<u>Chemical Characterization and Physico Chemical Properties of Cashew nut</u> (AnacardiumOccidentale) Oil and Cashew nut Shell Liquid

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Abstract: "Proximate composition and mineral concentration of Cashew nut (Anarcadiumoccidentale) were investigated using standard analytical methods. physicochemical characteristics of cashew nut shell liquid were also determined. The proximate composition (%) was as follows: moisture (7.2), ash (2.8), crude fat (49.1), crude protein (36.3), crude fibre (3.2) and carbohydrate (by difference) (1.4). The mineral composition (mg/100g) of cashew nut showed potassium (27.5 \pm 0.4) to be the highest, calcium (21.5 \pm 0.0), magnesium (19.3 ± 0.1) , sodium (8.2 ± 0.2) and phosphorous (14.0 ± 0.2) . Zinc and iron concentrations were lower. The physicochemical properties of cashew nut oil were as follows: colour (yellow), refractive index (1.458), specific gravity (0.962), acid value (10.7mgKOH/g), saponification value (137mgKOH/g), iodine value (41.3mgiodine/100g) and free fatty acid (5.4mgKOH/g). This is an indication that the oil is non-drying, edible and may not be used for soap making. The CNSL extracted was dark brown in colour. Ash and moisture content (%) were: 1.2 and 3.9 (for IND species), and 1.3 and 6.7 (for AFR species). Specific gravity and refractive index were 0.941 and 1.693 (for IND variety), and 0.924 and 1.686 (for AFR variety). Saponification, acid, free fatty acid (mg KOH/g) and iodine (mg iodine/100g) values were (58.1, 12.1, 6.1, 215 respectively (for IND species) and 47.6, 15.4, 7.8, 235.(for AFR species). The investigation showed that CNSL is a drying oil and it is useful in industries for paints, varnishes and surface coatings."

Keywords; Nutritive value, Iodine, Protein, carbohydrate, Fat.

Abbreviations: CNSL, Cashew nut shell liquid;

Introduction:

The cashew tree (AnarcardiumOccidentale) is a native of Brazil and the Lower Amazons. The cashew has been introduced and is a valuable cash crop in the Americas, the West Indies, Madagascar, India and Malaysia (Frankel,1991). As far back as 1967, Tyman and Morris described the composition of Cashew Nut Shell Liquid (CNSL). The economic importance of this special tree is such that while the tree is native to Central and South America, it is now widely distributed throughout the tropics, particularly in many parts of Africa and Asia. The Cashew

tree will tolerate a wide range of condition including drought and poor soil, but cannot withstand cold frost.

The major producing countries of Cashew are Tanzania, India, Mozambique, Srilanka, Kenya, Madagascar, Thailand, Malaysia, Indonesia, Nigeria, Senegal, Malawi and Angola. World Bank data estimates that 97% of production is from wild trees and only 3% is from established plantations (Rosengarten, 1984). Gibbon et al (1981) reported that many trees are found growing wild and that the plant germinates poorly, those that are cultivated are propagated by seed which are planted at a rate of 2-3 per hole due to poor germination rates.

Cashew nut is a high value edible nut. It yields two "Oils" one of these found, between the seed coat (or pericarp) and the nuts, is called the Cashew Nut Shell Liquid (CNSL). It is not a triglyceride and contains a high proportion of phenolic compound. It is used in industry as a raw material for brake lining compounds, as a water proofing agent, a preservative and in the manufacturing of paints and plastics. It is toxic and corrosive to the skin. Cashew apples are sometimes made locally into fruit drinks, wines and pickles. In some countries they are also Osmo-Sol dried to produce a date-like caramel.

An edible oil can be extracted from cashew nuts but no evidence of it being carried out commercially has been found. The cashew apple is very sour and astringent until fully ripe, when it becomes edible. In contrast to the nut, the apple was neglected until recently, although it is available in far greater tonnage. A number of processes have now been developed for converting the cashew apple into various products such as juice, jam, syrup, chutney and beverage (Winterhalter 1991).

The ability of cashew apples to supply and fortify the nutritional requirement for vitamin C, particularly in Africa was reported by Akinwale (2000). The author carried out a physicochemical analysis of some tropical fruits and compared them with those of cashew apple. Cashew apple juice was found to contain the highest amount of vitamin C (203.5mg/100ml.) of edible portion and when the cashew apple was blended with other tropical fruits it boosted their nutritional quality. The importance of the Cashew Nut Kernel Oil and Cashew Nut Shell Liquid (CNSL) cannot be overemphasized

The fat of nut is completely natural and unprocessed which is best for the body. It is especially rich in Linoleic acid (Omega-3) and is least damaging to heart and arteries. In fact, it constitutes about 47% of the total weight of the nut. Nuts often produce oil half their weight. This could be good news for people who feel weak or debilitated. Cashew has what is called the 'good fat. Cashew has the right combination of fat and the ratio of saturated to monounsaturated and polyunsaturated is 1:2:1 which is ideal for human consumption. The relative abundance of monounsaturated fatty acids in cashew nut is conducive to the promotion of good health and that the relative abundance of fat in cashew nut in no way poses a nutritional risk (Achal 2005). The

advantage of cashew kernel is that it has a rich, delightful taste and is meaty and acceptable as it is.

The Cashew Nut Shell Liquid (CNSL) is a versatile industrial raw material with diverse use in friction linings, paints and varnishes, laminating and epoxy resins, foundry chemicals and as an intermediary of chemicals. The innumerable industrial applications of CNSL are based on the fact that it leads itself to polymerization by various means. Simple phenols from petrochemicals have restrictions hence, the range of products obtained from them are few (Achal 2002, 2005).

Materials and Method Sample Collection:

The cashew samples were collected from the Cashew processing plant. All organic solvents and chemicals used in the analysis were obtained from the chemistry laboratory. The reagents used are of analytical grade (BDH). The cashew samples collected were cracked with manual cashew kernel cutter to separate the nuts from the shells. The nuts were dried at 40°C in the oven for 5 hours. Two hundred gramme of cashew nut and cashew nut shell were ground into small pieces using a mains- operated food grinder (HR 2811 Philip Model). The dried samples were kept in an air tight sample container in a refrigerator (4°C) until ready for analysis.

Analyses of sample:

Analysis of moisture, ash, crude protein and crude fat:

The recommended methods of the Association of Official Analytical Chemists (AOAC, 1984) were employed in determining the levels of moisture, ash, crude protein and crude fat. Moisture content was determined by heating 2.0 g of each sample to a constant weight in a crucible placed in an oven maintained at 105°C for 3.5hr

Ash was determined by the incineration of 1.0- g samples placed in a muffle furnace (LMF4 from Carbolite, Bamford, Sheffield UK) maintained at 550°C for 5 hours. Crude protein (% total nitrogen x 6.25) was determined by Khedjal method (Khedjahl 1883), using 1.0-g samples; crude fat was obtained by exhaustively extracting 5.0g of each sample in a Soxhlet apparatus using petroleum ether (boiling range 40-60°C) as the extractant (Onyeike&Onwuka, 1999). Total carbohydrate was obtained by difference.

Analysis of minerals in cashew nut:

The minerals, lead, iron, copper, zinc, magnesium and calcium were determined by atomic absorption spectrophotometry (Agte et al., 1995). 1.0-g samples in triplicate, were dry ashed in a muffle furnace at 550°C for 5h until a white residue of constant weight was obtained. The minerals were extracted from ash by adding 20.0ml of 2.5% HCl, heated in a steam bath to reduce the volume to about 7.0ml, and this was transferred quantitatively to a 50ml volumetric flask. It was diluted to volume (50 ml) with deionised water, stored in clean polyethylene bottles

and mineral contents determined using an atomic absorption spectrophotometer (Perkin-Elmer, Model 2380, USA). Sodium and Potassium were determined using flame photometry (Chapman & Pratt, 1961). Phosphorous was determined as PO 3- by the vanadium phosphomolybdate (vanadate colorimetry method) in which the phosphorous present as the orthophosphate reacts with a vanadate molybdate reagent to produce a yellow – orange complex, the absorbance of which was measured at 420nm.

Analysis of acid, saponification and iodine value:

The acid and peroxide values were determined using the method of Devine and Williams (1961). The saponification number was determined by the method of Williams (1950) while iodine value was obtained by the method of Strong and Kock (1974). Specific gravity was determined by a universal hydrometer and refractive index at 26°C was determined using Abbe refractometer.

Results and Discussion:

Proximate composition of cashew nut kernel (defatted):

The proximate compositions of the cashew nut kernel (defatted) studied are shown in (Table 1). From the data it was observed that the cashew kernel contained crude fat (49.1%) and protein (36.3%). It also contained 7.2% moisture, ash (2.8%), crude fiber (3.2%) and carbohydrate by difference (1.4%). Some of these values were in agreement with those reported by (Eromosele et al. 1994, Arogba et al. 1999, Achal et al. 2002). The moisture content of cashew nut was 7.2%. This value fell within the range of mean values of moisture of legumes (between 7.0% and 11.0%) reported by Arkroyed and Doughty (1964). Seeds with low moisture content could store for a longer time without spoilage. Ash content of cashew nut in this study was 2.8%. Previous studies showed ash content of kolanut, jackbean and cowpea to be 3.1%, 3.6% and 3.2% respectively (Arogba et al., 1999), and of cashew nut flour 4.4±0.1% (Aremu et al., 2006). An ash content of 1.5 - 2.5% for nuts has been recommended for suitability as animal feeds (Pomeranz and Clifton, 1981) but with the value of ash reported in this study, cashew nut may be unsuitable for animal feeds. This is in agreement with Aremu et al (2006). The values of fat and protein were also comparable to those obtained by Pearson (1976). The crude fat (49.1%) is comparable to the values for varieties of melon oil seeds (47.9 - 51.1%) reported by Ige et al. (1984); Pumpkin seed (49.2% and 47.01%)reported by Asiegbu (1987) and Fagbemi and Oshodi (1991) respectively. The crude fat content was higher than those reported for soybean seed (23.5%; Paul and Southgate, 1980). Aremu et al. (2006) reported 36.7% for crude fat in cashew nut flour; this may be due to differences in the specie of the cashew nut and the environment in which they are grown. Fat promotes the absorption of fat soluble vitamins hence it is very important in diets. This value of fat is an indication that cashew nut is a good oil seed particularly when compared with African yam bean with a fat content of 2.50% (Edem et al 1990). It is therefore a good source of edible oil that can be employed in cooking and food

industries. The high protein and fat content reported in this work were in agreement with the work of Arogba (1999) on cashew (AnacardiumOccidentale). The protein content (36.3%) is higher than previously reported for a number of seeds like sahm seeds (22.5%; Al-Jassir et al. 1995), Papaya seeds endosperm (20.49±0.79%; Passera et al 1981); soybeans, cowpeas, pigeon peas, melon, pumpkin and gourd seeds (23.1- 33.0%; Olaofe et al. 1994). That the protein content of the cashew nut is higher or comparable to previous reports shows that it is nutritiously rich (Achal et al 2002). The protein content of cashew nut analyzed suggests that it can contribute to the daily protein need of 23.6g for adults as recommended by the National Research Council (1974). Protein also plays a part in the organoleptic properties of foods in addition to being a source of amino acid (Okon 1983).

The crude fibre of cashew nut 3.2% compared favorably with the USDA nutrient database for the fiber content of cashew nut by weight percent which ranged from 3.0-3.8%. Aremuet.al (2006) recorded a lower value ($1.2 \pm 0.3\%$) for cashew nut flour. Crude fiber helps in the maintenance of normal peristaltic movement of the intestinal tract hence diets containing low fiber could cause constipation and eventually lead to colon diseases (piles, cancer and appendicitis) (Okon 1983).

The value obtained for carbohydrate (by difference) 1.4% is very low compared to the expected range of mean values for legumes (20 - 26 % of dry weight; Arkroyed and Doughty 1964). This could be due to the high levels of crude fat and crude protein in the studied sample.

Table 1.Proximate composition of cashew kernel (Defatted sample).

Composition	%
Moisture	7.2
Ash	2.8
Oil	49.1
Protein	36.3
Crude fibre	3.2
Carbohydrate (by difference)	1.4

Physicochemical properties of cashew kernel oil:

Table 2 presents the physicochemical properties of cashew nut oil. The oil extracted from the cashew nut is yellowish in color. It had a specific gravity of 0.962 which showed that it is less dense than water and a refractive index of 1.458 which showed that it is not as thick as most drying oils whose refractive indices fell between 1.475 and 1.485 (Duel 1951). The iodine value 41.3mg /100g of cashew nut is in close agreement with the value 44.4 ± 0.1 mg iodine/100g from previous work on cashew nut by Aremu et al (2006) and for Hausa melon seed, $38.50 \pm 0.67\%$ (Oladimeji et al., 2001). Oils are classified into drying, semi drying and non- drying according to

their iodine values. Since the iodine value of cashew kernel oil is lower than 100 it could only be classified as a non drying oil. The low iodine value indicates that the oil has a low content of unsaturated fatty acids which is evident in the acid and free fatty acid values of 10.7mgKOH/g and 5.4mgKOH/g respectively.

The saponification value of the cashew nut oil was (137mgKOH/g). This was lower than the values for some common oils like palm oil (196-205mgKOH/g), groundnut oil (188-96mgKOH/g), corn oil (187-196mgKOH/g) as reported by Cocks and Van Reed (1996), coconut oil (253mgKOH/g) and palm kernel oil (247mgKOH/g) (Pearson 1976). However this saponification value is within the same range of some edible oils reported by Eromosele et al (1994). The low saponification value is an indication that the oil may not be suitable for soap making.

Table 2.Physicochemical characteristics of cashew kernel oil.

Parameter	Concentration
Refractive index	1.458
Specific gravity	0.962
Saponification value (mgKOH/g)	137
Iodine value (mgiodine/100g)	41.3
Acid value (mgKOH/g)	10.7
Free- fatty acid (mgKOH/g)	5.4

Mineral composition of cashew nut:

The mineral content of cashew nut is shown in Table 3.K had the highest concentration $(27.5 \pm 0.4 \text{mg/}100\text{g})$. This is in line with previous work byOlaofe and Sanni (1988). This was followed by Ca $(21.5 \pm 0.0 \text{mg/}100\text{g})$, Mg $(19.3 \pm 0.1 \text{mg/}100\text{g})$ and Na $(8.2 \pm 0.3 \text{mg/}100\text{g})$. Mg has been reported to be involved in maintaining the electrical potential in nerves and activation of some enzyme systems (Ferro et al., 1987). The calcium content is in agreement with Aremu et al (2006). Calcium is responsible for bone formation. Phosphorous had a mean value of $14.0 \pm 0.2 \text{mg/}100\text{g}$. Phosphorous and calcium occur together in the body to maintain body blood. Fe $(0.6 \pm 0.1 \text{mg/}100\text{g})$ and Zn $(0.8 \pm 0.1 \text{mg/}100\text{g})$ were the least abundant of the minerals. This is in close agreement with the observation of Olaofe and Sanni (1988) and Aremu et al (2005).

Table 3. Mineral composition of defatted cashew nut kernel

Mineral	composition (mg/100g)
Magnesium (Mg)	19.3±0.1
Calcium (Ca)	21.5±0.0
Sodium (Na)	8.2±0.2
Zinc(Zn)	0.8 ± 0.1

Iron(Fe)	0.6 ± 0.1
Potassium(K)	27.5±0.4
Phosphorus(P)	14.0±0.2

Values are means \pm standard deviation of triplicate determinations

Physicochemical properties of cashew nut shell oil of Indian and Africancashew nut species:

The physico-chemical characteristics of cashew nut shell liquid from two varieties of cashew nut(Indian and African) shells are presented in Table 4. The oil extracted from the two cashew nut shells are both dark brown in color. The refractive indices of the oils (Indiansss and African species) were comparable (1.693 and 1.686 respectively). This shows that the oils are thicker when compared with most non- drying oils; 1.475 (Duel 1951) and 1.462 (Akintayo et al., 2002) for B. Sapida oil. Their specific gravities are 0.941 and 0.924 (IND and AFR species respectively) which indicate that they are both less dense than water. They are both viscous liquids with viscosity values at 56 centripores and 41 centripores. Moisture content of the two species are 3.9% and 6.7% for IND and AFR respectively. These values are comparable to the values $(5.7 \pm 0.2\%)$ reported for cashew nut flour by Aremu et al (2006) and 5.5% reported by Fagbemi and Oshodi (1981) for fluted pumpkin. The low moisture is an indication that the oils can have longer shelf lives. The ash content is low (1.2%) and (1.3%) for IND and AFR respectively).

As a result of this low ash, the oils can not be useful as animal feeds. The saponification values were low for both samples; 58.1mgKOH/g and 47.6mgKOH/g respectively. The low saponification values suggest that the oils contained high molecular weight fatty acids hence are unsuitable for soap making. The iodine values were high (215mg iodine/100g and 235mg iodine/100g) respectively which fell within the range 220-270mgiodine/100g) specified as drying oils. The high iodine value is an indication that the oil contained high degree of unsaturation therefore, it can be classified as drying oil and could find application in paints, varnishes and surface coatings. The total acidity expressed as the acid value takes into account the contribution of all the constituent fatty acids in the oil (Ekpa and Ekpe, 1995). This is a quality control parameter employed by paint manufacturers to monitor the concentration of acids in resins. The two oils contain appreciable amount of free fatty acid and this accounts for their applications as free fatty acid values were 6.1mgKOH/g and 7.8mgKOH/g for IND and AFR varieties respectively. Oils such as TelfariaOccidentalis (1.10±0.2), Chryosophyllumalbidum (1.81±0.1), Groundnut seeds (0.44 ±0.14) palm kernel (0.57±0.15) have been reported to have low fatty acid values and are edible oils (Dosunmu&Ochu, 1995; Onyeiki et al. 2002). CNSL is therefore not an edible oil.

Table 4. Physicochemical characteristics of cashew nut shell liquid (CNSL).

Parameter	IND specie	AFR specie
Size	Bigger	Smaller
Appearance	Dark brown liquid	Dark brown liquid
Nature	Viscous liquid	viscous liquid
Refractive index	1.693	1.686
Specific gravity	0.941	0.924
Viscosity (30oC) (centripore)	56	41
Moisture (%)	3.9	6.7
Ash (%)	1.2	1.3
Saponification value	58.1	
(mgKOH/g)		47. 6
Iodine value (mg/100g)	215	235
Acid value (mgKOH/g)	12.1	15.4
Free fatty acid (mgKOH/g)	6.1	7.8

The physical appearance and nature of the IND and AFR cashew nut species are presented in Table 5.

Table 5.Physical appearance of the IND and AFR species.

Parameter	IND	AFR
Size	Big	Small
Color of nut	pure white	white/ ivory

Feel /touch Very soft Soft

Taste Crispy Crispy

Flavour richly flavoured Flavoured

Conclusion:

The cashew kernel oil and cashew nut shell liquid are of high economic value in different ways. The result of this study showed that cashew nut is nutritionally richer than some other nuts and seeds. The high protein content in the cashew nut showed its potential to supply adequate amount of amino acids for children and adults. The physicochemical properties of the cashew nut oil indicated that it is non drying, edible (margarine) and may be unsuitable for soap production. The CNSL is highly useful in surface coating, paints, varnishes and resins as shown by the iodine value but cannot be used in soap production due to its low saponification value. The CNSL has got wide range of applicability for making raw materials for automobile brake lining such as liquid resin. It is also used for the manufacture of paint varnishes, epoxy resins and oil soluble resins and surface active agents. Further work could be done on CNSL to exploit the advantages of the resins obtained from it over phenolic resins.

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