermented *V. amygdalina* leaves

Samples	Fungal count (x 10^2 CFU/mL)	% Loss relative to the fresh sample*
Fresh	120	-
Light brine	49	59.16
Light salt	47	60.83
Light brine + Vinegar	43	64.17
Heavy salt	8	93.33
No salt	292	-

*% loss relative to fresh sample = $\frac{12000 - \text{fungal count after each treatment}}{12000} \times 100$

Table 2.10 shows the fungal counts of fresh and fermented leaves. In all cases, salting resulted in a decrease in fungal count. The fresh leaves had a higher fungal count (120 x 10^2 cfu/ml) than the salted samples (49, 47, 43 and 8 x10^2 cfu/ml, for light brined, light salted, light brine + vinegar treated and heavy salted leaves respectively). Unsalted leaves had the highest count (292 x 10^2 cfu/ml, about a two and half-fold increase, compared with the fresh leaves). Heavy salting was the most effective for the reduction of fungal load (93.3% reduction) and was therefore the most effective preservation treatment.

Table 2.11 shows the occurrence of fungal species and genera in fresh and salted *Vernonia amygdalina* leaves. *A. nige*r occurred in the fresh, light brined and the water treated (no salt) leaves. *A. flavus* was associated with all the samples (fresh and treated) and *Penicillium* with the light salted and water treated. *Fusarium* was associated with only the light salt and vinegar treated leaves.

TABLE 2.11. Occurrence of fungal species and genera, and aflatoxin in fresh and preserved *V. amygdalina* leaves

Leaves	*Aspergillus niger*	*Aspergillus flavus*	*Penicillium* spp.	*Fusarium* spp.	Aflatoxin
Fresh	+	+	-	-	**+**
Light brine treated	+	+	-	-	**+**
Light salt treated	-	+	+	-	**+**
Light brine + vinegar treated	-	+	-	+	**+**
Heavy salt treated	-	+	-	-	**+**
Water (no salt) treated	+	+	+	-	**+**

+: Present. -: Absent

Mycotoxins are small (MW ~ 700), toxic chemical products formed as secondary metabolites by a few fungal species that readily colonise crops and contaminate them with toxins in the field, between harvest and drying, and during storage. The major mycotoxin-producing fungal genera are *Aspergillus, Fusarium* and *Penicillium.* The most common mycotoxins are aflatoxins, ochratoxin A, fumonisins, deoxynivalenol, T-2 toxin, and zearalenone (Turner *et al*, 2009; Zheng *et al*, 2006).

A green colour characteristic of aflatoxins B_1 and B_2 (Surekha *et al*, 2011) was observed when leaf extracts were cleaned up, separated by thin-layer chromatography, and viewed under ultra violet light. Aflatoxins are highly toxic and carcinogenic secondary metabolites of *A. flavus, A. parasiticus* and *A. nomius. A. flavius* produces only aflatoxins B_1 and B_2, while the other two species produce both aflatoxins B and G. (Baydar, 2007). In this study, *A. flavus* was found to be associated with the leaves. Some species of *Fusarium* produce the mycotoxins zearalenone and fumonisin B_1, which are possibly carcinogenic in humans. One species of *Penicillium, P. verrucosum* produces ochratoxin, which is suspected to be a human carcinogen (GASGA, 1997).

TABLE 2.12. Frequency of occurrence of fungi isolates

Fungal isolates	Percentage frequency of occurrence
Aspergillus flavus	79.12
Aspergillus niger	74.21
Penicillium spp.	48.26
Fusarium spp.	19.36

Results (Table 2.12) show that the percentage frequency of occurrence of fungi associated with fresh, salted, and unsalted leaves was highest for *A. flavus* followed by *A. niger and Penicillium. Fusarium* had the lowest occurrence. Unlike the other treatments which gave leaves with two or more organisms, only *A. flavus* was found in the heavy salted leaves, which in addition, had the lowest fungal count. The effect of preservation treatments on the bacterial count of *V. amygdalina* leaves is shown in Table 2.13.

TABLE 2.13. Effect of salting on the bacterial count of *V. amygdalina* leaves

Leaves	**Bacterial count (cfu/ml)**	
Fresh (day 1)	0	
On day 3	40×10^2	
Treatments[a]		**% Decrease[b]**
Heavy salting	10×10^2	75.0
Light salting + vinegar	8×10^2	80.0
Light brining	16×10^2	60.0
Light salting	19×10^2	52.2

[a]Treatments of fresh leaves were for 14 days prior to bacterial counts

**% loss relative to 3-day old sample = $\frac{4000 - \text{bacterial count after each treatment}}{4000} \times 100$

Leaves were bacteria-free until the third day after harvesting, probably due to their antibacterial activity (Oboh and Masodje, 2009a). This activity diminished due to post mortem loss of physiological activity and subsequent breakdown of plant tissue resulting in loss of resistance to bacterial infection. Bacterial count of untreated *V. amygdalina* leaves on the third day was 40 x 10^2 cfu/ml; compared with this, preservation treatments decreased the microbial load. The largest decrease (80.0%) resulted from light brine + vinegar treatment; heavy salting resulted in a 75.0% decrease.

Bacterial genera associated with fresh and salted *V. amygdalina* leaves are shown in Table 2.14.

TABLE 2.14. Bacterial genera observed in fresh and salted *V. amygdalina* leaves

-: Absent. +: Present

Leaves	***Streptococcus spp.***	***Staphylococcus spp.***	***Lactobacillus spp.***
On day 3	+	+	-
Treatments			
Heavy salting	+	-	+
Light brine and vinegar	+	-	+
Light brining	_	+	+
Light salting	-	+	+

The fresh leaves yielded no bacterial growth. In the absence of any preservation treatment, the bacteria *Streptococcus* spp. and *Staphylococcus* spp. were observed on the third day. Only *Streptococcus* spp and *Lactobacillus* spp were observed in leaves preserved for two weeks in concentrated salt solution or light brine + vinegar, indicating that these treatments ensured a desirable microbial succession, by creating an environment suitable for the growth of these organisms but unfavourable for the growth of *Staphylococcus.* Strains of *Streptococcus* and *Lactobacillus* are employed as probiotics and are considered beneficial when they form part of the diet of humans (Saavedra *et al*., 1994; Granato *et al*., 2010)

Lactobacillus and *Staphylococcus* were present in the light brine and light salt treated leaves. These treatments were however, unsuitable for the growth of *Streptococcus.* Strains of *Staphylococcus*

are pathogenic and are implicated in food spoilage. Compared with the products of heavy salting and light brine and vinegar treatment, the absence of the acid-producing *Streptococcus* resulted in higher pH (Table 2.4) and the presence of *Staphylococcus* indicated poor preservation of the leaves (Table 2.14).

2.3. Fractionation and Rational Utilisation of *V. amygdalina* Leaves (Oboh *et al.*, 2016)

When used for food, *V. amygdalina* leaves are washed in water to remove most of the bitterness. Mostly, the water is thrown away and the residue is used as an ingredient. When the fresh leaves are used as medicine, the usual practice is to throw away the residue and drink the water extract. When used as a herbal tea, the dried and crushed leaves are extracted with hot water and the residue is discarded. Thus, clearly, the available methods for the utilisation of this valuable resource are very wasteful and a waste-free rational utilisation is needed.

The aim of this study was to develop a waste-free process for the utilisation of *Vernonia amygdalina* leaves by fractionation of the leaves. The leaves were pulped and pressed to yield the leaf juice (53%) and press cake (fibrous fraction, 47%). The juice was heated to coagulate its protein and filtered to yield the deproteinised juice (46.4%). The residue was pressed, washed and pressed again to give the leaf protein concentrate (LPC, yield, 3.8%).

Fig. 2.1: The hydraulic press used in the study.

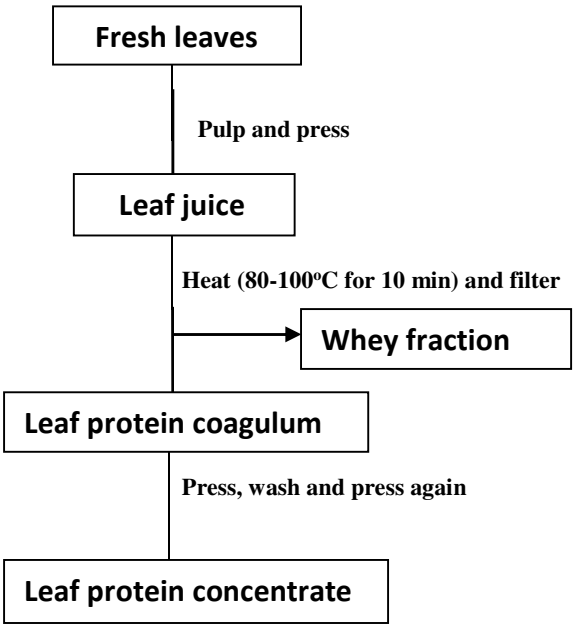


Fig. 2.2: Flow diagram of the leaf fractionation process (Fellows, 1987)

The fractionation scheme is shown in Fig. 2.2. Fresh leaves (10 kg) were rinsed with distilled water and pulped with a mortar and pestle followed by pressing in a hydraulic press (Fig. 19) to give the leaf juice and a fibrous fraction (press cake). The leaf juice was heated in batches to 80-100ºC for 10 min to coagulate and pasteurize the leaf protein. The protein coagulum was separated from the deproteinised juice by filtering through a cheese cloth followed by pressing in a hydraulic press (Fig. 2.1). The LPC was then washed with water and re-pressed. The fibrous fraction, leaf protein concentrate, leaf juice and deproteinised juice were stored in the deep freezer until required for analysis.

TABLE 2.15. Yields of fractions from fractionation of *V. amygdalina* leaves

Component	**Fresh wt (kg)**	**Dry wt (kg)**

Fresh leaf	10.00		1.98
Yields of fractions			
	Wet wt (kg)	**% by wet wt.**	**% by dry wt.**
Fibrous fraction	4.70	47	86.38
Fresh leaf juice	5.30	53	**-**
Deproteinised juice	4.64	46.4	7.45
Leaf Protein Concentrate	0.38	3.8	6.17

Pulping and hydraulic pressing of fresh leaves yielded a fibrous fraction (47%) and fresh leaf juice (53%). Heating of the fresh leaf juice yielded the leaf protein concentrate (3.8% of fresh leaves) and deproteinised juice (46.4% of the fresh leaves). Loss due to evaporation of water was 0.28%. Based on dry weight, the yield of the fibrous fraction was 86.38% while that of the leaf protein concentrate was 6.17%, with soluble solids in the deproteinised juice making up the balance.
Table 2.16. shows the proximate composition, β- carotene, and total phenolic content (TPC) of the fresh *V. amygdalina* leaves, and its fibrous and leaf protein fractions.

TABLE 2.16. Proximate composition, β-carotene and total phenolic content of fresh leaves, fibrous fraction and leaf protein concentrate

	Fresh leaves	**Fibrous fraction**	**Leaf protein concentrate**
Moisture (%)	80.24 ± 0.75	63.61 ± 0.38	67.83 ± 0.72
Ash (% DM)	12.19 ± 0.18^{a}	2.92 ± 0.17^{b}	2.89 ± 0.19^{b}
Crude protein (% DM)	11.95 ± 0.09^{a}	10.31 ± 0.32^{b}	40.12 ± 0.80^{c}
Crude fibre (% DM)	10.33 ± 0.04^{a}	13.10 ± 0.12^{b}	0 ± 0^{c}
Ether extract (% DM)	9.79 ± 0.09^{a}	8.27 ± 0.25^{b}	15.55 ± 0.30^{c}
Carbohydrate (% DM)	55.73 ± 0.17^{a}	64.91 ± 0.23^{b}	41.83 ± 0.85^{c}
β-Carotene (mg/100 g DM)	97.82 ± 0.37^{a}	33.33 ± 0.21^{b}	82.28 ± 0.20^{c}

Total Phenolic Compounds (mg GAE/g)	6.40	5.82	13.63

***DM = Dry Matter. Values are expressed as means ± SD (n = 3).[abc] Means with different superscripts on same row differ significantly (P < 0.05). **Gallic Acid Equivalent**

TABLE 2.17. Phytochemicals, β-carotene, lycopene and total phenolic content (TPC) of leaf juice and deproteinised juice

	Leaf juice	**Deproteinised juice**
Alkaloids	-	-
Flavonoids	+	+
Glycosides	+	+
Saponins	+	+
Terpenoids	+	+
Tannins	+	+
Total phenolic compounds (mg of GAE/litre)	713.59 ± 5.01[a]	812.82 ± 4.51[b]
β-Carotene (mg/l)	4.5 ± 0.20[b]	0.42 ± 0.02[a]
Lycopene (mg/l)	0.73 ± 0.05[b]	0.03 ± 0.01[a]

+ = Present; - = Absent. Values are expressed as mean ± SD (n = 3). [ab] Means with different superscripts on same column differ significantly (P < 0.05)

TABLE 2.18. Antibacterial[1] activities of fresh juice and deproteinised juice (DPJ)

Zone of inhibition (mm)

Zone of inhibition	**Gram positive bacteria**		**Gram negative bacteria**	
Sample	***B. cereus***	***S. aureus***	***E. coli***	***P. aeruginosa***
Fresh juice	- (<1)	- (<1)	- (<1)	+ (1)
DPJ	+ (1)	- (<1)	+ (1)	+ (2)

[1]Antimicrobial activities were expressed as inhibition diameter zones in millimetres (mm): - (negative) = < 1 mm; + (weak) = 1 to 4mm. [2] (), in parenthesis = Average zone of inhibition in mm. [3]Microorganisms used in the study were obtained from the Microbiology Unit, Department of Basic Sciences, Benson Idahosa University, Benin City (Table 2.19)

TABLE 2.19. Microbial strains used to test for antibacterial activity

Microbial group	Microorganism	Cultivation conditions
Gram-positive bacteria	*Bacillus cereus*	NA, 37°C
	Staphylococcus aureus	NA, 37°C
Gram-negative bacteria	*Escherichia coli*	NA, 37°C
	Pseudomonas aeruginosa	NA, 37°C
	Pseudomonas aeruginosa	NA, 37°C

NA = Nutrient Agar

Conclusion

Vernonia amygdalina leaves have been separated into three fractions namely, a fibrous fraction, a protein concentrate, and a deproteinised juice. A consideration of their composition indicates that the fibrous fraction would be suitable for use as an ingredient ("washed bitter leaf") in various food preparations, as a component of livestock feed and as raw material for conversion to bioethanol. The leaf protein concentrate was rich in protein, lipid and carbohydrate. This, coupled with its considerable content of phenolic compounds and β- carotene, indicates that it could be used as a nutritional supplement for humans and livestock. In the latter it could substitute for antibiotics, thereby reducing the cost of production and eliminating undesirable effects of such drugs on consumers of livestock products. The deproteinised juice could be drunk as a mineral and phenolic compounds-rich tonic, concentrated, or spray dried for use as a medicinal preparation and as a substitute for hops in craft beer.

2.4. *Talinum triangulare* (water leaf) (Oboh and Madojemu, 2016)

The pH, organoleptic characteristics, and nutrient content of *T. triangulare* leaves subjected to drying and salting preservation treatments are presented in Table 2.20, 2.21, 2.22 and 2.23.

TABLE 2.20. pH values for fresh and treated *T. triangulare* leaves

***T. triangulare* Leaves**	**pH**

Treatments	
Fresh (untreated)	6.49
Heavy salting	4.40
Light brining	-
Light salting	5.56
Light salt + vinegar	4.45

TABLE 2.21. Characteristics of fresh and fermented *T. triangulare* leaves

Property	Fresh	Light Salting	Light Brine + Vinegar	Heavy salting
Colour	Bright light green	Dull, light (slightly darker than the fresh) green	Dull light (slightly darker than the fresh) green	Bright light green
Taste	Fresh green leafy taste	Too offensive to taste	Bland taste with a hint of tanginess probably from the vinegar	Leafy taste but very salty
Odour	Fresh green leafy smell	Very offensive, rotten smell.	Mildly offensive (but no rotten smell).	Leafy smell similar to that of the fresh leaves.
Appearance and texture	Firm and succulent. Smooth feel.	Slimy and degraded	Succulent but not firm. Smooth feel	Succulent but not firm. Smooth feel.

TABLE 2.22. Beta-carotene, total carotene, vitamin C and moisture content of *T. triangulare* samples subjected to different preservation methods.

Leaves	β-Carotene (mg/100 g DW*)	Total carotene (mg/100 g DW)	Vitamin C (mg/100 g DW)	Moisture, % fresh wt)	Crude Fibre (mg/ g DW)

Fresh	0.570 ± 0.071	1.070 ± 0.045	1082.2 ± 82.040	87.60 ± 3.22[d]	4.250 ± 0.67
Treatments					
Light brine +vinegar	0.012 ± 0.001[a, b]	0.023 ± 0.001[a, c]	27.39 ± 2.739[a]	83.8 ± 1.10[d]	2.01 ± 0.73[a, e]
Heavy salting	0.011 ± 0.001[a, b]	0.020 ± 0.006[a, c]	17.29 ± 0.820[a]	84.20 ± 3.00[d]	1.85 ± 0.2[a, e]
Blanching and oven dried	0.382 ± 0.017[a]	0.911 ± 0.041[a]	404.0 ± 63.080[a]	-	1.74 ± 0.23[a]
Oven drying	0.259 ± 0.048[a]	0.381 ± 0.066[a]	238.9 ± 38.900[a]	-	1.6 ± 0.06[a]

Values were recorded as mean ± standard deviation of three independent samples. *DW: Dry wt. Test: [a]: values differ significantly compared with the fresh sample mean, P < 0.05. [bcde]values that have the same superscript are not significantly different for the same characteristic, P >0.05.

TABLE 2.23. Ash, iron, calcium and sodium content (dry basis) of fresh and preserved *T. triangulare* leaves.

Leaves	**Ash (mg/g)**	**Fe (µg/ g)**	**Ca (µg/ g)**	**Na (µg/ g$^-$)**
Fresh	3.90± 0.35	0.46±0.08	2.64 ± 0.36[e]	1.16 ± 0.07[f]
Treatments				
Light brine + vinegar	3.35 ± 0.6[b]	0.13±0.07[a]	4.84 ±1.22[a]	152.0 ± 41.2[a]
Heavy salting	4.45 ± 0.17[a]	0.11±0.02[a]	2.68 ± 0.77[e]	243.3 ± 8.25[a]
Blanching and drying.	2.10 ± 0.08[a, c]	0.29±0.14[a, d]	1.87 ± 0.91[a]	1.11 ± 0.04[b, f]
Drying without blanching.	2.03 ± 0.04[a, c]	0.29±0.16[a, d]	2.11 ± 0.91[a]	1.02 ± 0.04[b, f]

Values are recorded as mean ± standard deviation of three independent samples. t-Test: [a]values differ significantly compared with the fresh sample mean (P < 0.05), [b]not significantly different compared with the fresh sample, [cdef]values are not significantly different (P < 0.05) for the characteristic

TABLE 2.24. Percentage retention or increase (in parenthesis) of *T. triangulare* nutrients after treatments

Treatments	B-carotene (%)	Total carotene (%)	Vitamin C (%)	Moisture (%)	% Crude Fibre	% Ash	% Ca	% Na
Fresh	100	100	100	100	100	100	100	100
Light brine + vinegar	2.11	2.15	2.53	95.66	47.29	86.03	(183.3)	(13103.45)
Heavy salt	1.93	1.87	1.60	96.12	43.53	(114.10)	(101.52)	(20974.14)
Blanched and oven dried	67.02	85.14	37.33	-	40.82	53.85	70.83	95.69
Oven dried	45.94	35.61	22.08-	-	37.65	52.05	79.92	87.93

[a]Percentage retention or increase = $\frac{\text{Concentration of constituent in the treated leaves}}{\text{Concentration of constituent in the fresh leaves}} \times 100$

2.5. Medicinal Applications of Leafy Vegetables

Studies were undertaken to investigate the effect of aqueous extracts of *Vernonia amygdalina* and *Momordica charantia* leaves on the lipid profile of hyperlipidaemic adult male albino rabbits.

2.5.1. Effects of *V. amygdalina* aqueous extract on blood lipids of hyperlipidaemic rabbits (Oboh and Enobhayisobo, 2009)

This study investigated the effect of an aqueous extract of *Vernonia amygdalina* leaves on the lipid profile of hyperlipidaemic adult male albino rabbits.

Three groups of rabbits were employed in the study: a healthy control group fed only 1 ml groundnut oil/ kg body weight (A) and two groups (B and C), in which hyperlipidaemia was induced by feeding 100 mg/ ml groundnut oil/ kg body weight of a non-phosphorylated egg yolk extract for one week. For the next 14 days, Group B of the hyperlipidaemic rabbits received the egg yolk extract while Group C animals were given, in addition, 200 mg/kg body weight of the aqueous extract of *V. amygdalina* leaves twice daily. The control group (A) received only groundnut oil. All animals were fed grower's mash and water throughout the course of the experiment. Assay of lipids showed significant difference ($P<0.05$) in total cholesterol (TC), and low-density lipoprotein (LDL-C) between groups A and C. Very low-density lipoprotein (VLDL), triacylglycerol (TAG) and high-density lipoprotein (HDL-C) were not significantly different between the two groups. Relative to the control, treatment with the extract decreased plasma TC and LDL, but normalized VLDL, TAG and HDL-C. Change in the lipid concentration was progressive, with TC, TAG, VLDL and LDL-C being lower and HDL-C higher in the second week than in the first week after commencement of treatment.

Aqueous extract of *V. amygdalina* leaves may be effective for the control of these blood lipids in hyperlipidaemic individuals.

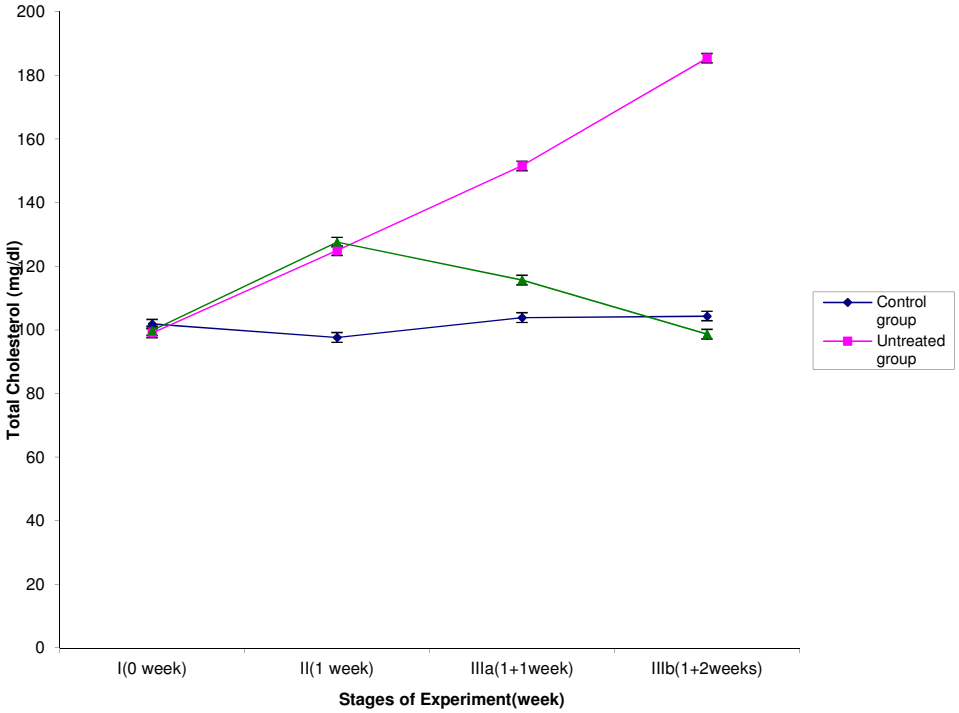


FIG. 2.3. Changes in total cholesterol of the control, untreated and treated groups at different stages of the experiment

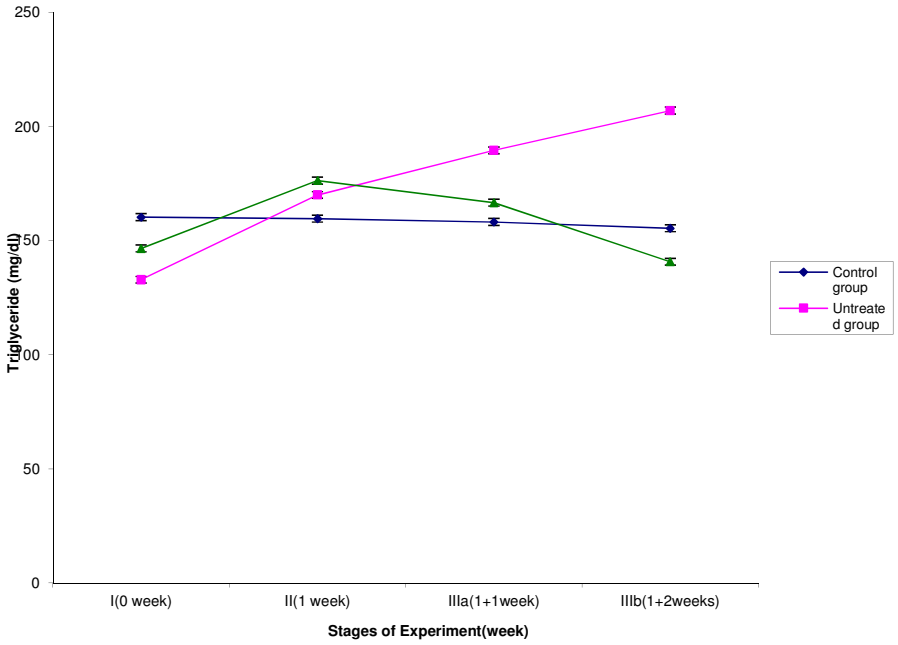


FIG. 2.4: Changes in the plasma LDL-cholesterol concentration of the control, untreated and treated groups at different stages of the experiment

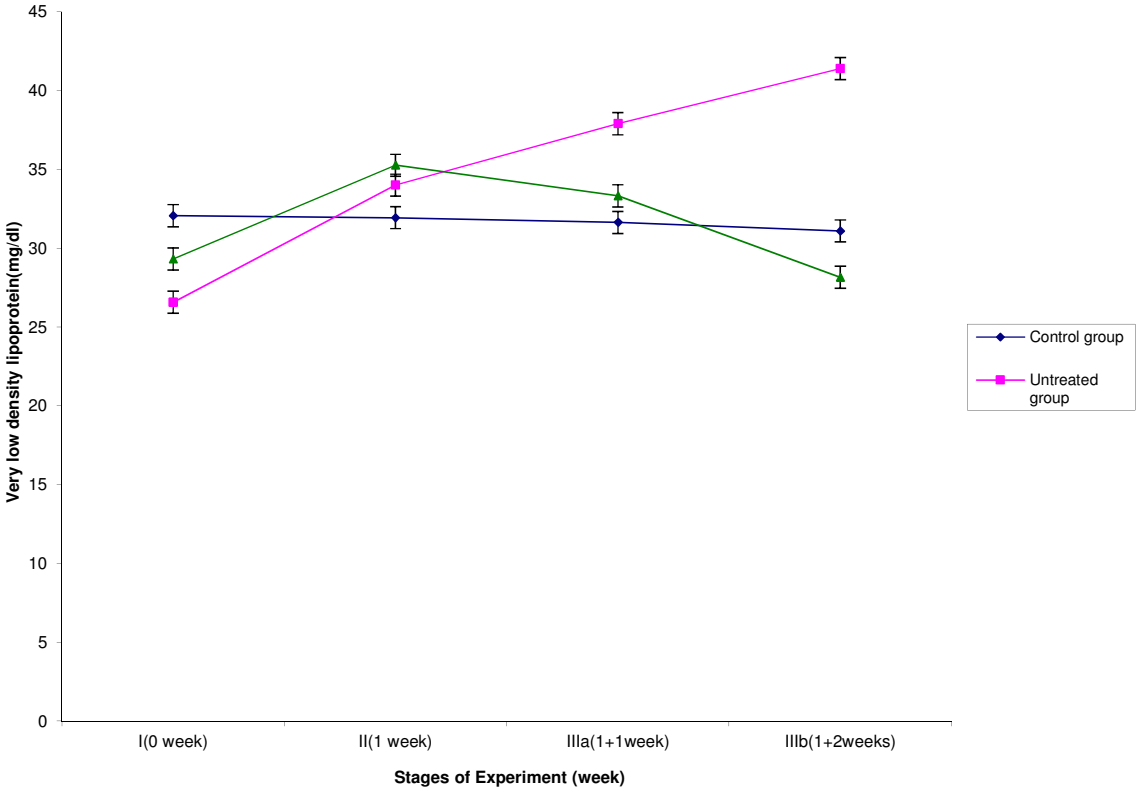


FIG. 24: Changes in the plasma very low-density lipoprotein concentration of the control, untreated and treated groups at different stages of the experiment

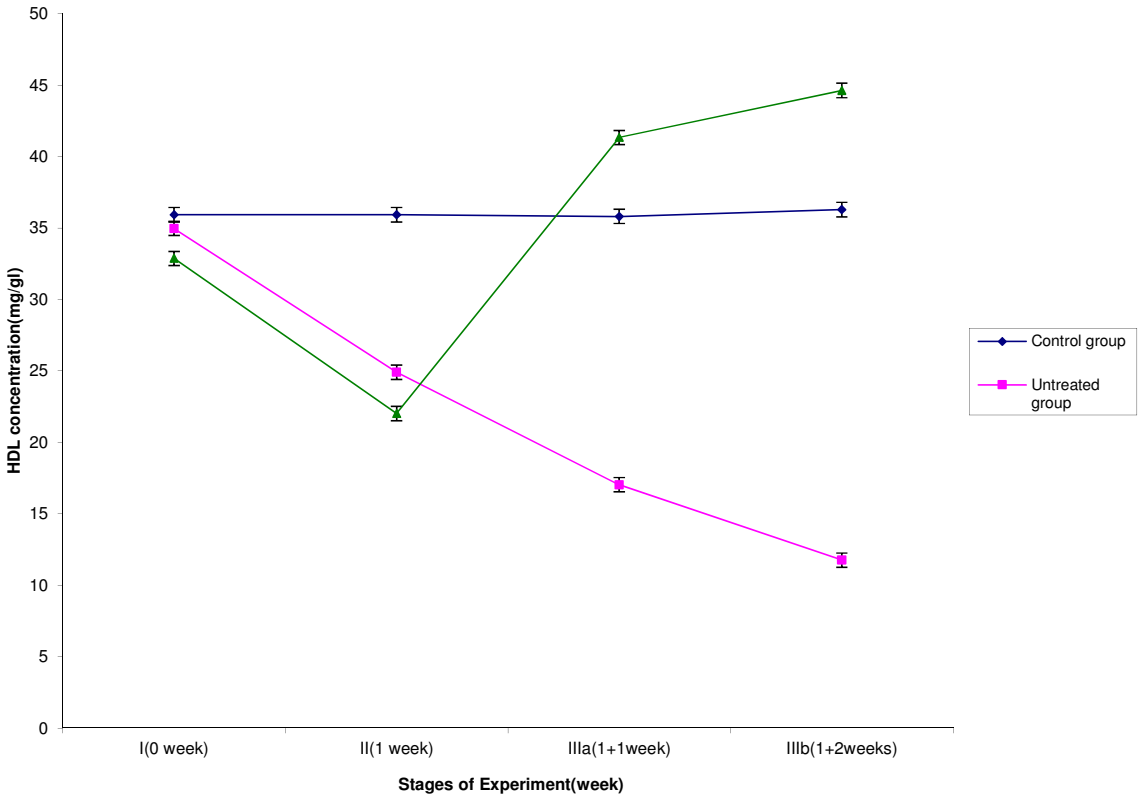


FIG. 2.5: Changes in HDL-cholesterol of the control, untreated and treated groups at different stages of the experiment.

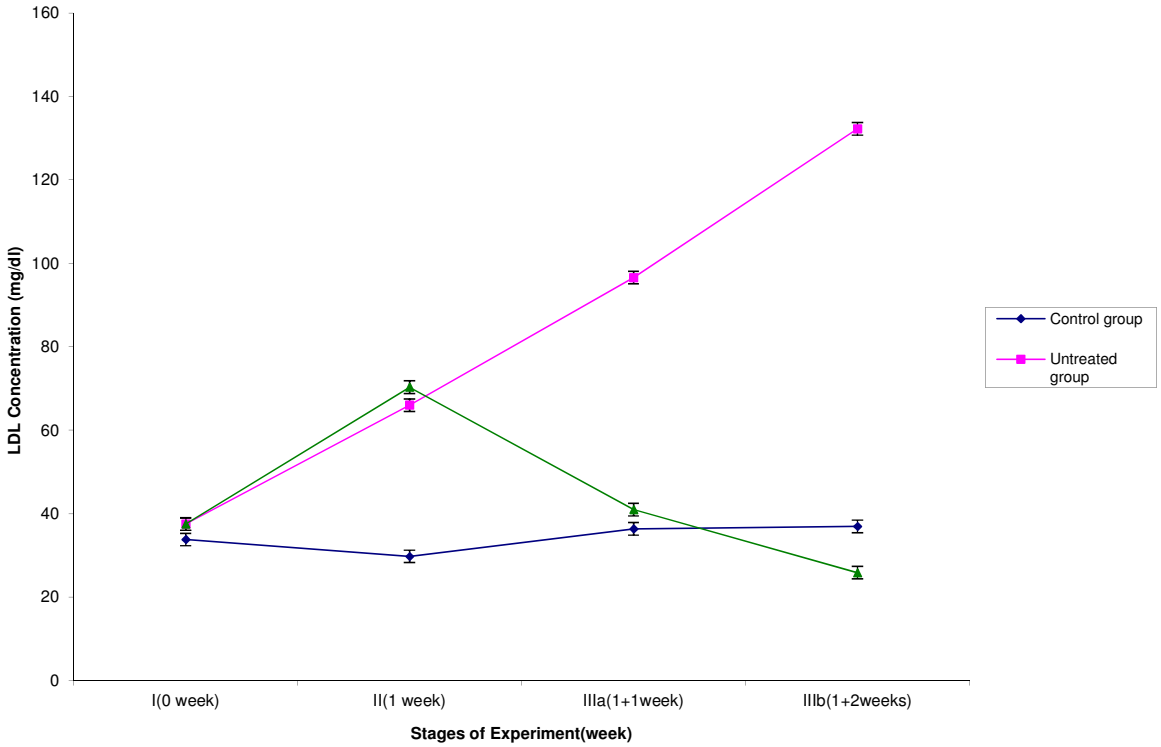


FIG. 2.6: Changes in LDL-cholesterol of the control, untreated and treated groups at different stages of the experiment.

Hyperlipidaemia was successfully induced in albino New Zealand rabbits by feeding them a basal diet supplemented with a non-phosphorylated egg yolk extract. Administration of an aqueous *V. amygdalina* leaf extract to the hyperlipidaemic animals caused a decrease in plasma TC, LDL-C, TAG, and VLDL and an increase in plasma HDL-C concentration. This indicates that aqueous *V. amygdalina* leaf extract may be useful for the control of these blood lipids in the prevention or treatment of coronary heart disease (CHD).

2.5.2. Effects of *Momordica charantia* aqueous extract on blood lipids of hyperlipidaemic rabbits (Oboh *et al.*, 2010)

This study investigated the effect of an aqueous extract of *Momordica charantia* leaves (ebi'siughu in Benin) on the lipid profile of adult male albino rabbits fed an atherogenic diet. Three groups of rabbits were employed in the study: a healthy control group fed only 1ml groundnut oil/ kg body weight (A) and two groups (B and C), which were fed 100 mg/ ml groundnut oil/ kg body weight of a non-phosphorylated egg yolk extract for two weeks. For the next 14 days Group B rabbits received the egg yolk extract while Group C animals were

given, in addition, 200 mg/kg body weight of the aqueous extract of *M. charantia* leaves twice daily. The control group (A) received only groundnut oil. All animals were fed grower's mash and water throughout the course of the experiment. Assay of lipids showed significant difference ($P<0.05$) in total cholesterol (TC), very low-density lipoprotein (VLDL), triglyceride (TG), high density lipoprotein (HDL-C) and low-density lipoprotein (LDL-C) between groups A and B, A and C and B and C. Relative to the control, feeding Groups B and C animals the lipid extract for 2 weeks increased TC, LDL-C, VLDL and TG but decreased HDL-C. Treatment of Group C animals with the leaf extract for two weeks resulted in a decrease in TC, LDL-C, TG, and VLDL, but in an increase in HDL-C. Changes in the lipid levels were progressive, with TC, TG, VLDL and LDL-C being lower and HDL-C higher in the second week than in the first week after commencement of treatment. Compared with the control, treatment with the leaf extract normalised TG and VLDL levels, increased HDL-C, but decreased LDL-C at the last stage of the experiment (week 4). Results indicate that aqueous extract of *M. charantia* leaves may (potentially) be effective for the control of these blood lipids in dyslipidaemia individuals.

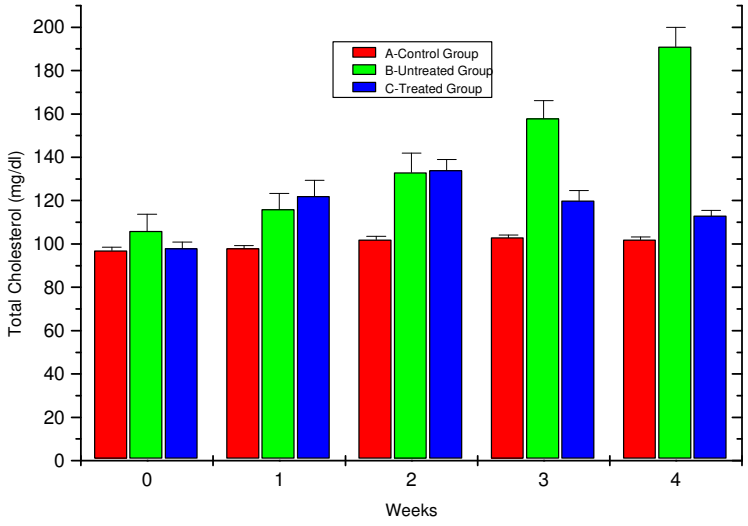


FIG. 2.7: Mean total cholesterol levels of the control, untreated and treated rabbits at different stages of the experiment.

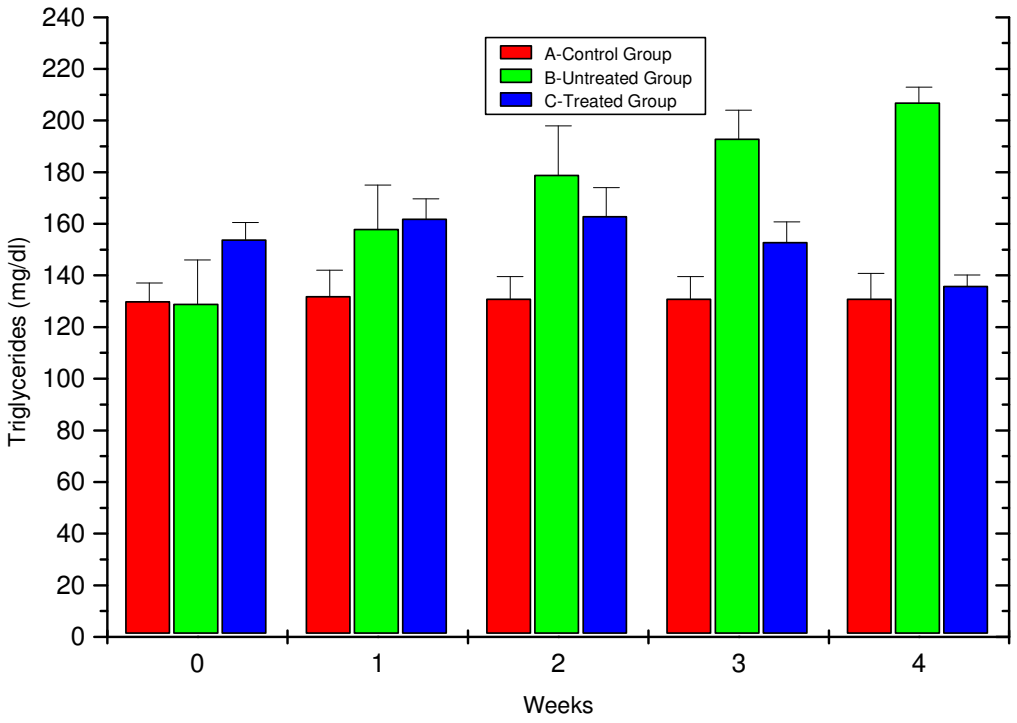


FIG. 2.8: Mean triacylglycerol levels of control, untreated, and treated rabbits at different stages of the experiment.

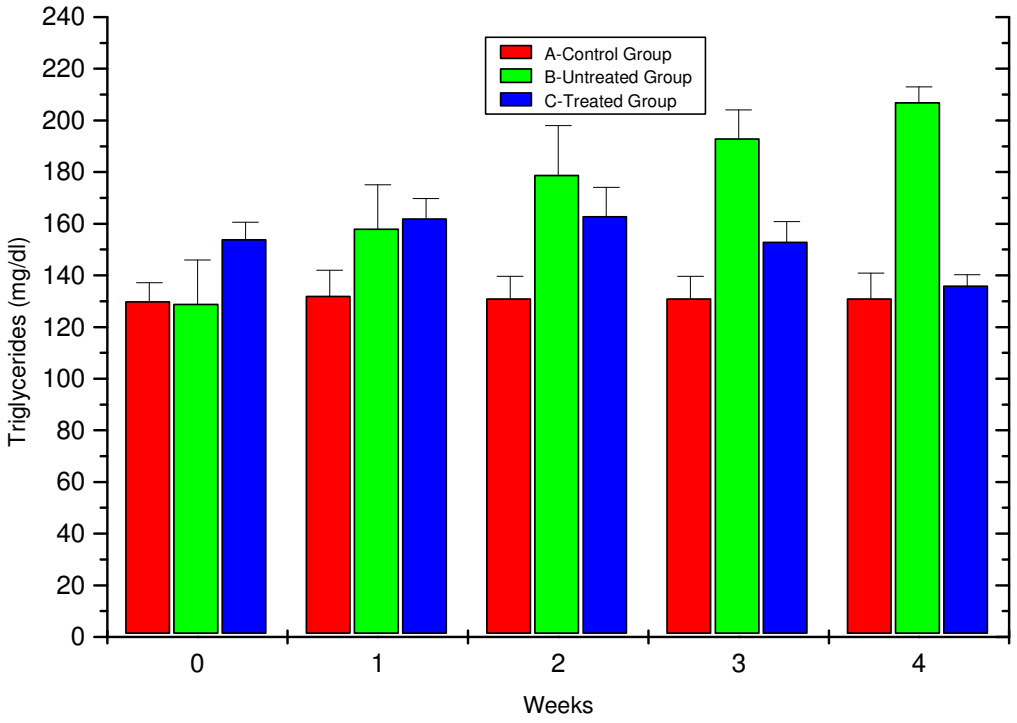


FIG 2.9. Mean very low-density lipoprotein levels of control, untreated, and treated rabbits at different stages of the experiment

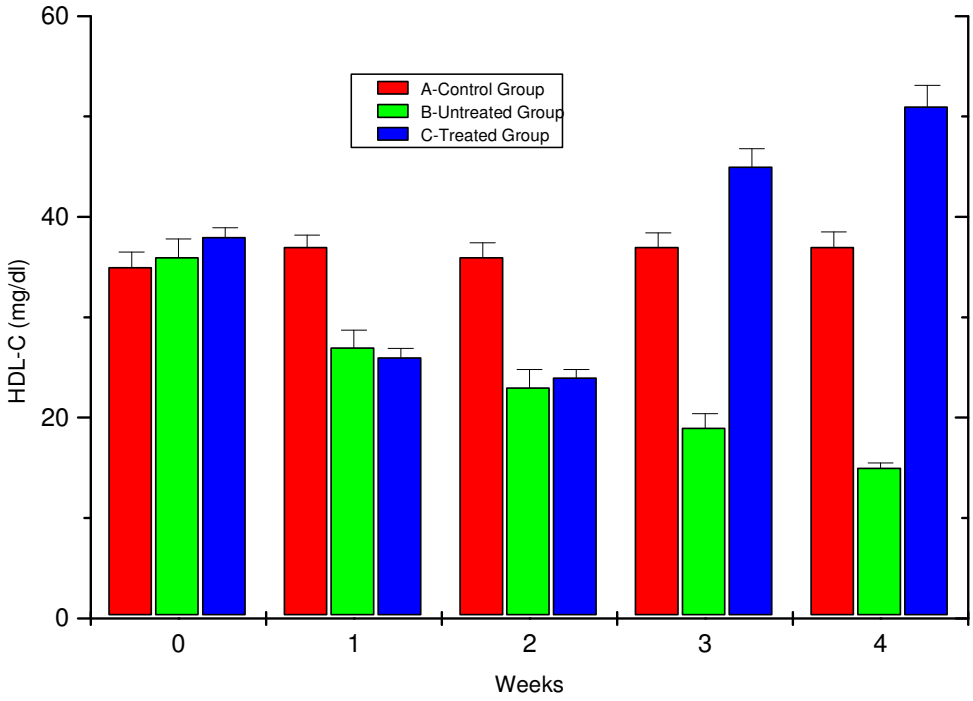


FIG. 2.10. Mean high-density lipoprotein levels of the control, untreated and treated groups at different stages of the experiment.

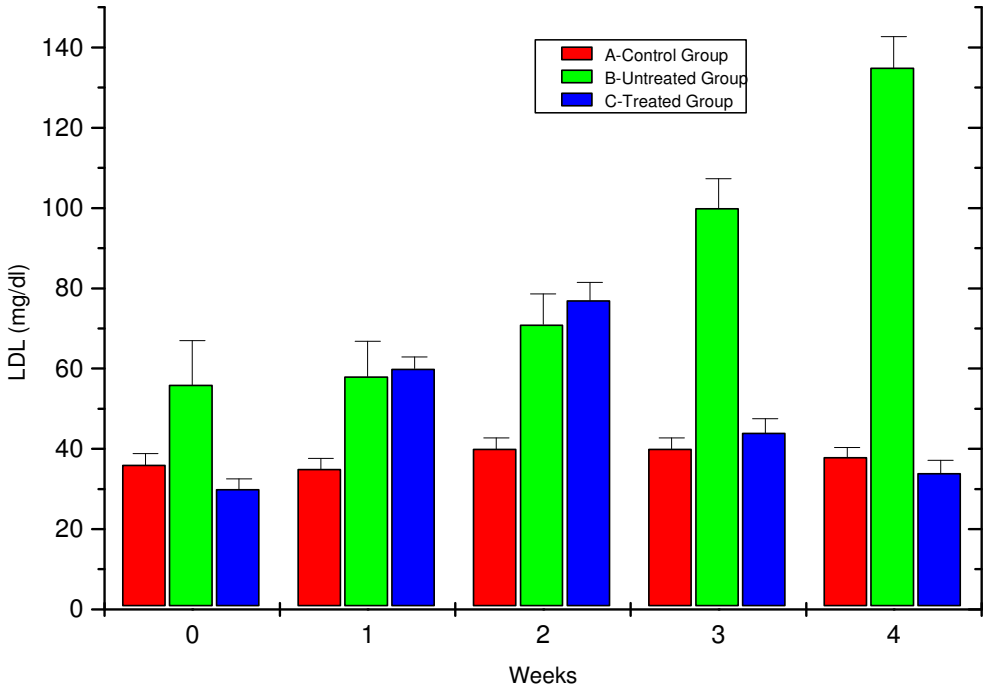


FIG. 2.11. Mean plasma low-density lipoprotein concentrations of control, untreated and treated rabbits at different stages of the experiment.

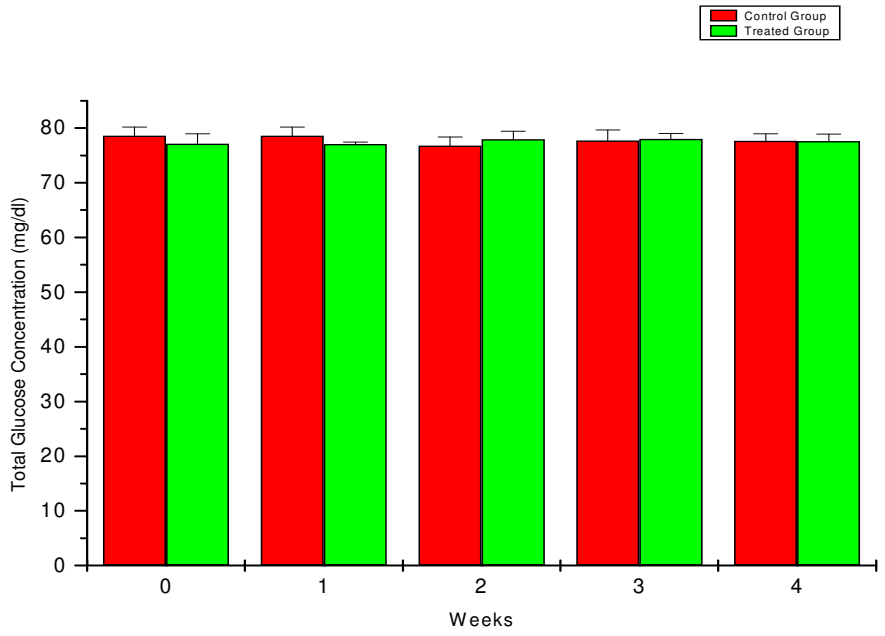


FIG. 2.12. Effect of *M. charantia* leaf extract on plasma glucose level

Non-phosphorylated egg yolk lipids (i.e., the acetone soluble egg yolk lipid fraction), consist mainly of cholesterol, triacylglycerols, cholesterol esters, and free fatty acids (Ramesh *et al.*, 1979), the fatty acyl chains of the triglyceride, cholesterol esters and the free fatty acids being mostly saturated. Cholesterol and saturated fatty acids are atherogenic (Wardlaw and Kessel, 2002), and non-phosphorylated egg yolk lipids due to their composition would be atherogenic. The increased TC, TG, LDL-C and VLDL and the associated decrease in HDL-C (i.e. dyslipidaemia) observed in groups B and C animals after feeding them with the non-phosphorylated lipid extract, (week 2) are in agreement with observed atherogenicity of dietary cholesterol and saturated fatty acids (Mensink *et al.*, 2002; Hayes, 2000; Bolton-Smith *et al.*, 1991).

Elevated low LDL-C and decreased HDL-C levels are well recognised cardiovascular disease (CVD) risk factors with recent evidence supporting the benefit of intensive LDL-C reduction and increasing HDL-C on coronary heart disease (CHD) risk (Evans *et al*., 2004).

Compared with the control, administration of the aqueous leaf extract to the dyslipidaemic rabbits decreased plasma LDL-C, increased HDL-C but normalized VLDL and TG. The decline in the levels of TC, TG, VLDL and LDL was progressive with the second week values being lower than those for the first week after treatment commenced. An opposing trend was observed for plasma HDL-C, which showed a progressive increase. This indicates a progressive effect of *M. charantia* extract on mechanisms involved in the control of plasma levels of these lipids.

That dyslipidaemia was induced by feeding the rabbits an atherogenic diet underscores the importance of not exceeding recommended levels, or where possible, the elimination of cholesterol and saturated fat from diets, for the prevention or management of CVD. The results show clearly that the administration of aqueous extract of *M. charantia* leaves reversed this condition in the rabbits, even when they were still being fed the atherogenic egg yolk lipid extract. This indicates that the extract could be beneficial for the control of blood lipids under conditions of poor dietary discipline.

Being a preliminary investigation of short duration, this study examined the effect of only one concentration (200 mg/kg body wt) and did not examine the long-term effect of different concentrations of leaf extract on plasma lipid levels. Long-term studies aimed at determining the optimum dose and toxicity of aqueous and organic extracts are therefore required.

Conclusions

Dyslipidaemia (i.e., increase in plasma TC, TG, LDL-C and VLDL and a decrease in HDL-C) was observed in adult male New Zealand rabbits fed a non-phosphorylated egg yolk lipid extract.

Administration of aqueous *M. charantia* or *V. amygdaline* leaf extracts to the animals caused a significant decrease in plasma TC, LDL-C, TAG, and VLDL and an increase in plasma HDL-C concentration, thereby normalising blood concentrations of these lipids. This indicates that

adequate concentrations of aqueous *M. charantia* leaf extract could be useful for the control of these blood lipids in the prevention and management of CVD.

3.0. PALM SAP STUDIES

3.1. Background to the study

Palm sap is the white, semi-translucent, sugary sap obtained by tapping the stalk of the immature inflorescence or the upper stem of palm trees, or by tapping the felled trees. In Nigeria, palm sap is obtained mainly from the African oil palm (*Elaeis guineensis* Jacq.) and the raffia (*Raphia* spp) palms (Francisco-Ortega and Zona, 2013; Oboh, 2022a) and is usually left to ferment, and drunk as such (palm wine, fresh or pasteurised and bottled), or distilled to yield a strong liquor. In 1969, palm wine production from both sources was estimated at roughly two million metric tonnes (Okereke, 1982). The trade in palm wine provides a source of income, not only for the tappers, but also to a wide range of market intermediaries (Okereke, 1982). In Nigeria, it was found that an oil palm estate may be better off devoting all its resources to the production of 9, 770 L /ha/ annum of oil palm sap than 10 tons of fresh fruit bunches (FFB) /ha/annum, with bright prospects for the sap and the possibility of higher yields through selection and breeding of varieties capable of yielding 100 L of sap per palm (14,800 L per ha) per annum (Udom, 1987). This indicates that in Nigeria, oil palm sap production could in some cases be preferred to FFB production in plantations, thereby becoming a readily available raw material for the following non-traditional products:

i. Palm sugar (as syrup, granulated sugar, and moulded solid sugar)

ii. Palm sugar-based products, such as confectionery, non-alcoholic beverages, and vinegar (Fellows and Hampton, 1992).

iii. Non-beverage alcohol, for use as an industrial solvent and biofuel

iv. Lactic acid for the food, cosmetics, pharmaceutical and chemical industries (Chooklin *et al*., 2011).

Production of these value-added products would increase the income of palm sap producers, which in turn would improve the rural economies where they are located.

3.2. Promising Novel Products from Palm Sap in Nigeria

3.2.1. Nutritious and functional sweetener (Oboh *et al.*, 2016)

The physico-chemical characteristics and antimicrobial activity of oil palm syrup, raffia palm syrup and honey were studied (Table 3.1, with *P. canariensis* syrup data for comparison). The materials contained mainly carbohydrate (64.76-68.79%) and water (28.05-31.50). They exhibited similar densities (1.23-1.26 g/ml) and pH (3.51-4.18), and had low ash (0.30-0.50%), protein (0.24-1.04%) and lipid (2.20-3.62%) content. They contained non-enzymatic browning products (browning intensity was 0.71 for honey, 0.159 for raffia palm syrup and 0.175 for oil palm syrup).

TABLE 3.1. Analytical characteristics of raffia, oil palm, *Phoenix canariensis* syrups, and honey

Characteristics	Honey[a]	Raffia palm syrup[a]	Oil palm syrup[a]	*Phoenix canariensis* syrup [b]
Protein (N x 6.25, %)	0.43 ± 0.04	0.24 ± 0.06	1.04 ± 0.04	-
Ash (%)	0.40 ± 0.02	0.30 ± 0.01	0.50 ± 0.01	1.78
Lipids (%)	3.12 ± 0.02	2.17 ± 0.03	2.20 ±0.03	Tr
Moisture (%)	28.05 ± 2.83	28.50 ± 4.95	31.50 ± 4.24	35.30
Carbohydrate (by difference) %	68.00	68.79	64.76	66.0
Energy (kcal/100 g) [a]	301.8	295.7	283.0	264
Browning intensity (Absorbance, 1% solution at 420 nm).	0.071	0.159	0.175	-
pH	4.18	3.76	3.51	-
Density	1.24	1.23	1.26	
Colour	Dark Brown	Dark Brown	Dark Brown	-

[a] Oboh *et al.* (2016); [b]Luis *et al.* (2012). [c]Energy was estimated from proximate composition using the following factors: Protein, 4.0 kcal/ g; carbohydrate, 4.0 kcal/ g; lipid, 9.0 kcal/ g.

They had modest content of Fe (2.35-3.30 mg/100g), and high Ca (37.06-79.05 mg/100g), and K (325.12-628.56 mg/100 g) content, with considerable contribution to the RDA values for these minerals.

TABLE 3.2. Mineral content of palm syrups and honey

MINERAL	Honey (mg/100 g DM[a])	Raffia (mg/100 g DM)	Oil palm (mg/100 g DM)
Ca	37.54±3.54 (3.8-9.4) [b]	37.06±2.8 (3.7-9.3)	79.05±1.47 (7.9-19.70)
Fe	3.30±0.42 (22.0-33.0)	2.35±0.65 (15-23.5)	2.90±0.14 (19.3-29.0)
K	325.12±7.8 (32.5)	545.75±3.73 (54.5)	628.56±12.07 (62.86)

[a]() in parenthesis: % of the Recommended Dietary Allowance (RDA) of minerals, which may be provided by 100 g of honey or palm syrup (RDA values: Ca= 400-100 mg, Fe= 10-15 mg, K= 1300 mg), [b]DM = Dry Matter

3.2.2. Antimicrobial activity of palm syrup against clinical strains of bacteria

The syrups derived from raffia and oil palm saps, and honey exhibited antimicrobial activity against clinical strains of *Pseudomonas aeruginosa, Bacillus cereus, Escherichia coli* and *Staphylococcus aureus* (Table 3.3). The antimicrobial activities of dilute solutions (0.1 ml, 0.5% aqueous solutions) of the honey (containing 0.36 mg dry matter) and syrups (raffia, 0.36 mg and oil palm, 0.34 mg dry matter) were similar to that of 10 µg of the antibiotic streptomycin. This indicates that the syrups exhibited considerable antibiotic activity against the test organisms compared with the purified and potent antibiotic streptomycin. The results suggest that in addition to their modest to high mineral and phytochemicals content (Table 3.4) the palm syrups could be useful (like honey) as an antimicrobial substance for food preservation and medicinal applications (e.g., treatment of burns). Thus, they may be regarded as functional foods.

Table 3.3. Antimicrobial activity expressed as zones of inhibition of bacterial growth (mm).

Material	Wt[a]	*Escherichia coli*	*Pseudomonas aeruginosa*	*Bacillus. cereus*	*Staphylococcus aureus*
Streptomycin	10 µg	6.0	6.0	5.0	6.0
Honey	0.36 mg[a]	7.0	6.0	4.0	6.0
Raffia palm syrup	0.36 mg[a]	8.0	4.0	6.0	7.0
Oil palm syrup	0.34 mg[a]	6.0	5.0	6.0	6.0

[a]**Amount of dry matter in 0.1 ml of a 0.5 % solution**

TABLE 3.4. Total phenolic content and phytochemicals of honey and palm syrups.

Characteristics	Honey	Raffia palm syrup	Oil palm syrup
Total phenolic content (TPC, mg GAE*/100g of syrup)	125.93±13.60	170.89±2.87	185.44±10.15
Alkaloids	-	+	-
Flavonoids	+	+	+
Glycosides	+	+	+
Saponins	+	+	+
Terpenoids	-	-	-
Tannins	-	-	-

*GAE: Gallic acid equivalent. +: Present. -: Absent

3.2.3. Antioxidant preservative based on palm syrup for cooked ground beef (Oboh *et al.*, 2021)

This study was undertaken to evaluate the effects of locally produced oil palm sugar and honey on the oxidation of cooked ground beef during short-term storage at 4°C.

TABLE 3.5. Chemical characteristics of oil palm syrup and honey[a]

Characteristics	Oil palm syrup	Honey
Consistency at ambient temperature	Viscous and sticky	Viscous
pH	3.90±0.01	4.31±0.01
Colour	Dark brown	Dark brown
Browning intensity (Absorbance of a 1% aqueous solution at 420 nm).	0.131±0.001	0.071±0.00
5-hydroxymethylfurfural (mmol/kg)[b]	1.009±0.002	1.073±.005

Both had pH in the acid range, in agreement with previous findings (Oboh *et al.*, 2016; Bogdanov, 2009); they had a dark brown colouration, but the palm sugar was darker, in keeping with its higher browning intensity (Table 3.5). Browning intensity is a measure of the extent of non-enzymatic browning and caramelisation. During evaporation of sap to syrup, amino acids and sugars present in oil palm sap undergo the Maillard reaction to produce brown coloured compounds (non- enzymatic browning). Further evaporation results in some caramelisation of the sugars, which contributes to the browning. Honey also becomes darker during storage and on heat treatment during processing (Anon., 2008). Maillard reaction products (MRP) exhibit antioxidant activity by scavenging oxygen radicals and by chelating pro-oxidant transition metals (Amin *et al*, 2010).

Hydroxymethyl furfural (5- HMF), a decomposition product of fructose was present in the palm syrup and honey. It is formed during storage or heat treatment of foods and is an indicator of the extent of these; it also contributes to the flavour of foods and may function as an antioxidant (Bogdanov, 2009). The oil palm sugar and honey contained moderate amounts of this substance. The browning intensity and 5-HMF values of oil palm sugar were in keeping with the long period of heat treatment required for the evaporation of palm sap to yield palm syrup. The honey was a commercial preparation and its processing history was not known.

The palm sugar and honey had high total phenolic content. The total phenolic content assay by the Folin-Ciocalteu reagent is also a measure of the reducing capacity of a substance, and would include, in addition to phenolic compounds, non-phenolic compounds, including vitamin C, 5-HMF and Milliard reaction products (Huang *et al.*, 2005). Phenolic compounds in foods have been reported to possess many useful properties. They act as antioxidants, metal chelators, antimutagens, anticarcinogens and antimicrobial agents (Cheynier *et al.,* 2005). Although there are numerous phytochemicals consumed in the diet, polyphenols constitute the largest group, and have attracted much attention due to their antioxidant properties. The antioxidant activity of regularly consumed fruits and vegetables reflects their phenolic and vitamin C content (Proteggente *et al*, 2002, Anhe *et al*, 2013). Wild yeasts present in palm sap contribute to the synthesis of its phenolic compounds, which in turn contribute to its sensory profile (Ayanru, 1989). It has been demonstrated that phenolic content has a strong positive correlation with the antioxidant activity of honeys (Gheldof *et al.*, 2002).

The antioxidant activity of the oil palm syrup and honey are shown in Table 3.6 Included for comparison are values for butylated hydroxytoluene (BHT), a synthetic phenolic antioxidant and food ingredient that is generally regarded as safe (GRAS). Using BHT as the standard, oil palm syrup had high DPPH scavenging activity and reducing power; honey had a high reducing power but a low DPPH radical scavenging activity.

TABLE 3.6. Antioxidant capacity of oil palm sugar and honey[a]

Characteristics	Oil palm sugar	Honey	BHT[b]
Total Phenolic Content (mg GAE[c]/100 g of extract)	168.65±0.65	125.15±1.36	-
DPPH Radical Scavenging Activity (%)[d]	73.94±0.70	12.01±2.98	84.07±2.55
Reducing Power (mg % AAE[e])[d]	39.71±1.00	47.44±0.05	5.12±0.02

[a]Values are expressed as mean ±SEM (n=3). [b]Values for 0.02% BHT (butylated hydroxytoluene) in 70% ethanol. [c]GAE: Gallic Acid Equivalent. [d]Values for 20% palm sugar or honey in distilled water
[e]AAE: Ascorbic Acid Equivalent

The β-carotene bleaching antioxidant activity of the oil palm syrup, honey, BHT and α–tocopherol preparations used in the study are shown in Table 3.7.

TABLE 3.7. β-carotene bleaching antioxidant activity of the test preparations

Product	Oil palm syrup[a]	Honey[a]	BHT[b]	α–Tocopherol[b]
β-Carotene bleaching antioxidant activity (%)	61.60±2.41*	68.80±1.70*	72.00±3.62*	43.50±2.56**

[a]0.75% aqueous solution. [b]0.75% solution in absolute ethanol. * Values are means ± standard deviation of three determinations. Values with different superscripts are significantly different at the level of p<0.05**

There was no significant difference between the values for the oil palm syrup, honey, and BHT; the value for α-tocopherol, however, was significantly lower.

The effects of oil palm syrup, honey, BHT, and α-tocopherol treatment on lipid oxidation in ground beef cooked at 75°C after 1, 3-, 7-, 10- and 13-days storage at 4°C are shown in Table 3.8.

TABLE 3.8. The effect of oil palm syrup, honey, BHT and α–tocopherol on lipid oxidation in cooked ground beef

Treatment	TBARS (mg malonaldehyde /kg of cooked beef), days					% inhibition[a] on day 13
	1	3	7	10	13	
Control (no treatment)	0.158±0.04*	0.325±0.06*	0.833±0.02*	0.933±0.07*	1.843±0.16*	-
Oil palm syrup	0.206±0.03*	0.446±0.05**	0.796±0.02*	0.543±0.02**	0.649±0.07**	64.85±1.06
Honey	0.165±0.03*	0.444±0.02**	0.796±0.03*	0.383±0.05***	0.611±0.10**	67.07±3.63
BHT	0.042±0.02**	0.009±0.02***	0.151±0.01**	0.185±0.02****	0.745±0.02**	59.37±3.45
α-Tocopherol	0.352±0.08***	0.627±0.03****	0.812±0.06*	0.935±0.06*	0.999±0.05***	45.62±2.84

***, **, ***, ****Values are means ±standard deviation of three determinations. Values with different superscripts within the same column were significantly different at the level of p<0.05. [a]% Inhibition: (TBARS value of the control on day 13 – TBARS value of treated sample on day 13)/ TBARS value of control on day 13**

These inhibition values exhibit a high positive correlation (r*=0.8260) with β-carotene bleaching antioxidant values for oil palm syrup, honey, BHT, and α-tocopherol (Table 3.9); for the natural antioxidants (oil palm syrup, honey and α-tocopherol) the correlation was even higher (r**=0.9828).

TABLE 3.9. Correlations between β-carotene bleaching antioxidant activity and % inhibition values

	β-Carotene bleaching antioxidant activity (%)	% Inhibition
Oil palm syrup	61.60	64.85
Honey	68.80	67.07
BHT	72.00	59.37
α-Tocopherol	43.50	45.62
Pearson's coefficients		
r*	0.8260	
r**	0.9828	

***r (0.8261) = correlation between the β-carotene bleaching antioxidant activities of oil palm syrup, honey, BHT, and α-tocopherol, and their corresponding % inhibition values.**

****r (0.9828) = correlation between the β-carotene bleaching antioxidant activities of oil palm syrup, honey, and α-tocopherol, and their corresponding % inhibition values.**

These correlations indicate a strong linear relationship between β-carotene bleaching antioxidant activity and inhibition of the oxidation of cooked ground beef.

The amount and type of lipids found in muscle foods, and their relative reactivity and accessibility to catalysts and inhibitors determine their susceptibility to oxidation (Erickson, 2002). In this study, time dependent degradation of the structure of the beef probably allowed deeper penetration of the test substances towards the end of the study, thereby increasing access to the lipids, not only of the hydrolytic and oxidizing enzymes and other pro-oxidants in the beef, but also to the antioxidants naturally present and those added *post mortem*. Under these circumstances, the resistance of meat to the development of rancidity would then depend on the balance between the antioxidants and pro-oxidants present in the animal tissue, their mode of action and the ability of the antioxidants to inhibit the activity of the pro-oxidants (Enser, 1987).

Iron heme protein, including myoglobin and haemoglobin, are abundant in muscle tissue (Livingstone and Brown, 1981). The ability of heme to promote oxidation has been demonstrated by several workers (Tapel, 1953). Non-heme iron participates in the production of the hydroxyl radical, a reactive oxygen species, via the chemical Fenton reaction, which is effective when Fe^{3+} can be recycled to Fe^{2+} by various reducing agents, for example, ascorbate. Levels of low molecular weight non-heme iron are initially low, being only 2.4 to 3.9% of the total muscle iron in beef. However, in muscle that has been processed and stored (such as in this study), increases in the catalytic low molecular weight iron fraction have been observed (Decker and Hultin, 1990; Kanner *et al*, 1988). Potential sources of non-heme iron are dislodgement of iron from the heme pocket by cooking (Igene *et al*, 1979; Schricker and Miller, 1983) and release of iron from the iron storage protein ferritin, by the reducing agents, cysteine and ascorbate (Decker and Welch, 1990). Cooked ground beef may contain cysteine due to hydrolysis by enzymes released during grinding. Oil palm syrup and honey have considerable iron (Oboh *et al.*, 2016) and ascorbate content (Oboh and Imafidon, 2018; Buba *et al*, 2013). Thus, in this study the presence of heme and non-heme iron (released by grinding and cooking) in the beef, and the presence of sufficient lipid substrate (membrane and storage fat, and fatty acid peroxides) set the stage for the increase in the oxidation observed in the beef (from 0.158 on day 1 to1.843 mg malonaldehyde/kg on day 13). This oxidation was then inhibited to various

degrees by the different treatments employed, which in all cases decreased the extent of the process.

Although there are many nutritional and medicinal benefits of honey, it may also have toxic constituents. It has been reported that honey can be contaminated with heavy metals such as lead, arsenic, mercury and cadmium, depending on its region of origin (Islam *et al*., 2014). Also, honey produced by bees from the nectar of various species, such as the rhododendrons, and other plants of the family Ericaceae, contain a group of closely related toxins, the polyhydroxylated cyclic diterpenes known as grayanotoxins. These toxins are harmful, and cause a very rare poisonous reaction called grayanotoxin poisoning or honey intoxication (Mayor, 1995; Demircan *et al.*, 2012; Jense*n et al*., 2012), which may be lethal at high enough concentration (Lensky, 1997; US FDA, 2012; Islam et al, 2014). There are no reports of these toxic principles in oil palm sap, and syrup produced from it may be considered safe. Also, although screening of the palm syrup and honey samples used in this study showed the presence of flavonoids, glycosides and saponins, terpenoids and tannins were absent (Table 3.10). Thus, the palm syrup and honey used in this study did not contain the toxin.

TABLE 3.10. Phytochemicals of oil palm syrup and honey.

Constituents	Oil palm syrup	Honey
Alkaloids	-	-
Flavonoids	+	+
Glycosides	+	+
Saponins	+	+
Terpenoids	-	-
Tannins	-	-

Key: +: Present. -: Absent.

CONCLUSION

The results of this study indicate that oil palm syrup and honey (each at a concentration of 7.5 g/kg) exhibited high inhibition of oxidation in cooked ground beef during storage for 13 days at 4^{o}C. They are therefore suitable (at this concentration) for use as antioxidant preservative ingredient for cooked ground beef during short term storage in the refrigerator.

3.3. Oil palm syrup, citric acid and *Aframomum melegueta* seeds (alligator pepper) as functional flavouring and sweetener in non-alcoholic still beverage formulations (Oboh and Imafidon, 2018).

Beverages are refreshing drinks. They include the carbonated non-alcoholic, and the non-carbonated or "still" beverages, such as fruit drinks, and fruit juices. Another important group of beverages is characterized by a common property of having an initially stimulating effect. These include alcoholic beverages, tea, coffee, and cocoa. Beverages provide water, an important nutrient, which is essential for good health, and prevention of dehydration; some contain carbohydrate to provide a sweet taste and as a source of energy to meet the body's caloric requirement, and natural or added vitamins (especially vitamin C), which are required daily for health and maintenance.

Non-alcoholic still beverages were prepared from palm sugar, *Aframomum melegueta* pepper, and citric acid, and their physico-chemical, nutritional, antioxidative and sensory properties were examined in order to determine their suitability as functional refreshing drinks of good nutritional value. Results for titrable acidity, pH, 5-hydroxymethylfurfural (5-HMF), and antioxidant capacity (total phenolic content, 2, 2-diphenyl-1-picrylhydrazyl radical scavenging activity, and reducing power), vitamin C, and carbohydrate content indicate that the beverage formulations had suitable chemical, nutritional, and antioxidant characteristics, and may be functional. Sensory evaluation of the formulations showed that they were acceptable and refreshing, thus presenting attractive ways of delivering the health benefits of oil palm sugar and *Aframomum melegueta* pepper (Tables 3.11, 3.12, 3.13, 3.14, 3.15, 3.16, 3.17).

Table 3.11. Beverage formulations

Beverage ingredients	**FORMULATIONS**			
	A	**B**	**C**	**D**
Citric acid	**-**	**0.5 g**	**-**	**0.5 g**
***A. melegueta* seed extract**	**-**	**-**	**10 ml**	**10 ml**
Palm sugar	**20 g**	**20 g**	**20 g**	**20 g**
Final volume (made up with distilled water)	**100.0 ml**	**100.0 ml**	**100.0 ml**	**100.0 ml**

Table 3.12. Chemical properties of oil palm syrup.

Characteristic	Value
Total carbohydrate (%)	66.22±4.44
Titrable acidity (%)	3.60±0.00
pH	3.48±0.01
Vitamin C (mg %)	170.0±0.05
5-Hydroxymethylfurfural (mmol/kg)	1.009.0±0.002

TABLE 3.13. Phytochemical groups present in oil palm sugar and alligator pepper aqueous extract

Phytochemical group	Oil palm sugar	*A. melegueta* pepper aqueous extract
Alkaloids	-	+
Tannins	-	+
Saponins	+	+
Glycosides	+	+
Terpenoids	-	+
Flavonoids	+	+

TABLE 3.14. Antioxidant capacity values for oil palm sugar solution, *A. melegueta* pepper extract, and BHT.

Characteristic	Oil palm sugar[a]	*A. melegueta* pepper aqueous extract	BHT[b]
Total phenolic content (mg GAE[c]/ ml)	0.216 ±0.010	0.130±0.005	-
DPPH radical scavenging activity (%)	28.31±0.99	12.40±0.20	84.07±2.55
β-carotene bleaching antioxidant activity (%)	26.58±2.42	51.27±0.57	72.00±3.62
Reducing power (mg % AAE[d])	39.69±0.77	-	5.12±0.02

Values are expressed as mean ±SEM (n=3). [a]20% syrup in distilled water [b]0.02% in 70% ethanol. [c]GAE: Gallic Acid Equivalent. [d]AAE: Ascorbic Acid Equivalent

All the sensory characteristics observed were pleasant. The beverage formulation containing palm sugar, alligator pepper and citric acid (which had the highest DPPH radical scavenging activity and reducing power) was the preferred product based on the sensory evaluation. Thus, the beverage formulations present pleasant ways for the delivery of the medicinal constituents of oil palm syrup and *A. melegueta* pepper, and the associated health benefits.

TABLE 3.15. Chemical characteristics of beverage formulations

Characteristic	Palm sugar +distilled water	Palm sugar+ citric acid + water	Palm sugar + *A. melegueta* pepper extract + water	Palm sugar +citric acid + *A. melegueta* pepper extract + water
Total carbohydrate (%)[a]	13.28±0.89	13.28±0.89	13.28±0.89	13.28±0.89
Titrable acidity (%)	0.72 ± 0.00	0.79 ± 0.00	0.19 ±0.01	0.80 ± 0.02
pH	3.48±0.01	3.12±0.01	3.51±0.01	3.14±0.01
Vitamin C (mg/100 ml)	34.00 ± 0.10	34.00 ± 0.10	36.00 ± 0.00	35.00± 0.00
5-Hydroxymethyl furfural (5- HMF), µmol/L	201.70±0.45	202.15±0.53	201.87±0.27	202.81±0.95

[a]Calculated from the total carbohydrate content value.

TABLE 3.16. Antioxidant capacity of beverage formulations

Characteristic	Palm sugar + distilled water	Palm sugar + citric acid + water	Palm sugar + *A. melegueta* pepper extract + water	Palm sugar + *A. melegueta* pepper extract + citric acid + water
DPPH radical scavenging activity (%)	28.31±0.99[a]	27.58±0.79[a]	54.10±2.09[b]	79.83±0.60[c]
Reducing power mg % ascorbic acid equivalent (AAE)	39.69±0.77[a]	39.91±1.10[a]	41.35±2.56[a]	45.19±0.19[b]

Data are reported as mean ± SD (n=3). [abc]Means with different superscripts on the same row differ significantly ($p < 0.05$).

Table 3.17. Comparison of DPPH and pH of formulations with reported values for beverages with reported health benefits

Beverage	Average DPPH radical scavenging activity (% inhibition)	pH
Palm sugar +*A melegueta* pepper + citric acid + water	79.83±0.60[a]	3.14±0.01[a]
Palm sugar + *A. melegueta* pepper + water	54.10±2.09[a]	3.51±0.01[a]
Pomegranate	50.10±1.90[b]	2.93-3.20[c]
Red wine	35.2±2.2[b]	3.30-3.50[d]
Palm sugar + water	28.30±0.99[a]	3.48±0.01[a]
Concord grape juice	28.20±6.10[b]	2.80-3.00[c]
Palm sugar + citric acid + water	27.58±0.79[a]	3.12±0.01[a]
Iced green tea	22.30±2.60[b]	3.72±0.01[c]
Blueberry juice	20.60±1.40[b]	3.11-3.33[c]
Cranberry juice	19.20±0.60[b]	2.30-2.50[c]
Acai juice	18.3±1.2[b]	2.05-3.50[c]
Orange juice	12.70±1.0[b]	3.30-4.19[d]

[a]This study, [b]Dawidowicz *et al*. (2012), [c]Seeram *et al*. (2008), [d]Anon. (1962).

Conclusion

Non-alcoholic, non-carbonated drinks were formulated from sugar derived from the sap of the African oil palm (*Elaeis guineensis* Jacq) tree, the aqueous extract of *Aframomum melegueta* seeds, and citric acid. Their antioxidant capacity, carbohydrate, vitamin C and phytochemicals content, coupled with their pleasant organoleptic characteristics indicate that they may be suitable for use as refreshing functional beverages.

3.4. Potentials of Palm Wine Infusions of Kola Nut and Alligator Pepper as Value Added Functional Beverages (Oboh *et al.*, 2022)

3.4.1. Background to the study

Effective dietary control of obesity, type-2 diabetes mellitus and its complications (especially where carbohydrates form the bulk of the diet and cost far less than food fat or protein, as exists in the tropics) requires in addition to a good understanding of the composition of local foods and beverages, the interplay of their macro- and micronutrients, and phytochemicals. Such knowledge would enable adequate combination of various foods and beverages, in combination with exercise and other lifestyle changes (with or without drug intervention), for effective management of fasting and postprandial blood glucose concentrations and control of oxidative stress. This should in turn broaden the range of dietary options available for individuals with type 2 diabetes mellitus (T2DM) and complications arising from the condition.

Palm wine is obtained from the spontaneous fermentation of palm sap, the white semi-translucent, sugary liquid obtained by tapping palm trees (Francisco-Ortega and Zona, 2013). In Nigeria, palm wine is obtained mainly from the saps of the African oil palm (*Elaeis guineensis* Jacq.) and the raffia palms (*Raphia* spp), which are left to ferment, and drunk as such (palm wine), or distilled to yield a strong liquor (the gin variously known as *kain-kain* or *ogogoro* in Nigeria, and *akpetesie* in Ghana). Palm wine is a rich nutrient medium containing sugars, ethanol, protein, amino acids, minerals, vitamins B and C, antioxidants (such as phenolic compounds), other phytochemicals, and beneficial microorganisms, (Okafor, 1978; Chandrasekhar *et al*., 2012; Hebbar, 2015; Oboh *et al.*, 2016; Oboh and Imafidon, 2018; Oboh *et al*., 2021, Oboh, 2022). Oboh *et al*. (2011) have reported low glycaemic index values for oil palm wine (11±5) and raffia wine (44.0±13).

In this study, the *in vitro* effects of infusions of wet *C. acuminata* and dried *A. melegueta* seeds on the pH, total phenolic content, reducing power, α-amylase inhibitory activity, and vitamin C content of oil palm wine were determined.

3.4.2. Our findings

Total phenolic and vitamin C contents and reducing power of the infusions were higher than those of palm wine. The infusions of *C. acuminata* seeds exhibited higher alpha-amylase inhibitory activity than the palm wine, while infusions of *A. melegueta* seeds had lower activity. The pH of palm wine and the infusions were within a narrow acidic range of 3.4-3.7. Findings suggest that there may be nutritional and functional benefits in the consumption of *C. acuminata* and *A. melegueta* seeds as accompaniment to palm wine, opening up possibilities for their use as nutritional and bioactive flavourings in the preparation of value-added functional beverages based on oil palm wine.

Palm wine had modest vitamin C content, reducing power and α-amylase inhibitory activity, and a high TPC (Table 3.17). The *C. acuminata* infusions had significantly higher values than palm wine, with percentage increase ranging from 125.441-246.391% for vitamin C content, 45.502-203.675% for TPC, 48.413- 127.317% for reducing power, and 86.843-136.388% for α-amylase inhibitory activity. These values were significantly higher than those for palm wine, but the increase did not follow any definite pattern because the kolanut samples were wet thereby limiting its solubility. Our use of wet kolanut was deliberate because kolanuts are usually eaten in that form. The pH of the palm wine and the extracts were within a narrow acidic range of 3.4-3.7, similar to values for several beverage preparations which are sold at a premium based on claims of functional properties, such as pomegranate juice (2.93-3.2), concord grape juice (2.8-3.0), red wine (3.30-3.50), blueberry juice (3.11-3.30), cranberry juice (2.30-2.50) and açaí juice (2.05-3.50) (Seeram *et al.*, 2008)

Table 3. 17. Vitamin C, pH, total phenolic content (TPC), reducing power, and α-amylase inhibitory activity of cold oil palm wine infusions of fresh *C. acuminata* seeds

Samples	**pH**	**Vitamin C (mg/100 ml)**	**Total phenolic content (µg GAE/ml)**	**Reducing power (mg % Ascorbic Acid Equivalent)**	**Alpha-amylase inhibitory activity (%)**
Palm wine (PW)	3.6	12.468±0.486[a*]	111.167±1.607[a]	10.521±1.402[a]	31.299±0.174[a]
PW + 0.5% CA[**]	3.5	35.272±2.520[b] (182.924) [***]	161.750±4.669[b] (45.502)	15.625±2.107[b] (48.513)	61.983±1.970[b] (98.035)
PW + 1.0% CA	3.4	41.112±0.134[c] (230.133)	263.917±1.778[c] (137.406)	14.467±1.265[b] (37.506)	84.899±1.238[c] (171.252)
PW + 1.5% CA	3.6	37.908±0.618[b] (240.042)	337.583±10.181[d] (203.672)	20.920±2.776[c] (98.840)	68.169±0.348[d] (117.799)
PW + 2.0% CA	3.4	39.504±1.867[b] (216.843)	318.000±12.219[d] (186.056)	19.525±4.702[c] (85.581)	71.262±1.477[e] (127.681)
PW + 2.5% CA	3.5	43.188±0.517[d] (246.391)	312.625±7.528[d] (181.221)	26.214±4.467[c] (127.317)	60.836±4.345[b] (94.370)
PW + 3.0% CA	3.7	30.299±3.190[b] (143.014)	303.042±4.877[d] (172.601)	21.157±2.633[c] (101.093)	58.480±4.606[f] (86.843)
PW + 3.5% CA	3.7	28.108±5.420[b] (125.441)	323.708±13.438[d] (191.191)	21.463±3.332[c] (104.002)	73.987±2.665[g] (136.388)

***Mean±SD. Results with different superscripts are significantly different (*p*<0.05). **CA = *C. acuminata.* ***() In parenthesis, percentage increase relative to palm wine**

Phenolic compounds and vitamin C found in foods are responsible, to a large extent, for their antioxidant capacity and beneficial biological activity (Proteggente *et al.*, 2002, Anhe *et al.*, 2013). The health benefits of polyphenols are generally attributed to both specific and non-specific mechanisms, dependent on a broad antioxidant activity, and specific mechanisms which include interaction with key signalling proteins, and inhibitory effects on key enzymes associated with diseases, such as α-amylase and α-glucosidase in type 2 diabetes mellitus (T2DM) (Fraga *et al.,* 2010, Anhe, 2013; Gonçalves and Romano, 2017).

Dietary phenolic compounds can modulate glucose homeostasis. This they do by decreasing the postprandial glucose response through inhibition of SGLT 1 (sodium-dependent glucose transporter 1) and GLUT 2 (glucose transporter 2) that aid glucose transport across the intestinal brush border membrane (Pico and Martinez, 2019). Polyphenols may protect pancreatic cells from glucotoxicity and improve insulin secretion thereby alleviating T2DM by acting on insulin secreting cells (Hanhineva *et al*., 2010). Obesity-linked T2DM is associated with a low-grade inflammatory state, which leads to insulin resistance, and subsequently, T2DM (Marette, 2002; Freedman *et al.*, 1991; Wellen and Hotamisligil, 2005; Weisberg *et al*., 2003; Xu *et al.*, 2003). It has been proposed that polyphenols can protect against T2DM through anti-inflammatory effects (Rodriguez-Sanabria *et al.*, 2010; Kostyuk *et al*., 2011; Vitaglione, 2010).

In this study, addition of kolanut increased the *in vitro* α-amylase inhibitory activity of palm wine at all the concentrations considered (Table 3.17). *In vivo*, α-amylase present in saliva and pancreatic juice cleaves internal α-1, 4 bonds of the component amylose and amylopectin of dietary carbohydrate (starch) to oligosaccharides and disaccharides, which are ultimately converted into glucose by α-glucosidase. Liberated glucose is then absorbed and may result in postprandial hyperglycaemia in T2DM. The inhibition of these enzymes delays the process of carbohydrate hydrolysis and absorption, thereby decreasing significantly, postprandial increase in blood glucose levels after consumption of a carbohydrate-rich meal. This forms the basis of an important strategy in the management of T2DM and reduction of chronic complications associated with the disease (Oboh *et al*., 2010).

Excessive generation of highly reactive free radicals (largely due to hyperglycaemia) leads to oxidative stress, resulting in damage to DNA, lipids, and proteins, coupled with disruption in cellular homeostasis and accumulation of damaged molecules (Jakus, 2000), which may further accelerate the development and progression of diabetic complications (Penckofer *et al*., 2002; Johansen *et al*., 2005). The use of natural antioxidants is a complementary therapy in the management of diabetes (Rahimi *et al*., 2005; Srinivasan, 2005; Golbidi, 2011; Obi *et al*., 2011).

The considerable TPC and *in vitro* reducing power of the palm wine kolanut infusions indicate high reducing (antioxidant) capacity. These, and the increased *in vitro* α-amylase inhibitory activity and vitamin C content indicate possible nutritional and functional benefits *in vivo,* of consumption of kolanuts along with palm wine. Inhibition of human pancreatic α-amylase (HPA) by vitamin C has been reported by Borah *et al*. (2019). These authors found that ascorbic acid inhibited HPA activity via non-competitive antagonism from two allosteric sites, by channelling the inhibition towards the active site cavity via the triose-phosphate isomerase (TIM) barrel.

Dried *A. melegueta* seeds are usually consumed in much smaller quantities than kolanuts, due to their peppery flavour. Lower concentrations (than for kolanuts) were therefore employed in this study (Table 3.18). Addition of melegueta pepper increased vitamin C content, TPC, and *in vitro* reducing power (by 65.047 to 81.922%, 3.26 to 65.029%, and 191.85 to 233.875% respectively), indicating beneficial effects of its infusion in palm wine over the range of concentrations studied. In addition, the low IC_{50} (29.0 mg/ml) for reducing power of the palm wine infusions of melegueta pepper indicated a high *in vitro* antioxidant capacity.

The results suggest that consumption of melegueta pepper as a complement to palm wine drinking may be beneficial from the viewpoint of increased intake of antioxidants, including vitamin C and phenolic compounds. As in the case of kolanut, these findings indicate that combination of palm wine and melegueta pepper may provide a suitable and safe refreshment for individuals with chronic health conditions caused by highly reactive free radicals, potentially, through the inhibition, *in vivo,* of their generation and propagation, thereby resulting in amelioration of their effects.

There was decrease in the α-amylase inhibitory activity of the palm wine on addition of the pepper (Table 3.18). Compared with palm wine, residual activity in the pepper infusions, varied from 16.01% for the lowest, to 42.12% for the highest concentration, suggesting that the addition of melegueta pepper to palm wine may impair the modest potential of the latter for dietary regulation of blood glucose concentration through the inhibition of pancreatic and salivary α-amylase.

Table 3.18. Vitamin C content, pH, total phenolic content, reducing power, and α-amylase inhibitory activity of cold palm wine infusions of dried *A. melegueta* seeds

Samples	pH	Vitamin C (mg/ 100 ml)	Total phenolic content (µg GAE/ml)	Reducing power (mg % Ascorbic Acid Equivalent)	Alpha-amylase Inhibitory Activity (%)
Palm wine (PW)	3.6	12.468±0.486[a*]	111.167±1.607[a]	10.521±1.402[a]	31.299±0.174[a]
PW+ 0.2% *A. melegueta*	3.6	20.578±4.427[b] (65.047) **	114.791±4.284[a] (3.260)	30.705±0.644[b] (191.845)	5.011±0.106[b] (16.010) ***
PW+ 0.4% *A. melegueta*	3.5	22.398±1.565[b] (79.644)	128.250±5.773[b] (15.367)	33.188±0.894[b] (215.445)	6.115±0.185[b] (19.537)
PW+ 0.6% *A. melegueta*	3.7	22.682±1.512[b] (81.922)	159.000±8.880[c] (43.028)	33.709±0.291[b] (220.397)	10.945±0.748[c] (31.969)
PW+ 0.8% *A. melegueta*	3.7	22.058±4.275[b] (76.917)	183.458±6.771[d] (65.029)	35.127±0.839[b] (233.875)	13.183±0.555[d] (42.120)
IC_{50} (mg/ ml)		-	-	29.0	-

*Mean ±SD. Results with different superscripts are significantly different ($p<0.05$). **(): In parenthesis percentage increase relative to palm wine.
***(): Percentage retention compared with inhibition by palm wine alone.

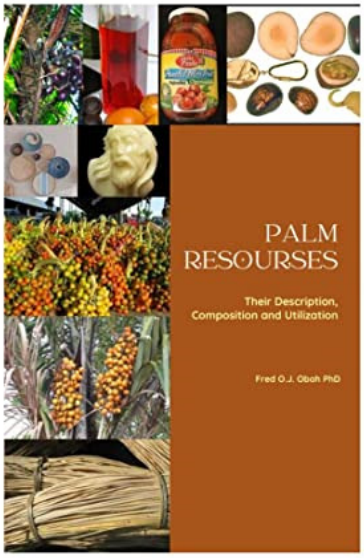
Oil palm wine is rich in nutrients and bioactive phytochemicals, including the water-soluble vitamin C and the vitamins B, amino acids, minerals and phenolic compounds, as well as lactic acid bacteria with possible probiotic properties and benefits for gut health (Chandrasekhar *et al*., 2012). Kolanuts and melegueta pepper, in addition to their functional properties, have considerable macronutrient and mineral content (Borquaye *et al.*, 2017). Thus, their addition to palm wine would further enrich it by improving its nutritional composition, flavour, and functional properties.

In this study, vitamin C content and *in vitro* functionality of palm wine infusions of *Cola acuminata* P. Beauv. Scott and Endl and *Aframomum melegueta* (Roscoe) K. Schum seeds were determined. Various oil palm wine infusions of fresh *Cola acuminata* and dried *Aframomum melegueta* seeds were prepared and their pH, total phenolic and vitamin C contents, *in vitro* reducing power, and *in vitro* α-amylase inhibitory activity were determined. Total phenolic and vitamin C contents and reducing power of the infusions were higher than those of palm wine. The infusions of *C. acuminata* seeds exhibited higher alpha-amylase inhibitory activity than the palm wine, while infusions of *A. melegueta* seeds had lower activity. The pH of palm wine and the infusions were within a narrow acidic range of 3.4-3.7. Findings suggest that there may be nutritional and functional benefits in the consumption of *C. acuminata* and *A. melegueta* seeds as accompaniment to palm wine, opening up possibilities for their use as nutritional and bioactive flavourings in the preparation of value-added functional beverages based on oil palm wine.

3.4.3. Conclusion

This study showed increase in the vitamin C content and reducing (antioxidant) capacity of palm wine on addition of *C. acuminata* and melegueta pepper, suggesting benefits of their consumption as accompaniment to the drinking of palm wine. Also, *C. acuminata*-palm wine infusions exhibited high *in vitro* α-amylase inhibition, with potential for control of postprandial blood glucose levels *in vivo.* The potential nutritional and functional benefits of the consumption of palm wine infusions of *C. acuminata* and *A. melegueta* seeds open up possibilities for their use as nutritional and bioactive flavourings in the preparation of value-added functional beverages based on oil palm wine.

4. OTHER BOOKS BY THE AUTHOR



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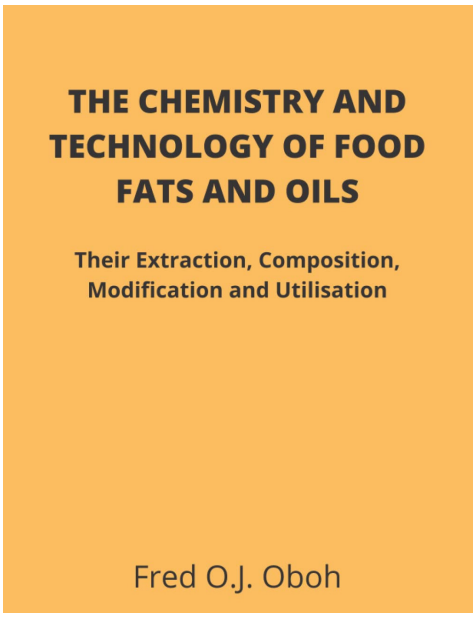
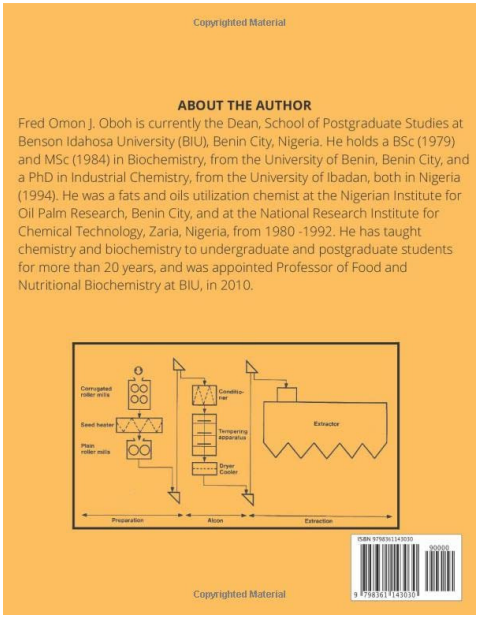
This book is about palm produce, products based on them, and their utilisation. The applications of the resources available from the five major cultivated palms (the coconut palm (*Cocos nucifera*), the date palm (Phoenix dactylifera), the African oil palm (Elaeis guineensis), the carnauba wax palm (*Copernicia cerifera*), and the areca nut palm (Areca catechu)) are well known. However, there are other palms that bear produce that are currently exploited for the provision of a broad range of resources, including fats and oils, sap, wax, starch, flours, vegetable milks, fibre, cabbage, handicraft, shelter, and furniture materials, charcoal e.tc. These resources, previously only of local or regional importance, are increasingly emerging on international markets as ingredients for cosmetics and other personal care products, food and beverages, nutritional supplements and pharmaceuticals, vinegar, handicraft and others. They also feature increasingly, as raw materials for the industrial production of fuel materials, such as biodiesel and bioethanol, oleochemicals, and bioplastics. Increased utilisation of their produce has led in some cases, to unsustainable exploitation of some of these palms. Due to the economic and nutritional benefits of the products from these lesser-known palms, it is an aim of this book to highlight these developments and the current interventions aimed at their rational and sustainable exploitation as

ingredients for cosmetics and other personal care products, food and beverages, nutritional supplements and pharmaceuticals, vinegar, handicraft and others.





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This book focuses on the chemistry, industrial extraction, modification, and utilisation of fats and oils and the residues from their extraction, for food applications. Good extraction and processing techniques ensure that the oil is extracted in an efficient manner, yielding valuable by-products (e.g., lecithin and protein concentrates and isolates, suitable for inclusion in human food preparations and livestock feed) along the processing chain. It is therefore important to have an understanding of the chemistry of oilseeds, oils and fats, to enable appropriate design and applications of the various technologies involved in their extraction, modification, and utilisation.
In this book, descriptions of processes, are taken from trade brochures made available by manufacturers of equipment, academic journals, books, and other sources, including the author's research results. Oleaginous materials discussed include oilseeds, fruit mesocarp, animal, as well as marine sources (fish, krill, and algae).

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PREVIOUS INAUGURAL LECTURES

S/N	NAME OF LECTURER	LECTURE TOPIC	DATE
1.	Professor Johnson Olajide Oyedeji	Bricks with Little Straws: How efficient are the meat and egg-type chickens?	27 July 2010
2.	Professor R. A. Masagbor	Language: A Complementarity of Being	17 April 2012
3.	Professor A. A. Borokini	Female Genital Mutilation: The Nexus between Anthropology, Law and Medicine	19 May 2015
4.	Professor Ernest B. Izevbigie	From Growth Biology to HIV associated Neuropathy to the Discovery of Anti-Cancer Agents: Economic Implications	8 December 2015
5.	Professor Andrew O. Oronsaye	The Anatomy of Nigeria Federalism and the Physiological Imperatives for Sustainable Development	22 March 2016
6.	Professor Rex O. Aruofor	Economic Systems Engineering- Poverty, Unemployment and Underdevelopment: A Quest for Solution and Imperatives for Developing the Nigerian Economy	6 March 2017
7.	Professor Sam Guobadia	It's the Environment	19 October 2017
8.	Professor (Mrs.) Clara Leyibo Igeleke	Microbes The Good and The Bad, and The Fascinating: Man the Effective Manager"	26 November 2019
9.	Professor (Mrs.) Nora Omoregie	Educational Administration and Quality of Products of the school system	2 April, 2021

10.	Professor Duze Chinelo Ogoamaka	Nigeria's Legacy in Education, Nigeria's Education System and Sustainable National Development: Thought for Food	13 July 2022
11.	Professor Theresa Uzoamaka Akpoghome	Taming the Beast: IHL in a Bleeding Environment	26 July 2022
12.	Professor Alexandra Esimaje	Because War is much too serious to be left to the Military, Corpus Linguistic is a thing and it is a very Useful Thing too	18 October 2022
13.	Professor Mark Osamagbe Ighile	The Poet Prophetic Voice in the Wilderness of our Time: an Oral, Literary and Biblical Prognosis	8 November 2022
14.	Professor Augustine E. Akhidime	Financial Gatekeepers, Watchdogs and Bloodhounds in the Eyes of the Storm of Public Trust; and the House that is Divided Against Itself	22 November 2022
15.	Professor Ehimen Pius Ebhomielen	Take Responsibility: Comprehensive accountability culture is mandatory for all and sundry	13 December 2022
16.	Professor Kingsley Osamianmionmwan Obahiagbon	From Medieval to Modernity: Odyssey of an Information Scientist (informatics)	17 January 2023

BIOGRAPHY OF THE AUTHOR

Frederick Omonkhegbe Joseph Oboh, a Professor of Biochemistry, is the Dean, School Postgraduate Studies, at Benson Idahosa University, Benin City, Nigeria. Professor Oboh was born in Irrua, Ishan Division, Western Region, Nigeria, on the 8th of December, 1957. He attended St. Joseph's Catholic Primary School, Igueben (founded in 1918) from 1964 to 1968, and Edo College, Benin City, from January 1969 to May 1973 (theirs was the first set to write the West African School Certificate Examinations in May-June, and spent only about five or 6 months in form 5, depending on the subjects taken). He proceeded to higher school in September of the same year, and in the same school, but subsequently secured admission to read science at the University of Benin, Benin City, where he resumed in January 1975 for the 5-term predegree programme. At the successful completion of his predegree studies, he chose biochemistry out of the various options available to him (i.e., biochemistry, chemistry, industrial chemistry, optometry, geology, and the biological sciences – botany, microbiology, and zoology), and graduated with a BSc (Hons) Degree in 1979.

He did his national service in Niger State (1979-1980) and had his primary assignment at the Pathology Department, General Hospital, Minna. At the end of his service, he was appointed to the position of Research Officer-in-Training (ROT, similar to the position of Graduate Assistant in the university) at the Nigerian Institute for Oil Palm Research. After a year as an ROT, he proceeded to the University of Benin, Nigeria, on in-service training, where he acquired an MSc degree in Biochemistry in 1984. He latter proceeded to the University of Ibadan, where he earned a PhD degree in Industrial Chemistry in 1994.

Professor Fred Oboh, has been, at various times:

Member, National Youth Service Corps. Place of primary assignment: Pathology Laboratory, General Hospital, Minna, Niger State -September 1979- September 1980.

Research Officer-in-Training, Nigerian Institute for Oil Palm Research, Benin City: –
1980 – 1984.

Research Officer 1, Nigerian Institute for Oil Palm Research, Benin City: - 1984-1988.

Senior Research Officer, Nigerian Institute for Oil Palm Research, Benin City: - 1988.

Principal Research Officer and Research Leader, Organic Chemicals Programme, National Research Institute for Chemical Technology, Zaria, Nigeria: 1989 – 1992.

Executive Director, RIOGROUP: 1992 – 1996.

Managing Director, Standard Technologies (Nig) Ltd: 1997 – 2001.

Senior Lecturer in Chemistry, Department of Chemical Sciences, Igbinedion University, Okada, Edo State - January 2002 – Oct 4, 2006.

Senior Lecturer in Biochemistry, Department of Basic Sciences, Benson Idahosa University, Benin City – October 5, 2006 – November 15, 2006.

Associate Professor of Biochemistry, Department of Basic Sciences, Benson Idahosa University, Benin City (November 16, 2006 – September 30, 2010).

Head, Department of Basic Sciences, Benson Idahosa University, Benin City (October 1, 2008 – February 21, 2011).

Professor of Biochemistry, Department of Basic Sciences, Benson Idahosa University, Benin City (Since October 1, 2010).

Dean, Faculty of Basic and Applied Sciences, Benson Idahosa University, Benin City (February 21, 2011-January 27, 2012).

Dean, Faculty of Science, Benson Idahosa University, Benin City (September 2020-July 2021).

Dean, School of Postgraduate Studies, Benson Idahosa University, Benin City (Since August 1, 2021).

Professor Fred Oboh has been a member of the Senate of Benson Idahosa University since 2008, and was a member of the Committee that produced the Academic Culture Document (2011/2012). He has been Acting Vice Chancellor on a number of occasions.

Professor Fred Oboh spearheaded the development of the curricula for the MSc Biochemistry and MSc Microbiology programmes in 2010, and defended them before the Postgraduate Committee; subsequently, the programmes passed National Universities Commission verification. He was also a member of the committee that wrote the curriculum for BSc Chemistry and Industrial Chemistry (2017).

Subsequently, he chaired the committee that developed the curricula for the BSc in Nursing Science and the Bachelor of Medical Laboratory Sciences programmes, and signed the MOU documents between Faith Mediplex and Neuropsychiatric Hospital Uselu on behalf of the Vice Chancellor, Benson Idahosa University:

He participated in the review of the curricula for the following programs from time to time, such as pegging the maximum credit units registerable in a session at 48, at 24 credits per semester and the change to the 6-month continuous industrial training consisting of the second semester of 300L in addition to the long vacation, for BSc Biochemistry, BSc Microbiology and BSc Computer Science, and BSc Physics.

Professor Oboh has taught chemistry and biochemistry to both undergraduate and postgraduate students, and supervised BSc and MSc projects for over 20 rears. He has also served as External Examiner for undergraduate and postgraduate industrial chemistry examinations, and has participated in National Universities Commission (NUC) accreditation. He participated in the review of the following:

i. National Universities Commissions' instruments for the accreditation part-time programmes (2019)
ii. National Universities Commissions' instruments for institutional accreditation (2019)

Before embarking on a career in academics, Professor Fred Oboh was a palm produce utilisation chemist at the Nigerian Institute for Oil Palm Research and the National Research Institute for Chemical Technology from November 1980 to 1992. He was a member of the End-Use Research Task Force, which metamorphosed into a full-fledged End-Use Research Programme for the development of food fats and oleochemicals (1985-1986). He was also a member, Date Palm Research Programme from 1987- 1988. From 1989 – 1991, Professor Oboh was Head and Research Leader, Organic Chemicals Programme, National Research Institute for Chemical Technology, Zaria, Nigeria.

Professor Fred Oboh's articles have been published in foreign and Nigerian journals, and in edited proceedings of an international conference. He has authored two full length books (an e-book and a paperback), both published on Amazon. He has reviewed articles for various Nigerian and foreign journals over the years. He was a member, University Research and Publications Committee, Igbinedion University, Okada (2003-2006), and is an Editorial Board member/reviewer, Benson Idahosa University Journal of Basic and Applied Sciences.

Professor Oboh's research interest is focussed on the utilisation of plant resources, including palm produce (pulp and kernel oils, residues from their extraction, and palm sap and products derived from it), tropical fruit juices, spices, and leafy vegetables.

Prof. Fred Oboh is a member of the following learned societies: The Nigerian Society of Biochemistry and Molecular Biology, the Society of Chemical Industry (UK), the Society for Economic Botany (USA), the Science Association of Nigeria, and the Chemical Society of Nigeria.

Professor Fred Oboh is married to Ijeoma Oboh, a Professor of Hydrobiology and Fisheries, and they are blessed with children.