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Spectroscopic Determination of Sugar Components of *Vitex doniana* Fruit Syrup Following Derivatization

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Abstract: The fresh fruits of black plum (*Vitex doniana*) were collected from several randomly selected trees in a farm site in Uromi metropolis, Esan North-East Local Government Area of Edo state and then processed into an extract in form of syrup. The sugars were identified using a combination of 1D ^{1}H NMR and GC-MS. For the NMR analysis, 5 mg of the sample was dissolved in deuterated DMSO (DMSO-d_6), a common solvent for NMR analysis. Then the sample, was analysed with 1D ^{1}H NMR at 500 MHz to obtain the spectrum showing the chemical shifts, peak multiplicity and coupling constants of the prospective sweeteners (sugars) in the sample. While characterization of the specific sugars in black plum fruit syrup was done using GC-MS spectroscopic techniques via derivatization. This method converts the sugars in the sample to the respective trimethylsilyl- derivatives of the sugars, which are volatile and amenable for GC-MS analysis. The sugars identified in *Vitex doniana* fruit syrup are fourteen (14) and are presented based on the percentage of each sugar constituents and contribution to the sweetness profile of the syrup as obtained from their raw area percentage based on the total ion current. The sugars identified are Alpha.-D-Glucopyranose (16.11%), Glucopyranose (11.19%), D-Glucose (11.15%), d-(+)-Xylose (8.95%), 2-Deoxy-pentose (8.92%), Glucofuranoside (6.84%), beta.-D-Galactopyranoside (6.37%), D-Fructose (6.16%), alpha.-DL-Arabinofuranoside (6.14%), alpha.-DL-Lyxofuranoside (4.85%), Ribitol (4.58%), 2-Keto-d-gluconic acid (3.62%), D-Xylofuranose (3.05%). While the least contributor is the alpha.-D-Galactopyranose (2.07%). The high sugar content of *Vitex doniana* fruit syrup makes it very sweet and people enjoy licking it, discourage microbial growth, hence reduced deterioration and increased shelf-life. It is therefore recommended for human consumption in every household. It is also suggested that further research should be carried out on its economic status and feasibility of the seed as feed supplement in animal feed. Proper exploitation of the fruit and utilization of the syrup can help conserve foreign exchange expended on the importation of syrup, and substitute for other syrups in industrial and food uses.

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1. Introduction

Black plum (*Vitex doniana*) is a plant widely used by several communities in Nigeria for many purposes, including production of wine and jam. Ripe mature black plum fruits for food use, usually are collected from the ground instead of plucked (Okigbo, 2001). With increasing emphasis on upgrading traditional plant food resources in Nigeria, there is the need for better understanding of available plants including the severally underutilized species. *Vitex doniana* represents one of our neglected underutilized forest resources. Although major research on the health benefits of plant-rich diets has lied emphasis on established vitamins, the current data are controversial and the drive towards identification of more constituents and plant food sources continues (Ochieng and Nandwa, 2010). In addition, the economic value of *Vitex doniana* has not been exploited to its maximum despite the documented uses. Black plum of the family verbanacae is a tree crop that grows in open woodland and savannah regions of tropical Africa; it is the commonest of Vitex species in West Africa. It produces fruits which are plum like, sweet and edible. The fruit is green when mature and changes to dark brown when fully ripe, with the pulp surrounding a hard stone containing 1 to 4 seeds. It is a savannah specie and therefore can be found in northern, western and eastern Nigeria.

Plants and other components of natural origin have being applied throughout the world for human and animal health care for age long time. This is especially in Africa where underdevelopment and poverty have made a large percentage of the people depend almost totally on traditional medical practices and folkloric application of plants (Ajoku *et al.,* 2001; Enzo, 2006). The efficacy of some of these traditional herbal remedies has been shown by several researchers. One of such plant popular for it wide use in Africa native folklore is *V. Doniana* Sweet. The plant is indigene to Nigeria, Botswana, Ethiopia, Kenya, Lesotho, Namibia, Niger, Senegal, Somalia, South Africa, Sudan, Tanzania, Uganda, Zambia. It is locally known as Vitex (English), dinya (Hausa), ucha koro (Igbo) and oori-nla (Yoruba) (Burkill, 2000; Glew *et al.,* 1997). In folkloric medicine, various parts of the plant are used as remedy for infectious conditions such as infertility, anaemia, jaundice, leprosy, dysentery, colic, gonorrhea, backaches, headaches, febrifuge, conjunctivitis and other eye troubles, stiffness, measles, rash, fever, chickenpox, hemiplegia, as tonic galactagogue to aid milk production in lactating mothers, anodyne, ankylostomiasis (ancylostomiasis), rachitis, leprosy and liver disease, kidney troubles and dearth of vitamin A and B. the twigs are used as chewing sticks for cleaning the teeth. The blackish extract gotten by boiling the leaves, bark, root and/or fruits is applied as ink and dye for clothes (Burkill, 2000; Irvine, 1961).

The generic name, 'Vitex', is an ancient Latin name for the genus. Apart from the commercial relevance of this plant in timber and wood production, not much research on its chemical and antimicrobial activity has been done. It is in the light of the above, that this work aim to link scientific findings with some of these folkloric uses with the intentions of attracting more research interest to plant in trending lead/hit prospects in drug discovery. Black plum are branded as juicy seed bearing structure of flowering plant that may be consumed as food (Hyson, 2002). Fruits are not given the place they deserve in the diet of Nigerians due to lack awareness of their nutritive value, cost and challenges in storage and distribution (Sai, 1997). The diet of most rural and urban dwellers is deficient in protein resulting in increased incidence of malnutrition and rise in dietary diseases; a situation in which children and especially pregnant and lactating women are most susceptible (Black, 2003). In developing nations, various types of edible wild plants are exploited as sources of food to give supplementary nutrition to the inhabitants (Aberoumand and Deokule, 2009). Food and Agricultural Organization (FAO) reported that at least one billion people are assumed to use wild food in their food (Burhingame, 2000). In Ghana alone, the leaves of over 300 species of wild plants and fruits are eaten while about 150 wild plant species have been earmarked as sources of emergency food in India, Malaysia and Thailand (Umar *et al*., 2007). Also, in South Africa about 1400 edible plant species are consumed (Hassan and Umar, 2004). It is therefore paramount to note that the addition of edible wild and semi-cultivated plant resources could be valuable to nutritionally marginal populations, or to certain susceptible groups within the population, especially in developing countries where poverty and climatic changes are inflecting havoc to the rural dwellers (Aberoumand and Deokule, 2009). The genus Vitex consists of over 270 species, mostly trees and shrubs, and is confined to tropical and sub-tropical regions, although some species are also present in the temperate zones (Padamalatha *et al*., 2009). Among them is *V. doniana* also called black plum. Information of its botany is reported by Agbede and Ibitoye (2007). Nnajiofor (2003) investigated the fermentation of *V. doniana* (black plum) juice for the preparation of wine, while Agbede and Ibitoye (2007) studied the sugar composition as well as the anti-nutritional components in its fruit. Egbekun *et al*. (1996) revealed that *V. doniana* fruit could serve as a vital source of nutritive sweetener while Ladeji *et al*. (2004) investigated the anti-diarrhoea potency of stem bark of *V. doniana*. Despite its application as food and medicine in this part of the world, there has been minimal or no report on its proximate, vitamin and mineral composition. There had been no worry about food security since 1930 in United States; the booming food export has even returned a beneficial effect on the economy. Many nations cannot lay claim to this because over 870 million people are malnourished or hungry according to the United Nations Food and Agriculture Organization (Woteki, 2013). There is a reason for other countries to resolve this fundamental issue of feeding their people in order to ensure food security. The dependence on some crop species (rice, maize, wheat and cassava) in the supply of calorie need demand of man and high cost of readily available fruits and vegetables are among the propelling forces behind micronutrients deficiency prevailing in Africa. While there had been many interventions through food bio-fortification, diet diversity is the most commendable approach. Strategies based on nutrient rich foods like vegetables are regarded essential to be a basic objective in the fight against malnutrition and under-nourishment. In Nigeria like most other African nations, rural dwellers depend on leaves collected from the wild as their major source of leafy vegetables. These vegetables include leaves of annuals and shrubs and also leaves of trees. Most often, the trees are considered as sources of fruits and seeds while their leaves are left to rot.

Derivatization is a process of chemically modifying a compound to produce a compound which has properties that are suitable for analysis using a GC or HPLC. Derivatization is a technique in chemistry which transforms a chemical compound into a product (reaction's derivate) of similar chemical structure called a derivative. The most commonly used trimethylsilylation reagent for derivatization is the Tri-

Sil HTP Reagent (HDMS: TMCS: Pyridine). The reagent rapidly produces TMS derivatives of polar compounds for GC analysis and biochemical synthesis. The versatile reagent is ideally suited for GC determinations of a range of compounds such as sugars, alcohols, phenols, steroids, sterols, organic acids and some amines. GC and GC-MS are excellent techniques for the analysis of carbohydrates; nevertheless the preparation of adequate derivatives is necessary. The different functional groups that can be found and the diversity of samples require specific methods.

2. Materials and Methods

The fresh fruits of black plum (*Vitex doniana*) were collected from several randomly selected trees in a farm site in Uromi metropolis, Esan-North East Local Government Area of Edo state. The plant was identified by the Ethnobotanist and registered with a voucher specimen number NIPRD/01/03/CCPF/384/3 and deposited at the herbarium of the National institute for pharmaceutical research and development (NIPRD), Idu Industrial area, Abuja.

Extraction was done using a modified method described by Abu (2002) and Aiwonegbe (2018). The fruits were kept under ambient temperature in the laboratory. The fruits were sorted to select the fresh ones and then cleansed to remove sand and other debris. Thereafter, washing with portable water and removal of the thin epicarp. The fruits were then milled through a 90 µm sieve to press out the succulent mesocarp and separate the stony seed from the pericarp. The pulp was blended in a waring blender for a few seconds and warm water at 30^{o}C was added to the mixture. The mixture was then stirred continuously for five minutes with a wooden paddle to obtain the syrup.

Spectroscopic techniques 1D ^{1}H NMR and GC-MS were used. For the NMR analysis, 5 mg of the sample was dissolved in deuterated DMSO (DMSO-d_6) a common solvent for NMR analysis. Then the sample was analysed with 1D ^{1}H NMR at 500 MHz to obtain the spectrum showing the chemical shift, peak multiplicity and coupling constants of the prospective sweeteners (sugars) in the sample. While the characterization of the specific sugars in black plum fruit syrup was done using GC-MS spectroscopic techniques. Derivatization procedure: the black plum syrup was dried in a desiccator to remove water. The dried sample was treated with 5 mL of Tri-Sil HTP reagent (Thermo Scientific, Product number TS-48999, Lot number TG-267519). This method converts the sugars in the sample to the respective trimethyl derivatives of the sugars, which are volatile and amenable for GC-MS analysis. GC-MS Analysis: Modified method of Okhale *et al.* (2018) was used for the GC-MS analysis.

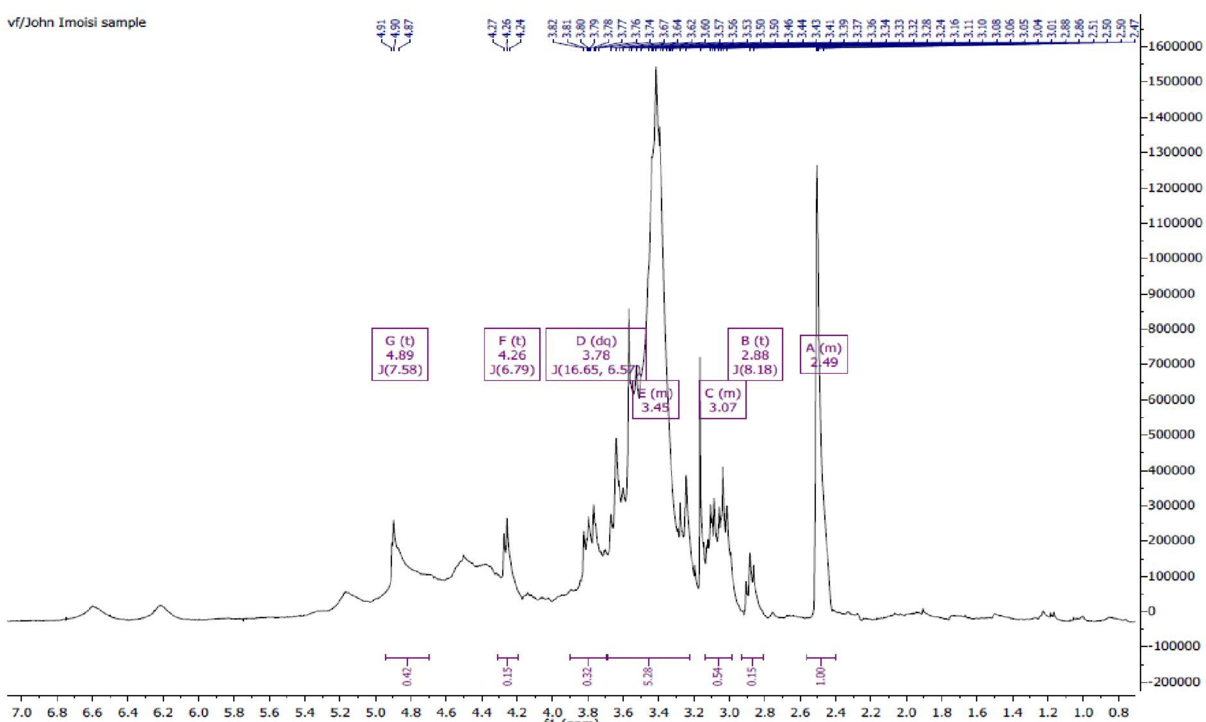

Figure 1: ^{1}H NMR Spectrum of the Sugars in *Vitex doniana* fruit Syrup

The black plum syrup was derivatized with Tri-Sil HTP reagent and analyzed by GC-MS using Shimadzu QP-2010 GC with QP-2010 Mass Selective Detector [MSD, operated in the EI mode (electron energy = 70 eV), scan range of 45-700 m/z, and scan rate of 3.99 scans/sec], and Shimadzu GCMS solution data system. The Gas chromatography column was HP-5 MS fused silica capillary with 5% phenyl-methylpolysiloxane stationary phase, with length of 30 m, internal diameter of 0.25 mm and film thickness of 0.25 µm. The carrier gas was helium with flow rate of 1.61 mL/min. The program used for gas chromatography oven temperature was 60-160 ^{0}C at a rate of 15^{0}C/min, then held at 160 ^{0}C for 2 min, followed by 160-280 ^{0}C at a rate of 10 ^{0}C/min, then held at 280^{0}C for 2 min. The injection port temperature was 250 ^{0}C. While ion source temperature was 200^{0}C; interface temperature was 250 ^{0}C. 1.0 µL of sample was injected using autosampler and in the split mode with ratio of 20:80. Individual constituents were identified using NIST Mass Spectra Library (NIST). The percentage of each sugar reported as raw area percentage based on the total ion current.

3. Results

From figure 1 above, the syrup was seen to contain a very high percentage of sugars.

Typical ^{1}H NMR chemical shifts of carbohydrate ring protons for sugars are 3-6 ppm (4.5-5.5 ppm for anomeric protons). Modern high field NMR instruments used for carbohydrate samples, typically 500 MHz or higher, are able to run a suite of 1D, 2D and 3D experiments to determine a structure of carbohydrate compounds. In the case of simple mono- and oligosaccharide molecules, all proton signals are typically separated from one another (usually at 500 MHz or better NMR instruments) and can be assigned using 1D ^{1}HNMR spectrum only.

GC-MS Results of the Chemical Structures of Sugars Components *Vitex doniana* Fruit Syrup.

Table 1: Sugars and Trimethylsilyl Sugar Derivatives of *Vitex doniana* Fruit Syrup

PEAK	Name of sugar (as the trimethylsilyl derivative)	SUGARS
1.	1, 3, 4, 5, 6-pentakis-O-(trimethylsilyl)-	D-Fructose
2.	3, 4, 5-tris-O-(trimethylsilyl)-pentose	2-Deoxy-ribose
3.	Methyl 2, 3, 5- tris-O-(trimethylsilyl)-	alpha.-DL-Arabinofuranoside
4.	Pentakis-O-(trimethylsilyl)-	2-Keto-d-gluconic acid
5.	Methyl 2, 3, 5, 6-tetrakis-O-(trimethylsilyl)-	Glucofuranoside
6.	1, 2, 3, 4, 6-pentakis-O-trimethylsilyl)-	Glucopyranose
7.	Methyl 2, 3-bis-O-trimethylsilyl)-	beta.-D-Galactopyranoside
8.	1, 2, 3, 5-tetrakis-O-(trimethylsilyl)-	D-Xylofuranose
9.	Methyl 2, 3, 5-tris-O-(trimethylsilyl)-	alpha.-DL-Lyxofuranoside
10.	1, 2, 3, 4, 5-pentakis-O-(trimethylsilyl)-	Ribitol
11.	1, 2, 3, 4, 6-pentakis-O-(trimethylsilyl)-	alpha.-D-Glucopyranose
12.	Tetrakis-O-(trimethylsilyl)-ether	d-(+)-Xylose
13.	1, 2, 3, 4, 6-pentakis-O-(trimethylsilyl)-	alpha.-D-Galactopyranose
14.	2, 3, 4, 5, 6-pentakis-O-(trimethylsilyl)-	D-Glucose

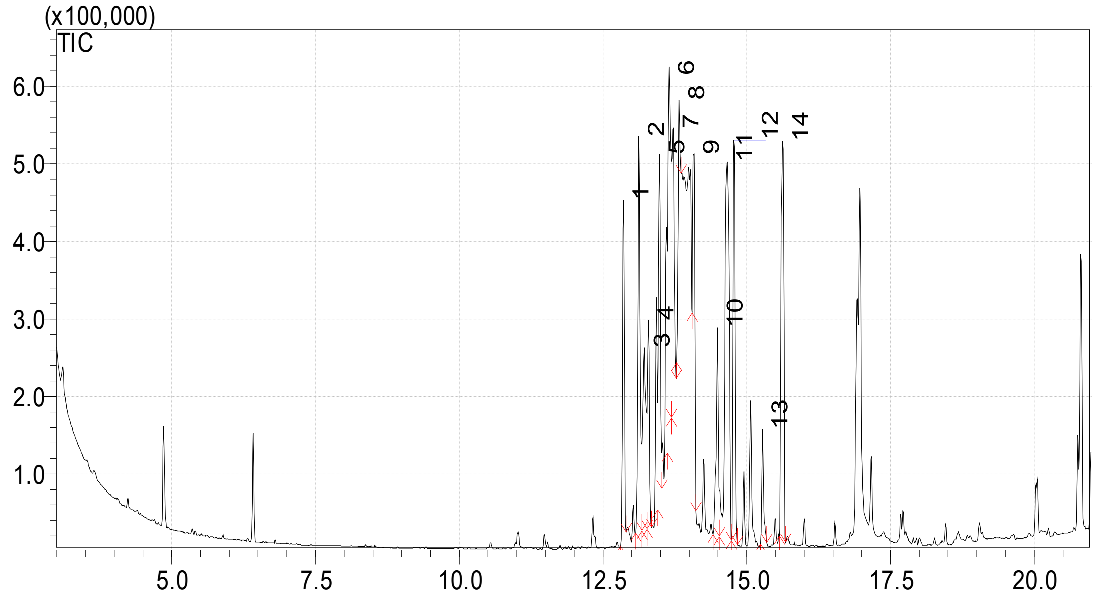

Figure 2: GC-MS Spectrum of the Sugar Components of *Vitex doniana* Fruit Syrup

4. Discussion

Carbohydrates are especially prominent constituents of plants and usually form over one-half of the total plant substance. They serve not only as a source of available energy but also as reserve food and as structural materials. They are one of the main groups of food substances (carbohydrates, proteins, and fats) to be synthesized in the plant from simple organic substances. The empirical composition of carbohydrates may be expressed by the formula $C_nH_{2n}O_n$. With regard to their specific chemical properties, carbohydrates may contain a potential aldehyde, -CHO, or ketone, C=O, group. In general, the substances belonging to this class of compounds may be divided into three broad groups: monosaccharides, oligosaccharides, and polysaccharides. Monosaccharides have five carbon atoms (pentoses) or six carbon atoms (hexoses) and have a sweet taste (Kenji, 2005). The second group of carbohydrates, oligosaccharides, is made up of two or more monosaccharide units linked to one another through a glycosidic bond. These are the disaccharides, trisaccharides, tetrasaccharides, etc., and may or may not have reducing properties. No sharp line of distinction can be drawn between the oligosaccharides and the third group of carbohydrates, the polysaccharides, which represent large aggregates of monosaccharide units (starch, cellulose, pectin, etc.). The main function of carbohydrates upon ingestion by an animal organism is that of a fuel. They are metabolized to other products with the release of carbon dioxide, water, and energy. In addition, certain products of carbohydrate metabolism aid in the breakdown of many food stuffs, acting as catalysts in biological oxidations. Carbohydrates can also be used as a starting material for the biological synthesis of other types of compounds in the body, such as fatty acids and certain amino acids. Regardless of the form in which a carbohydrate happens to be ingested, it must be transformed into a monosaccharide for absorption and metabolism, thus emphasizing the significance of monosaccharides in food stuffs. In spite of the increasing awareness of the specific carbohydrate role as human food, however, many problems in this field are far from being solved owing to chemical and structural complexity of the sugars (Domb *et al*., 1998).

Much work has been devoted to the preparation of derivatives for different families of carbohydrates before their GC-MS analysis. These have been focussed on two main aims: (i) to simplify the derivatization process; (ii) to reduce the number of peaks in the chromatogram. At present, there are a number of derivatization methods with one or two steps which can be satisfactorily carried out in the laboratory (Blau and Halket, 1993). The large number of chromatographic peaks per sugar is still mentioned as a problem and different methods have been developed to reduce this effect. However, in certain cases multiple peaks may be an aid for carbohydrate identification. In the last few years the number of emerging derivatization methods has been limited. These new applications are resolved with optimization and experiment designs in order to find specific conditions for each sample which afford the best yield and reproducibility. In certain cases, the use of two different derivatives provides important structural information, either through MS fragmentation or through retention data (Blau and Halket, 1993). In conclusion, derivatization along with the coupling of GC with MS allows invaluable information about composition and structure of real samples. Silylation is used to enhance GC performance. The silyl reagents have two desirable results: increase analyte volatility and decrease surface adsorption.

Silyl derivatives are formed by displacement of active hydrogen on -OH, -SH, and -NH groups. Compounds containing active hydrogen atoms amendable to silylation are acids, alcohols, thiols, amines, amides, and enolizable ketones and aldehydes (Blau and Halket, 1993). Their silyl derivatives generally are more volatile, less polar, and thermally more stable. The choice of a silyl reagent is based on its reactivity and selectivity toward the compound, the intended application, the stability of the derivative, and the abundance and nature of reaction byproducts. Sterically crowded reagents with bulkier R groups are generally less reactive, but give more stable derivatives after silylation. *"Silyl derivatives generally are more volatile, less polar, and thermally more stable."*

The sugars identified in *Vitex doniana* fruit syrup are fourteen (14) and are presented in table 1. Based on the percentage of each sugar constituents and contribution to the sweetness profile of the syrup as obtained from their raw area percentage based on the total ion current without standardization from table 1. Alpha.-D-Glucopyranose is highest with a value of (16.11%) and therefore, the largest sweetness contributor. The next highest contributor to the sweetness profile is Glucopyranose with a value of (11.19%). While the next are in the following order D-Glucose (11.15%), d-(+)-Xylose (8.95%), 2-Deoxy-pentose (8.92%), Glucofuranoside (6.84%), beta.-D-Galactopyranoside (6.37%), D-Fructose (6.16%), alpha.-DL-Arabinofuranoside (6.14%), alpha.-DL-Lyxofuranoside (4.85%), Ribitol (4.58%), 2-Keto-d-gluconic acid (3.62%, D-Xylofuranose (3.05%). While the least contributor is the alpha.-D-Galactopyranose (2.07%).

Of the 16 possible aldohexose sugars, only one occurs free to any extent. This is D-glucose, D-galactose is occasionally encountered in trace amounts, and because of its distribution in mannans, D-mannose may be occasionally encountered. The L-series of aldohexoses is not known to occur in the free-state (Shallenberger and Moyer, 1961). Glucose is a simple with the molecular formula $C_6H_{12}O_6$. Glucose is the most abundant monosaccharide, a subcategory of carbohydrates. Glucose is mainly made by plants and most algae during photosynthesis from water and carbon dioxide, using energy from sunlight. There it is used to make cellulose in cell walls, which is the most abundant carbohydrate (Domb *et al*., 1998). In energy metabolism, glucose is the most important source of energy in all organisms. Glucose for metabolism is partially stored as a polymer, in plants mainly as starch and amylopectin and in animals as glycogen (Domb *et al*., 1998). Glucose circulates in the blood of animals as blood sugar. The naturally occurring form of glucose is D-glucose, while L-glucose is produced synthetically in comparatively small amounts and is of lesser importance (Kenji, 2005). Glucose is a monosaccharide containing six carbon atoms and an aldehyde group and is therefore referred to as an aldohexose. The glucose molecule can exist in an open-chain (acyclic) and ring (cyclic) form, the latter being the result of an intramolecular reaction between the aldehyde C atom and C-5 hydroxyl group to form an intramolecular hemiacetal (Kenji, 2005). Glucose is a primary source of energy for living organisms. It is naturally occurring and is found in fruits and other parts of plants in its free state. In animals, glucose arises from the breakdown of glycogen in a process known as glycogenolysis. Glucose, as intravenous sugar solution, is on the World Health Organisation's list of essential medicines, needed in a basic health system (WHO, 2013). The name glucose derives through the French and from the Greek which means "sweet" in reference to must, the sweet, first press of grapes in the making of wine. The suffix "–ose" is a chemical classifier, denoting a sugar (Thenard *et al*., 1838).

Fructose, or fruit sugar, is a simple ketonic monosaccharide found in many plants, where it is often bonded to glucose to form the disaccharide sucrose. It is one of the three dietary monosaccharides, along with glucose and galactose, they are absorbed directly into blood during digestion (Dubrunfaut, 1847). Pure, dry fructose is a sweet, white, odorless, crystalline solid, and is the most water-soluble of all the sugars (Fruton, 1972). Fructose is found in honey, tree and vine fruits, flowers, berries, and most root vegetables. Commercially, fructose is derived from sugarcane, sugar beets, and maize. All forms of fructose, including fruits and juices, are commonly added to foods and drinks for palatability and taste enhancement, and for browning of some foods, such as baked goods (William, 1857). About 240,000 tonnes of crystalline fructose are produced annually

(Wolfgang, 2004). Excessive consumption of fructose may contribute to insulin resistance, obesity, elevated LDL cholesterol and triglycerides, leading to metabolic syndrome (Malik and Hu, 2015).

Eight aldopentose sugars are known, four belonging to the D-series, and four enantiomorphic compounds, belonging to the L-series. Only four occur naturally, but not in any great abundance in the free-state. These are D-xylose, D-ribose, and D- and L-arabinose (Shallenberger and Moyer, 1961).

Ribitol, or adonitol, is a crystalline pentose alcohol formed by the reduction of Ribose. It occurs naturally in the plant *Adonis vernalis* as well as in the cell walls of some Gram-positive bacteria, in the form of ribitol phosphate, in teichoic acids.

Xylose is a sugar first isolated from wood, and named for it. Xylose is classified as a monosaccharide of the aldopentose type, which means that it contains aldopentose type, which means that it contains five carbon atoms and includes an aldehyde functional group. It is derived from hemicellulose, one of the main constituents of biomass. Free xylose, in trace amounts, has been reported in onion, strawberries, prunes, apples, pears, grapes, juniper berries, barley malts, brew house worts, maple syrup, asparagus, the white and the yolk of eggs, corn, tomatoes, apricots, bamboo shoots, potatoes, beans, alfalfa, beer, and mangoes. Xylose is not generally fermented by yeasts (and hence appears in wines). Large quantities in the diet cause cataracts in rats. It is also reported to be a minor component of citrus pectic acid and a component of the glycosidic moiety of the alkaloid tomatin found in tomatoes.

2-Deoxy-D-ribose is a good example of a 2-Deoxy-pentose, is a D-ribose in which the hydroxyl group at position C-2 is replaced by hydrogen. It has a role as a human metabolite, a Saccharomyces cerevisiae metabolite and a mouse metabolite. It is derived from D-ribose.

Galactose, (*galacto*- + -*ose*, “milk sugar”), sometimes abbreviated Gal, is a monosaccharide sugar that is about as sweet as glucose, and about 65% as sweet as sucrose (Spillane, 2006). It is a C-4 epimer of glucose (Kalsi, 2007). Galactan is a polymeric form of galactose found in hemicellulose, and forming the core of the galactans, a class of natural polymeric carbohydrates (Zanetti and Capra, 2003).

Pyranose is a collective term for saccharides that have a chemical structure that includes a six-membered ring consisting of five carbon atoms and one oxygen atom. There may be other carbons external to the ring. The name derives from its similarity to the oxygen heterocycle pyran, but the pyranose ring does not have double bonds. A pyranose in which the anomeric OH at C-1 has been converted into an OR group is called a pyranoside. The pyranose ring is formed by the reaction of the hydroxyl group on carbon 5 (C-5) of a sugar with the aldehyde at C-1. This forms an intramolecular hemiacetal. If reaction is between the C-4 hydroxyl and the aldehyde, a furanose is formed instead (Robyt, 1998). The pyranose form is thermodynamically more stable than the furanose form, which can be seen by the distribution of these two cyclic forms in the solution (Ma *et al*., 1998). A furanose is a collective term for carbohydrates that have a chemical structure that includes a five-membered ring system consisting of four carbon atoms and one oxygen atom. The furanose ring is a cyclic hemiacetal of an aldopentose or a cyclic hemiketal of a ketohexose (Reginald *et al.,* 2005). The name derives from its similarity to the oxygen heterocycle furan, but the furanose ring does not have double bonds. The furanose ring will have either alpha or beta configuration, depending on which direction the anomeric hydroxyl group is pointing. In a D-configuration furanose, alpha configuration has the hydroxyl pointing up. It is the opposite in an L-configuration furanose. Typically, the anomeric carbon undergoes mutarotation in solution, and the result is an equilibrium mixture of alpha and beta configurations. Arabinose is an aldopentose – a monosaccharide containing five carbon atoms, and including an aldehyde (CHO) functional group.

For biosynthetic reasons, most saccharides are almost always more abundant in nature as the “D”-form, or structurally analogous to D-glyceraldehyde. However, L-arabinose is in fact more common than D-arabinose in nature and found in nature as a component of biopolymers such as hemicellulose and pectin. Arabinose was originally commercialized as a sweetener, arabinose is an inhibitor of sucrase, the enzyme that breaks down sucrose into glucose and fructose in the small intestine (Krog-Mikkelsen *et al*., 2011). This inhibitory effect has been validated both in rodents and humans (Seri *et al*., 1996). Therefore arabinose could be used in foods to attenuate the peak of glycemic response after the consumption of sucrose. The long-term effects of arabinose consumption on blood glucose paraments and fasting blood glucose levels are unknown. Foods that contain arabinose are usually designed for prediabetic and diabetic patients. These foods are especially popular in Japan and China, where arabinose is legally used as a food additive. Arabinose is a potential prebiotic, because it cannot be absorbed by human intestine and could be utilized by probiotics such as bifidobacteria (Degnan and Macfarlane, 1993). L-Arabinose occurs as a glycosidic component of hemicellulose, gum, and pectin. Arabinose is reported to be a free, but minor sugar component of onions, grapes, strawberries, commercial beer, corn, and alfalfa.

Vitex doniana fruit syrup contained 14 sugars when compared to Date juice (syrup) which contains 3 sugars. *Vitex doniana* fruit syrup was used as a simple natural food resource for the analysis because of its potential usage as an alternative substrate for most toxic non-nutritive sweetners such as Cyclamate, Saccharin, Miraculin, e.t.c. Also, *Vitex doniana* fruit syrup contains more sugars when compared to floral honey which contains only two sugars fructose and glucose averaging 38.2 and 31.3% of the total mass. Hence, qualifying and quantifying its sugar content is a crucial step.

Therefore, gas chromatography mass spectrometry (GC-MS) via derivatization was used as a qualitative and quantitative method to identify and estimate the respective types of sugar in the *Vitex doniana* fruit syrup sample. The results demonstrate that the analysed *Vitex doniana* syrup contains glucose, fructose, galactose, xylose, arabinose and ribose. This analysis was obtained by measuring the retention time of individual standard sugars. In addition, the mass spectra of the *Vitex doniana* fruit syrup samples contained characteristic fragments of glucose, fructose and sucrose.

Thus, GC-MS results determined the appropriate chemical and instrumental assays for quantifying the sugars in *Vitex doniana* fruit syrup. Therefore, they confirmed the identified sugars and provided the sugar contents of the sample (Füzfai *et al*., 2008). Gas chromatography mass spectrometry (GC-MS) is widely used for sugar identification and quantification. Consequently, the reduced sugars must be oximated before analysis to block the prochiral moiety of the reduced sugar molecules. As a result, two new structural isomers, the syn and anti-forms, are obtained (Blau and Halket, 1993). Otherwise, five forms for each reduced sugar will be formed during the GC-MS process. Oximation is not conducted for non-reduced sugars, for example, disaccharides, because they are devoid of prochiral centres (Füzfai *et al*., 2008). To derivatize a functional group, such as (-OH), a silylation reagent, for example, trimethylsilyl (TMS) must be used. The produced derivatives are less polar and more volatile. Silylation must be applied for both reduced and non-reduced sugars (Blau and Halket, 1993).

Conclusion

The study has shown that the edible pulp of black plum (*Vitex doniana*) fruit is a good source of sugars, and that acceptable syrup could be solely produced from the extracted juice. The syrup is an intermediate moisture food with a very high sugar content and fourteen (14) different types of sugars account for its unique taste. The high sugar content of *Vitex doniana* syrup will probably discourage microbial growth and hence deterioration. Proper exploitation of the fruit and utilization of the syrup can help conserve foreign exchange expended on the importation of syrup, and as substitute for other syrups in industrial and food uses. It can be concluded from the characteristics of the *Vitex doniana* fruit syrup, that it is a potential source of food grade sweetener.

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