



TOWARDS THE STUDY OF MINERAL INDICATION PLANTS: PHYSICO - CHEMICAL CHARACTERISTICS OF SOME VEGETABLE PLANTS (PART I)

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ABSTRACT

This paper presents a data on physical and chemical properties of fourteen vegetable oils derived from thirteen different mineral indicating plant source. These plants include *Solanum nodiflorum* Jacq., *Momordica balsamina*, *Cassia occidentalis* L., *Erythrina senegalensis* DC., *Khaya senegalensis* (Desr.) A. Juss, *Melia azedarach* L., *Arachis ricinus communis* L., *Senanum radiatum*, *Balanite hypogea* L., *Elacis guineansis* Jacq. and *Butyrospermum parkii* (Don). Apart from oil palm (*Elacis guineansis*) they are all seed oils. Seven of the oils are edible, the others are regarded as non-edible but found various uses in Africa. Eight of these oils are well known and are sold freely in Nigeria markets.

INTRODUCTION

The studies include several samples of unsaponifiable fractions of olive husk oil, the mechanism and stability of the oils to oxidation, the pharmacological properties of low-energy biological peroxidation of fat by oil and the polar substances of leather fats and oil. We have collected the information in the various research efforts. The common application of oils and fats are numerous and are well documented (1-4). Whatever use is made of any particular oil or fat depends on its properties; be it physical, chemical or pharmacological. The physico - chemical characteristics of any fat or oil therefore provide individual information on the quality, composition and the probable uses of such oils and fats. In addition, such information will always provide a

positive proof of ore, 'behavior in use' of the oil and fat.

The study was prompted while computing ore-indicating plants especially plants especially the deep - rooted members (5). Deep - rooted members of the association of indicator plants have been found over uranium in ore buried at depth up to 20m (6). Different species of such plants take up different amounts of organic and inorganic materials from the soil. However, this paper is concerned with the physico - chemical properties of fourteen oils derived from thirteen local plants. Eight of these oils are well known and sold freely in the market. All the oils except the red palm oil and the palm kernel oil derived from the fruit and the nut of the palm tree (*Elacis guineansis* Jacq) are derived from seeds.

EXPERIMENTAL

The two oils from palm tree were obtained using the indigenous technology; rendering and pressing respectively. The others were obtained by solvent extraction. The work of Price (7) in conjunction with methods described in the British Standards 684 (8) was used in the estimation of volatile matter. All the remaining parameters were determined using the procedures described in the British Standard 684 (8). The Abbe refractometer was used in the determination of index (9). The method according to Daniels et al and the Ostwald viscometer was used in determination of viscosity (10). Ramat Polytechnic fabricated the apparatus used in the smoke point determination. Physical states, colour and odour of samples were assessed visually.

Extraction:

(a) Solvent Extraction

Crushed seed/nut (200g) was hexane in a Soxhlet extractor for six hours. The oil was recovered by evaporating over a rotary evaporator

and allowed to stand under vacuum at about 30°C overnight. The physical state of the oil including colour and odour were recorded.

(b) Indigenous Extraction

(i) Pressing: The nut/seed (100g) was roasted and crushed. Warm water (10cm³) was added and by continuous pressing, oil separated out. The process of adding warm water and pressing was continued until very little or more oil separated out. This method was used for the extraction of palm kernel oil and the groundnut oil.

(ii) Rendering: The palm fruit (200g) was first boiled and then shred in a wooden mortar to remove the fleshy part and was well macerated. The melt and float on the surface was withdrawn and boiled for five hours.

Pressing and Rendering produced higher amounts of the products use in the analysis.

Determinations

Density of oil:

Dried clean borosilicate density bottle was first calibrated at 25°C by weighing it and then filled with distilled water and stoppered such that the capillary was completely filled with water. The bottle and its content were thermostated at 25°C until no further change in volume occurred. The bottle and stopper were cleaned and reweighed. The whole process was repeated for water at 27°C to obtain (W₁)g. The overall experiment was repeated for each oil and the density of oil at 27°C was obtained using equation:

$$\rho = \frac{W_0 - W_1}{V(T - 25)}$$

α = Coefficient of expansion,

W₀ = weight of water at 25°C

W₁ = weight of water at 27°C

$$D_{27} = W_2/W_1 \times 1/1 + \alpha(T - 25)$$

W₁ = weight of water obtained in the calibration test.

W₂ = weight of oil in test; T = 27°C

Viscosity (η):

This was determined using the Ostwald viscometer at 36°C. The flow time for 20cm³ of oil was measured 6 times. Water was used as reference. Viscosity was derived using equation;

$$\eta_1/\eta_2 = t_1\rho_1/t_2\rho_2$$

Here t₁ and t₂ are time flow for water and oil. η_1 and η_2 viscosity for water and oil while ρ_1 and ρ_2 are density for water and oil respectively [8].

Ash:

The oil (10g) held in an already weighed crucible was heated carefully to ignition point and was allowed to burn spontaneously. After burning was completed, the crucible and content were heated to constant weight in a furnace whose temperature was maintained at 600°C. The experiment was repeated for each test sample and ash percentage was determined using the equation: A₁ = 100 W₂ / W₁; W₁ and W₂ are weights of residue and oil [9].

Acidity:

Warm ethanol (50ml) neutralized with 0.1M sodium hydroxide using phenolphthalein as indicator was added to 4.0g of oil. The mixture was brought to boiling and the hot mixture was further titrated with 0.5M sodium hydroxide solution. The acid value (A) for the various oils was calculated using the equation:

$$A = 2V/W$$

V = volume of alkali required.
W = weight of oil

The method used excludes free fatty acids, soaps mineral matters and readily volatile substances. The phenolphthalein used in this experiment had 0.1% (v/v) solution of methylene blue.

Acid value and Mean Molecular Mass

The oil (2g) was refluxed for one hour with ethanolic potassium hydroxide (25cm³) and the solution was made up to (100cm³) with distilled water. Hydrochloric acid was added until the solution became acidic (pH2). The acidified solution was extracted and washed three times with portions of distilled water (50cm³). The ether solution was evaporating to dryness. Acetone (2cm³) was added, air-dried, and sample was later heated in the oven at 80°C to constant weight (wg). The weighed acid (wg) from above was dissolved in neutral 95% ethanol titrated with 0.2M sodium hydroxide, using phenolphthalein as indicator, until pink colour remained. The acid value (A²) and the molecular mass (M₂) were determined using equation: A_s = 11.22 V/W; V is volume of alkali required, W is the weight of oil. Table 3 shows the overall results.

Specification value and mean molecular mass

Ethanolic potassium hydroxide solution (25cm³) was added to the oil (2g). The mixture was refluxed for one hour. The hot solution was titrated with standard 0.5M hydrochloric acid using phenolphthalein (1cm³) as indicator. A blank potassium hydroxide solution (25cm³) was also determined under the same condition. The saponification value for each oil was calculated using equation: S = 28.05(T₂ - T₁)/W; T₂ = volume of titrant for blank, T₁ = volume of oil in gm, W = weight of oil. The saponification values (S) obtained were used to calculate the mean molecular mass (M) of the oils using equation; M = 56.10 x 3/S. The table 2 shows the result obtained for the individual oils.

Unsaponifiable matters.

The oil (2g) was refluxed with alcoholic hydroxide (25cm³) for one hour. The reaching mixture was diluted with distilled water (50cm³) and extracted four times with diethyl ether (25cm³) while warm. The ether extracts were pooled together and washed first with distilled water (20cm³) followed by 0.5M aqueous potassium hydroxide (20cm³) and then by distilled water (20cm³). This cycle of washing was repeated twice. All the aqueous wash were pooled together and extracted once with diethyl ether (50cm³). The ether extract thus derived was washed repeatedly with distilled water (20cm³) until neutral to phenolphthalein. The ether solution were pooled together and the concentrated to about 3cm³. To this solution, equal volume of acetone (3cm³) was added and solvents evaporated to dryness over a steam bath. The residue obtained was heated to constant weight at an oven temperature of about 80°C. This was dissolved in neutralized 95% ethanol 10cm³ and titrated against 0.1M alcoholic sodium hydroxide using phenolphthalein as indicator. Percentage unsaponifiable matter (U) was calculate from equation: U = 100W₂/W₁; W₁ = weight of oil sample, W₂ = weight of residue [8].

Impurities:

a) Determination of total dirt:

The oil (2g) was dissolved in petroleum ether (40°C), analar grade (100cm³). The solution was allowed to stand at room temperature overnight and was filtered through an already weighed Whatmann filter paper No. 41 which was dried in an oven at 105°C. This was dried to a constant weight at the oven temperature of 105°C and was preserved for the determination of organic dirt. The total dirt (Td) was calculated using equation: $Td = 100 (W_3 \times W_2) / W_1$. W₃ = weight of paper + impurities, W₂ = weight of paper alone, W₁ = weight of oil.

b) Determination of organic dirt:

The residue together with the paper was ashed in the furnace. The percentage organic dirt (Od) was calculated using the equation: $Od = 100 (W_3 \times W_4) / W_1$.

Iodine value:

a) Standardization of the 0.1M Sodium Thiosulphate solution:

Potassium dichromate (0.2g) was dissolved in distilled water (60cm³). To this, 40cm³ of potassium iodide solution (10%) together with concentrated hydrochloric acid (3.5cm³) were added. The reacting mixture was allowed to stand at room temperature for ten minutes and the liberated iodine was titrated with the sodium thiosulphate solution using starch as indicator. The weight of iodine (e) equivalent to 1cm³ of sodium thiosulphate was calculated using the equation: $E = 2.588 W_5 / T_1$; W₅ = weight of potassium dichromate in gm, T₁ = volume of thiosulphate required.

b) Preparation and standardization of Hanu's iodine monobromide solution:

Pure iodine (13.62g) was dissolved with heating in 99.5% glacial acetic acid (825cm³). The quality of the acetic acid was such that sulphuric acid (10cm³) containing a saturated solution of potassium dichromate (0.05cm³) will not turn the acetic acid (10cm³) green. The solution was cooled and enough bromine (Xg) was determined using equation: $Xg = 800 T_6 / T_7$; T₆ = volume of standard sodium thiosulphate equivalent to (10cm³) of iodine, T₇ = volume of standard sodium thiosulphate equivalent to 1cm³ of bromine. The amount of (25cm³) T₆ and T₇ were determined as follows:

First the solution without bromine (25cm³) was titrated with the standard sodium thiosulphate solution to obtain T₆. Then another portion (5cm³) derived from the acid (200cm³) to which bromine (3cm³) were added was titrated with the thiosulphate to obtain T₇.

c) Determination of Hanu's Iodine value:

The oil (0.5g) was dissolved in trichloromethane (10cm³). Hanu's iodine (25cm³), prepared as described above was added and the mixture was allowed to stand for 30minutes with occasional shaking. Potassium iodine (10%, 15cm³) solution together with 0.001M copper

sulphate solution (5cm³) was later added followed by distilled water (100cm³) to wash down any free iodine. The liberated iodine was titrated with the standardized sodium thiosulphate solution until the initial yellow colour disappeared. Two blanks were determined and the mean was used in further calculations. The Hanu's Iodine value (H) was calculate using equation: $H = 100e(T_8 - T_9) / T_7 W_4$; T₈, T₉ are titre values required for sample and mean titre value for the respectively; W₄ = weight of oil used while e = iodine equivalent to thiosulphate solution (1cm³).

Thiocyanogen value:

The oil (2g) was weight into a 500cm³ glass stoppered bottle. Thiocyanogen (0.1N, 25 cm³) solution prepared for this experiment was added. The mixture was allowed to stand for a few hours. The reaction mixture was agitated by rotation. Distilled water (200cm³) was then added. The liberated iodine was titrated with a standardized (0.1N) sodium thiosulphate solution. Two blanks were titrated and the mean value was taken for use in the further calculations of the thiocyanogen value. This was calculated in terms of iodine using equation:

Thiocyanogen value = $100e (T_2 - T_1) / W$; T₁ = volume in cm³ of sodium thiosulphate required for sample; T₂ = volume in cm³ of sodium thiosulphate required for blanks; W = weight of oil use; e = weight in gm of iodine equivalent to 1cm³ of sodium thiosulphate solution.

Peroxide value:

The oil (2g) was dissolved in glacial acetic acid and chloroform mixture (2:1 V/V, 20cm³) in the dark room. After aspirating for a while with carbon dioxide gas, saturated solution of potassium iodide (1cm³) was added and aspiration was allowed to continue for one hour. The content was then transferred into a 500cm³ conical flask; the reaction flask was further rinsed with distilled water and added to the conical flask. The solution was titrated with 0.002M thiosulphate solution using starch indicator. The peroxide value (P) of the 0.002M sodium thiosulphate per gramme of the sample was calculated using the equation: $P = V/W$; V = volume of 0.002M sodium thiosulphate required by sample; W = weight in gramme of sample taken.

Smoke Point

The cup was filled with the oil, making sure that the top of the meniscus was exactly at the filling line with a well directed beam of light across the center of the cup. The sample was heated until it gave a continuous team of smoke. The temperature was recorded as the smoke point. The procedure was repeated for each sample.

The Refractive Index of Oil:

The oil was rendered optically clear and water free by first heating the oil at 55 - 60°C to a constant weight and the filtered using a Whatmann No. 41 filter paper. The refractive index was measured at 589.3nm at a temperature of 20°C

except in the cases of red palm oil and the seed oil of *Butyrospermum parkii*, which were semi-solid at the experimental temperature. For these two,

measurements were taken at 63°C and 61°C respectively and the results were corrected for 20°C.

RESULTS AND DISCUSSION

Table 1 shows the characteristic colour and odour of the oils. Sample numbers 1,2,6,7,8,9,10 and 11 were yellowish; samples 3,4,5 and 13 were brownish while sample 14 was ash. Tables 2 and 3 show the physico-chemical compositions of the vegetable oils, these include the thiocyanogen value, saponification value, mean molecular mass, iodine value, organic dirt, ash content and smoke point in table 2 and in table 3; impurity, acid value, pure mean mass, unsaponifiable matter, refractive index, density, viscosity, volatile matter and peroxide value. *Ricinus communis* had the highest thiocyanogen value of 158g/100g while the least was *Butyrospermum parkii* with 39g/100g. The thiocyanogen value of 114.6g/100g is high among the edible plant oils. Sample 11 had the highest

saponification value while the least is sample 4. Samples 10 and 13 had the highest iodine values of 89.20 and 89.10g/100g respectively while 14 had the lowest of 39.05g/100g. The percentage of organic dirt was generally low.

These results have given us insight into the physico-chemical properties and composition of the oils analysed hence making it easier for industrial values to be attached for each oil depending on its composition and purity.

This work can be a basis for understanding certain characters of the oils. More work is in progress on other oils and also on the properties observed from their uses as ore indicating plants.

Table 2: Chemical Composition of Vegetable oil Samples

Sample No.	Thiocyanogen value (T) g/100g	Saponification value (S)	Mean Mol. Mass	Iodine value g/100g	% Organic dirt (O _d)	% Ash content	Smoke point (°C)
1	125.00	171.10	938.58	80.30	0.05	0.07	148.00
2	73.33	251.05	670.38	46.70	0.00	0.00	0.00
3	126.00	136.04	1237.14	79.20	0.05	0.09	155.00
4	112.12	84.15	2000.00	84.70	0.00	0.00	0.00
5	105.77	169.70	991.95	81.40	0.15	0.85	138.00
6	87.50	152.87	1100.94	88.00	0.00	0.07	151.00
7	158.00	231.41	227.28	86.90	0.00	0.35	152.00
8	72.19	189.34	888.88	77.00	0.00	0.08	174.00
9	98.50	225.80	743.35	80.30	0.55	0.34	142.00
10	114.60	142.65	1188.14	89.20	0.25	0.65	204.00
11	96.30	265.93	568.72	86.90	0.55	0.50	130.00
12	53.90	237.00	710.07	39.60	1.10	0.02	126.00
13	75.60	228.60	736.19	89.10	0.95	1.05	122.00
14	39.00	112.20	500.00	39.05	0.95	0.00	135.00

Table 1: Physical properties of the Vegetable oil Samples

Sample No	Plant Name	Family	Note	Physical State 30°C	Colour	Odour
1	<i>Solanum nodiflorum</i> Jacq.	Solanaceae	M	Liquid	Yellow	Sharp
2	<i>Momordica balsamina</i> L. Syn. <i>M. charanta</i> L.	Cucurbitaceae	M	Semi solid	Light Yellow	Pungent
3	<i>Cassia occidentalis</i> L.	Caesalpinoideae	M	Liquid	Brownish yellow	Pungent
4	<i>Ethrina senegalensis</i> DC.	Papilionoideae	M	Liquid	Brown	Sharp & Pungent
5	<i>Khaya senegalensis</i> (Desr.) A. Juss.	Meliaceae	M	Liquid	Brown	Sharp & Pungent
6	<i>Melia azedarach</i> L.	Meliaceae	M/E	Liquid	Light yellow	Sharp
7	<i>Ricinus communis</i> L.	Euphorbiaceae	M	Liquid	Yellow	Sweet
8	<i>Jatropha curcas</i> L.	Euphorbiaceae	M	Liquid	Light yellow	Sweet
9	<i>Sesamum radiatum</i> Schum. & Thonn.	Pedaliaceae		Liquid	Yellow	Odourless
10	<i>Balanites aegyptiaca</i> (L.) Del.	Zygophyllaceae		Liquid	Yellow	Odourless
11	<i>Arachis hypogea</i> L.	Papilionoideae		Liquid	Yellow	Odourless
12	<i>Elaeis guineans</i> Jacq.	Palmae	E/M	Liquid	Reddish yellow	Odourless
13	<i>Elaeis guineans</i> Jacq.	Palmae				

156

69

Table 3: Chemical Properties of Vegetable oil Samples

Sample No.	% Impurity W/W	Acid Value (A ₂)	Pure Mass	% Unsaturation (U) matter W/W	Refractive Index (25°C)	Density x (ρ) 25°C	Viscosity (η) gcm ⁻¹ sec ⁻¹	% Volatile Matter W/W	Peroxide Value (P) (cm ²)
1	0.05	3.79	1111.10	60.55	1.47	0.96	2.45	0.60	1.85
2	-	-	660.54	11.10	1.47	-	-	-	1.25
3	0.00	12.06	169.85	31.90	1.47	0.91	0.26	0.70	1.10
4	0.00	6.73	216.00	58.65	1.56	-	-	-	0.95
5	0.00	3.93	121.99	61.20	1.45	0.91	0.42	0.90	0.55
6	0.02	12.48	505.60	33.05	1.46	0.90	0.29	0.85	0.40
7	0.00	6.73	-	-	1.47	0.94	2.83	0.50	0.70
8	0.25	5.47	194.00	42.20	1.45	0.89	0.19	0.30	0.45
9	1.85	11.23	-	-	1.46	0.91	0.29	0.20	0.95
10	1.00	8.13	-	-	1.45	0.91	0.29	0.10	0.90
11	0.80	3.93	-	-	1.46	0.90	0.29	0.20	0.30
12	1.25	10.66	-	-	1.46	0.90	0.63	1.60	0.40
13	1.15	6.31	-	-	1.45	0.91	0.23	0.30	0.35
14	0.95	5.89	-	-	1.46	0.91	0.89	-	0.55

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