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Analysis of the Pulp and Pulp Oil of the Tucum (*Astrocaryum vulgare* Mart) Fruit

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ABSTRACT

Pulp composition, lipid classes, fatty acid composition, fatty acid distribution in triglycerides and triglyceride composition of pulp oil from the fruit of the Astrocaryum vulgare *(Mart) palm have been studied. Triglycerides were the major species, accounting for 86·8% of the oil. Palmitic and oleic acids were the dominant fatty acids in whole oil, triglycerides and in the 2-position of triglycerides.*

A. vulgare *pulp oil contained a broad range of triglycerides, the major types of which were* S_2U *(31·4 mol.%) and* SU_2 *(43·1 mol.%).* S_3 *and* U_3 *accounted for 6·9 mol.% and 18·6 mol.%, respectively.*

Proximate analysis of pulp gave: protein, 5·9%; crude fibre, 5·7%; ash, 1·9%; carbohydrate, 19·5%; oil, 22·0% and moisture, 45·0%.

INTRODUCTION

The palm *Astrocaryum vulgare* (Mart), also known as Tucum or Awarra, grows principally in Brazil, the Guianas, Peru, Venezuela and neighbouring areas (Eckey, 1954). The fruits yield pulp (fruit coat), oil and kernel fats. The pulp oil is used locally for soapmaking while the kernels are exported or milled in the country of origin to produce fat for local consumption mainly for edible purposes (Eckey, 1954). Although modest amounts of kernels have featured in international trade (Eckey, 1954; Balick, 1979), only wild palms have been exploited.

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Previous authors have given data on the composition of whole fruit (Eckey, 1954) and analytical data on the pulp and kernel oils. However, such information has been largely inadequate or obscure. Current knowledge about the *Astrocaryum vulgare* palm suggests that its products are superior to similar products from other sources (Eckey, 1954; Teixeira de Carvalho *et al.*, 1973; Balick, 1979). This development calls for a more detailed study of the chemical composition of the products of this palm with a view to enhancing their utilization. The present investigation was undertaken to provide information on the chemical constitution of the pulp and pulp oil of the *A. vulgare* palm fruit as a basis for their utilization.

MATERIALS AND METHODS

Fruits

Astrocaryum vulgare fruits were obtained from the Palmatum of the Nigerian Institute for Oil Palm Research (NIFOR). The pulp was scraped from the shell and put immediately in an oven with air circulation at 100°C until all moisture was removed. Moisture content (%) was calculated from the difference between the wet and dry weights of the pulp.

Extraction of oil

The dried pulp was pounded in a mortar and subjected to Soxhlet extraction with hexane for 6 h (10 g pulp/100 cm^3 hexane); solvent hexane was removed in a rotary evaporator at 40°C and the oil dried to constant weight at 100°C to remove any trace of moisture. The result was calculated as % oil (wet basis) in the original pulp.

Analysis of pulp and pulp oil

Protein, crude fibre and ash contents of pulp were determined by official methods (AOAC, 1970). Saponification value, iodine value and slip point of pulp oil were determined according to official methods (Cocks & Van Rede, 1966).

The lipids of *A. vulgare* pulp oil were separated by preparative thin-layer chromatography on 0·75 mm thick plates (20 × 20 cm coated with silica gel G, Merck). The plates were developed in an 80/20/1 volume mixture of petroleum ether (40–60°C)/diethyl ether/acetic acid (Sanders, 1980). The lipid classes were identified through the use of authentic samples, spraying with specific reagents (Beiss, 1964; Dittmer & Lester, 1974) and by reference

to relative R_f values. The various bands were located under iodine vapour, the iodine evaporated, the bands scraped into small chromatographic columns and eluted exhaustively with diethyl ether. The ether was evaporated completely and the lipids weighed in a Mettler balance.

The composition of fatty acids at the 2-position of triglycerides was determined by lipolysis with pancreatin previously defatted essentially according to the procedure of Tan *et al.* (1981), with modification. A mixture of 40 mg triglycerides; 60 mg enzyme; 2 ml ammonia buffer (pH 9); 0·3 ml, 22% $CaCl_2$; and 0·1 ml of a 10% solution of sodium taurocholate was agitated vigorously for 10 min at 40°C. The reaction was stopped by adding 0·5 ml of 6N HCl. Hydrolysis products were extracted with diethyl ether, the extract washed with distilled water, dried over anhydrous sodium sulfate, concentrated and dissolved in chloroform for thin-layer chromatography. The extracted lipids were chromatographed on thin-layer plates (20 × 20 cm, 0·5 mm thickness, silica gel G, Merck) using a petroleum ether (40–60°C)/diethyl ether, 60:40 v/v mixture containing 1·6% formic acid. The resolved bands were made visible with iodine vapour. The monoglyceride band was scraped off the plate and eluted with petroleum ether/diethyl ether, 1:1 (v/v).

Whole fat, triglycerides, and 2-monoglycerides were converted to methyl esters by H_2SO_4-catalyzed methanolysis (Urakami *et al.*, 1976). The esters were extracted with analytical grade hexane, washed with distilled water, dried over sodium sulfate, concentrated and injected into the gas chromatograph. Fatty acid compositions were determined isothermally at 180°C on a 1·82 m × 2·4 mm glass column packed with 10% polyethylene glycol adipate (PEGA) on 100/120 mesh Diatomite C AW. The carrier gas was nitrogen at a flow rate of 35 ml/min. The instrument was equipped with a flame ionization detector.

Triglyceride composition was calculated according to the 1,3-random 2-random distribution hypothesis (Coleman, 1961).

Carotenoid content was measured spectrophotometrically using 1 cm matched silica cells. Pulp oil was dissolved in cyclohexane (2·5% w/v) and the spectra recorded in the range 350–550 nm. For the quantitative determination of total carotenoids the absorbance was read at 417 nm (Vasconcellos *et al.*, 1980).

RESULTS AND DISCUSSION

The oil content of pulp was 22·0% based on wet weight. Protein, ash, carbohydrate and moisture contents were 5·9%, 1·9%, 19·5% and 45·0%, respectively (Table 1). On a moisture-free basis the pulp contained 40·0% oil.

TABLE 1
Percentage Composition of Pulp and Physico-Chemical Characteristics of Pulp Oil from *Astrocaryum vulgare* Palm Fruits

Pulp	*Mean ± SD*
Crude protein	5·9 ± 0·3
Crude fibre	5·7 ± 0·3
Ash	1·9 ± 0·1
Carbohydrate	19·5 ± 0·6
Oil[a]	22·0 ± 0·9
Moisture	45·0 ± 1·1

[a] 40·0% based on dry weight of pulp.

Physico-chemical characteristics	*Mean ± SD*
Saponification value	188·6 ± 0·2
Iodine value	63·5 ± 0·3
Slip point (°C)	28·0 ± 1·0
Carotenoids (mg/kg)	135·5 ± 0·1

Pulp oil, which was bright red in colour, had the following physical and chemical properties: saponification value, 188·6; iodine value, 63·5; and slip point, 28·0°C (Table 1). These saponification and iodine values are typical for fruit coat fats (Hilditch & Williams, 1964).

On a dry weight basis, oil content of pulp was slightly higher than that given by Eckey (1954), who gave an oil content of 38·0% and saponification value, iodine value and slip point of 220, 46·4 and 27–35°C, respectively. Although slip point of oil in this study fell within the range given by that author (Eckey, 1954), there were appreciable differences in saponification and iodine values. The iodine value indicates that the *A. vulgare* pulp oil examined in the present study was more unsaturated. These differences may be important in breeding *A. vulgare* palms for particular traits. The carotenoid content of *A. vulgare* pulp oil was 135·5 mg/kg.

A. vulgare pulp contained a low amount of protein and would be a poor source of protein isolates, concentrates and amino acids. However, it should be a good source of oil and carbohydrate.

The lipid classes and fatty acid composition of *A. vulgare* pulp oil are shown in Table 2. Included for comparison are the fatty acid compositions of the principal fruit coat oils of commerce; palm oil, olive oil, and beef tallow. As is generally true for fruit coat fats (Hilditch & Williams, 1964), the

TABLE 2
Lipid Classes and Fatty Acid Composition (wt%) of *A. vulgare* Pulp Oil in Comparison with those of some other Oils

Lipid[a] *% by wt (Mean ± SD)*	*TG*	*DG*[b]	*MG*	*FFA*	*ST*	*HC/SE*	*PL*
	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

Fatty acid	A. vulgare *(Mean ± SD)*	*Palm oil*[d]	*Olive Oil*[e]	*Bleachable*[f] *fancy tallow*
12:0	t[c]	0·8	—	—
14:0	t	1·3	—	3·0
14:1	—	—	—	0·5
15:0	—	—	—	0·5
16:0	30·4 ± 0·1	47·2	7–15	25·0
16:1	—	—	—	2·5
17:0	—	—	—	1·5
18:0	2·2 ± 0·4	5·1	—	21·5
18:1	59·9 ± 0·2	36·2	70–85	42·0
18:2	2·9 ± 0·1	9·4	4–12	3·0
18:3	—	—	—	—
20:0	4·6 ± 0·2	—	—	0·5

[a] TG = triglyceride, DG = Diglyceride, MG = monoglyceride, FFA = Free fatty acid, ST = sterol, HC/SE = Hydrocarbon/sterol ester, PL = Polar lipid.
[b] Made up of *sn* 1,-3,- = 0·42% and *sn* 1,-2 (2,-3-) = 8·27%.
[c] Trace: could not be calculated.
[d] Oboh (1984).
[e] Hilditch & Williams (1964).
[f] Ooi and Pee (1985).

principal fatty acids present in *A. vulgare* pulp oil were palmitic (30·4%) and oleic (59·9%); stearic, linoleic and arachidic acids accounted for 2·2%, 2·9% and 4·7%, respectively, of *A. vulgare* pulp oil fatty acids. Short and medium chain fatty acids were present in trace amounts. *A. vulgare* pulp oil, when compared with palm oil and tallow, appears to offer some advantages. It has a lower content of saturated fatty acids and an oleic acid content far higher than those of palm oil and tallow. Its low content of linoleic acid indicates a higher stability towards oxidation than palm oil. Also shown in Table 2 is the lipid class composition of *A. vulgare* oil. The oil was made up mainly of triglycerides, which accounted for 86·8% of the oil.

Diglycerides accounted for 8·69% and monoglycerides free fatty acids, sterols, hydrocarbons and sterol esters, and polar lipids accounted for 0·58%, 1·12%, 1·25%, 1·25% and 0·33%, respectively. Although free fatty

acids and partial glycerides are formed as a result of normal metabolic processes, their amounts in oil-bearing materials can increase greatly as a result of *in situ* hydrolysis brought about by contact of lipolytic enzymes with oil in the presence of moisture, as a result of bruising of fruits, which brings pulp oil into contact with compartmentalized lipase, or by infection by lipolytic organisms. Low amounts of free fatty acid and monoglyceride, but an appreciable amount of diglyceride, have been reported for the mature *Elaeis guineensis* palm fruit coat (Jacobsberg & Jacqmain, 1977). This unexpected level of diglyceride has been linked with the synthesis of oil in the fruit coat (Jacobsberg & Jacqmain, 1977). The low fatty acid, low monoglyceride and the relatively high diglyceride content of *A. vulgare* fruit coat (pulp) oil may have arisen through mechanisms similar to those in operation in the *E. guineensis* palm fruit coat. Diglycerides exert an effect on the crystallinity of oils by impeding the $\alpha \rightarrow \beta'$ and $\beta' \rightarrow \beta$ phase transitions of saturated triglyceride polymorphs, leading to a softening of the consistency of fats (Berger, 1975; Okiy, 1978; Timms, 1985; Hernquist *et al.*, 1981). They thus act as crystal modifiers and serve to improve the fluidity of oils. Free fatty acids are removed from oils during processing and although partial glycerides are retained, the monoglycerides in *A. vulgare* oil should not be in sufficient quantity to have any effect on the crystallinity of the oil. The implication of the relatively high diglyceride content of *A. vulgare* oil is that the diglycerides should increase its fluidity and the yield of liquid fraction if the oil is subjected to fraction to separate liquid from solid components. Also the resulting liquid fraction should have an enhanced fluidity because diglycerides are usually concentrated in the liquid fraction during fractionation (Traitler & Dieffenbacher, 1985; Deffense, 1985). *A. vulgare* oil diglycerides were mainly of the *sn* 1-, 2-(2-, 3-) type which have been found to impede the $\beta' \rightarrow \beta$ polymorphic transformation (Hernquist *et al.*, 1981).

The positional distribution of fatty acids on *A. vulgare* pulp triglycerides is presented in Table 3. As in the whole oil, the medium chain fatty acids lauric and myristic occurred at very low levels in the triglyceride fraction and in the derived 2-monoglycerides (i.e. 2-position of the triglycerides). Generally, the fatty acid composition of *A. vulgare* triglycerides was similar to that of the whole oil and the major fatty acids of the 2-position of triglycerides were palmitic (21·2%) and oleic (68·4%).

A characteristic of oils, which is largely responsible for their exhibiting a particular crystal habit on crystallization, is their palmitic acid content and the distribution of this acid in their triglycerides. Oils with a moderate to high palmitic acid content and a moderate amount of this acid in the 2-position of their glycerides exhibit a β' (beta prime) crystallization (Weidermann, 1978). Examples of β'-oils are palm oil and tallow (Berger *et al.*, 1978). The palmitic acid content of *A. vulgare* pulp oil and the amount of

TABLE 3

Fatty Acid Distribution on *Astrocaryum vulgare* Pulp Triglycerides (Mean ± SD)

Fraction	*Fatty acid composition (mol.%)*							
	12:0	*14:0*	*16:0*	*16:1*	*18:0*	*18:1*	*18:2*	*20:0*
Triglyceride[a]	0·3 ± 0·1	0·6 ± 0·1	36·5 ± 0·1	1·1 ± 0·2	2·2 ± 0·2	54·5 ± 0·1	2·2 ± 0·1	2·6 ± 0·2
2-Monoglyceride[b]	0·8 ± 0·2	1·1 ± 0·2	21·2 ± 0·2	0·8 ± 0·2	1·4 ± 0·3	68·4 ± 0·3	2·2 ± 0·1	4·1 ± 0·3
Proportion 2-position[c]	88·9	61·1	19·4	24·2	21·2	41·8	33·3	52·6
Proportion 1-3-position[d]	11·1	38·9	80·6	75·8	78·8	58·2	66·7	47·4

[a] Isolated on thin-layer chromatography (Sanders, 1980).

[b] From pancreatic lipase cleavage (Tan *et al.*, 1981).

[c] Proportion in 2-position $= \dfrac{\text{mol.\% in 2-monoglyceride}}{\text{mol.\% in triglyceride} \times 3} \times 100$

(Mattson & Volperhein, 1961).

[d] Proportion in 1,3 positions = 100 − proportion in 2-position.

this acid in the 2-position of its glycerides indicate that the oil would exhibit a β' crystallization. Fats exhibiting a stable β' polymorphic form tend to crystallize in small needles. Such fats appear smooth, provide good aeration and have excellent creaming properties (Thomas, 1978; Berger *et al.*, 1978). Because of these characteristics, such fats are used in margarines and shortenings. The fatty acid compositions of the 2-positions of *A. vulgare*, palm oil and tallow triglycerides are shown in Table 4.

Another significance of the level of palmitic acid in the 2-position of *A. vulgare* pulp oil triglycerides is that it indicates that the oil would have a good digestibility. This, coupled with the fact that *A. vulgare* pulp oil should have a good oxidative stability (due to its low content of linoleic acid), should make the oil ideal for utilization in baby food formulations (Traitler & Dieffenbacher, 1985).

Under a strict random distribution the proportion of fatty acids at any position on the triglyceride molecule should be $33\frac{1}{3}$. As in the case of palm oil (Coleman, 1961; Rossel *et al.*, 1985), palmitic and oleic acids displayed a non-random distribution. Oleic acid was acylated preferentially at the 2-position (proportion at the 2-position = 41·8%) and palmitic acid displayed a high specificity for the 1,3-positions (proportion at the 1,3-positions = 80·6%) of *A. vulgare* pulp triglycerides (Table 3). However, while it displays a high specificity for the 2-position in palm oil (Oboh, 1984), linoleic acid was

TABLE 4
Fatty Acid Composition of the 2-Positions of *Astrocaryum vulgare* Pulp Oil Palm Oil and Tallow Triglycerides (mol.%)

Fatty acid	A. vulgare[a] (*Mean* ± *SD*)	*Palm oil*[b]	*Tallow*[c]
12:0	0·8 ± 0·2	—	—
14:0	1·1 ± 0·2	0·8	6·1
14:1	—	—	3·4
16:0	21·2 ± 0·2	16·4	6·7
16:1	0·8 ± 0·2	—	7·5
17:0	—	—	1·0
17:1	—	—	2·2
18:0	1·4 ± 0·3	0·8	6·3
18:1	68·4 ± 0·3	62·7	58·8
18:2	2·2 ± 0·1	19·1	5·9
18:3	—	0·2	1·1
20:0	4·1 ± 0·3	—	—

[a] Present work.
[b] Calculated from wt% mean values given by Rossel *et al.* (1985).
[c] From Luddy *et al.* (1973).

randomly distributed among the three positions of *A. vulgare* triglycerides. The medium chain fatty acids lauric and myristic and the long chain fatty acid arachidic favoured the 2-position while palmitoleic and stearic acids were preferentially esterified at the 1,3-positions.

The triglyceride composition of *A. vulgare* pulp oil was calculated from triglyceride fatty acid composition and the fatty acid composition of their 2-positions according to the 1,3-random 2-random distribution hypothesis of Coleman (1961). The composition of palm oil is included for comparison (Table 5). *A. vulgare* pulp oil had a broad range of triglycerides. The major

TABLE 5
Triglyceride Composition (mol.%) of *Astrocaryum vulgare* Pulp Oil and Palm (*Elaeis guineensis*) Oil

Triglycerides[a]	A. vulgare *oil*	E. guineensis *Palm oil*[c]
SSS[b]	6·9	9·0
SSU	14·3	7·7
SUS	17·1	39·9
USU	7·4	1·7
UUS	35·7	34·3
UUU	18·6	7·4
SSS	6·9	9·0
SSO	13·7	6·3
SSL	0·6	1·4
SOS	16·6	30·6
SLS	0·5	9·3
OSO	6·8	1·1
LSL	—	0·1
OOS	33·0	21·5
LOS	1·5	4·8
OLS	1·1	6·5
LSO	0·6	0·5
LLS	0·1	1·5
OOO	16·5	3·8
OOL	1·5	1·7
LOL"	—	0·2
LLL	—	0·1
OLL	0·1	0·5
OLO	0·5	1·1

[a] Triglyceride composition calculated according to the 1,3-random-2-random distribution hypothesis (Coleman, 1961).
[b] Saturated fatty acids; U: unsaturated acids; O: monounsaturated fatty acids; L: linoleic acid.
[c] Berger *et al.* (1978).

triglyceride types were UUS which accounted for 35·7% (mainly OOS, 33·0%), UUU 18·6% (mainly OOO, 16·5%), SUS 17·1% (mainly SOS, 16·6%) and SSU 14·3 (mainly SSO, 13·7%). The trisaturated triglycerides accounted for 6·9%. Palm oil, also with a broad range of triglycerides, by contrast, is made up mainly of two triglyceride types SUS 39·9% (mainly SOS, 30·6%) and UUS 34·3% (mainly OOS, 21·5%) and a higher trisaturated triglyceride content than *A. vulgare* pulp oil (9·0% for palm oil against 6·9% for *A. vulgare* pulp oil).

Due to its high content of the lower melting triglycerides SU_2 and U_3 (melting point $< 20°C$ which together account for 61·7% of its triglycerides), *A. vulgare* pulp oil should be a good source of low-melting olein for cooking and frying. The presence of a high amount of diglycerides should enhance the fluidity of its liquid fraction. The multiplicity of triglycerides should also make *A. vulgare* oil very useful in such applications (for example margarine fat formulations) where multicomponent systems are required in order to prevent grain formation. However, due to its low content of SOS type triglycerides, *A. vulgare* pulp oil would be a poor source of these important triglycerides which find use as cocoa butter replacers (Gordon *et al.*, 1978).

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