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Sterols, Methyl Sterols, Triterpene Alcohols and Fatty Acids of the Kernel Fat of Different Malagasy Mango *(Mangifera indica)* Varieties

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ABSTRACT

The kernel fat content of 16 different mango varieties collected from the Northwestern part of Madagascar island were examined. The fat content (22-54%) was determined by chloroform/methanol extraction. Investigation by gas liquid chromatography (GLC) revealed 15 fatty acids, mainly palmitic (7-12%), stearic (22-40%), oleic (41-48%) and linoleic (7-17%). Significant correlations were observed among the main fatty acids. Testing for the sterol fraction in 15 mango varieties allowed us to separate and quantitatively analyze 7 sterols by GLC. The main sterols were β-sitosterol (47-76%), stigmasterol (12-23%) and campesterol (7-12%). The stigmasterol/campesterol ratio (1.2:2.3) was lower in mango kernel fat than in cocoa butter. Among the 4-methyl sterol fractions, gramisterol, lophenol, obtusifoliol and citrostadienol were tentatively identified by GLC. Lupeol, cycloartenol, α- and β-amyrins and friedelinol were tentatively identified by GLC in the triterpene alcohols fractions.

INTRODUCTION

Mango *(Mangifera indica)* fruits are widely grown in tropical countries. The world mango production amounted to some 13 million tons in 1978 (1). On Madagascar island, more than 7 native varieties are found and 33 ameliorated varieties have been introduced (2,3). The Malagasy mango production is higher than 200,000 tons a year and in this country, after consumption of the mango fruit, the mango stones remain as waste. Studies of the fat content extracted from these mango kernels have been recently investigated (1,4-7). The composition of mango kernel fat is similar to that of cocoa butter, Borneo tallow, illipe *(Shorea stenoptera)* butter and karite or shea *(Butyrospermum parkii)* butter and could be used in the food industry as a substitute for these fats (8-10). Taking into account its low commercial value, partial substitution for cocoa butter represents an interesting possibility. In a recent study, Baliga and Shitole (8) have fractioned mango fat from acetone at low temperature in 1 or 2 stages to segregate suitable solid fractions having physical properties close to cocoa butter. Although the positional distribution of the fatty acids in the triglycerides of mango kernel fat varieties of African origin has been studied by Van Pee et al. (1,11, 12), we know nothing about the unsaponifiable matter composition of the kernel fat. Some triterpenoids of the leaves (13) and the root bark (14) of *M. indica* have been investigated. This paper presents results on several characteristics of mango kernel fats. Sterols, methyl sterols, triterpene alcohols and fatty acids of kernel fats of 16 mango varieties found in Madagascar were examined.

EXPERIMENTAL

Materials

Sixteen ripe mango fruit varieties were collected from the Mangatsika Station (Mahajanga area) in December 1981. The physical and chemical characteristics of the ripe mango fruits and kernels are given in Table I. The determinations were made from at least 6 randomly selected fruits. Moisture of mango kernels and unsaponifiable matter of kernel fats were determined according to NFT 60-201 and 60-205 Norms (15). The fat content was determined after extracting the powdered kernels in a Soxhlet apparatus with a chloroform/methanol mixture (2:1, v/v) for 8 hr.

For the tentative identification of fatty acid methyl esters, commercial saturated even-numbered methyl esters (Fluka, Buchs, Switzerland) and unsaturated and polyunsaturated methyl esters (Sigma Chemical Co., St. Louis, Missouri) were used as standards. For the tentative identification of sterols, commercial cholesterol and lanosterol (Fluka) were used as standards.

Methyl Ester Preparation

The methyl esters of the 16 mango fats were prepared by transesterification of the oils in methanol containing 1%

TABLE I

Physical and Chemical Characteristics of Malagasy Mango Fruits and Kernels

Sample	Variety	Kernel/fruit ratio[a]	Kernel moisture (%)	Fat kernel content[b] (%)	Unsaponifiable matter of the fat kernel (%)
1	Bory or ronde	0.07	37	29	3.21
2	Hieso or S	0.08	40	31	1.79
3	Rano verte	0.11	54	27	0.96
4	Rano jaune	0.08	54	27	0.96
5	Diego	0.07	33	30	1.42
6	Vato	0.11	45	26	1.03
7	Zanzibar	0.14	42	24	1.08
8	Amelie	0.02	50	36	1.76
9	Beverley	0.04	32	27	1.52
10	Cogshall	0.02	39	38	1.24
11	Divine	0.07	22	32	1.04
12	Kent	0.02	31	24	2.77
13	Ruby	0.05	34	29	0.94
14	Smith	0.03	33	30	1.22
15	Spring field	0.02	33	35	2.60
16	Zill	0.04	36	32	2.38

[a]in weight.
[b]dry weight basis.

(v/v) sulphuric acid for 3 hr. The resulting mixtures were diluted with cold water, chilled in an ice bath and then extracted repeatedly with diethyl ether. Combined extracts were dried over sodium sulphate, evaporated in vacuo and then analyzed by gas liquid chromatography (GLC).

GLC of Fatty Acid Methyl Esters

A Girdel 300 PTF 6 gas chromatograph equipped with a flame ionization detector (FID), a glass injector and a glass capillary column (35 m, 0.35 mm i.d.) coated with Carbowax 20 M (0.15 μm df) were used for the analyses. Temperatures were 190 C for the column, 210 C for the detector and 200 C for the inlet. The flow rate of helium used as carrier gas was 5 ml/min with a split ratio of 5/100. Characterization of individual fatty acid peak was made by comparison with those obtained with known oils (peanut, olive and sunflower) and by comparing their equivalent chain length with previous results (16). All GLC data reported are given as area percentages.

Thin Layer Chromatography (TLC) of the Unsaponifiable Matter

The unsaponifiable matter was dissolved in carbon tetrachloride (5%). This solution (150 μL) was deposited on a 0.25 mm thick, 60 F 254 silica gel plate (Merck, Darmstadt, W. Germany) and developed using chloroform/diethyl ether (9:1, v/v). Cholesterol and lanosterol used as standards were spotted to identify sterols and 4,4-dimethylsterols. The 4-methyl sterol band was between the sterol and 4,4-dimethylsterol bands. The developed plate was sprayed with Rhodamine-B and bands were examined under 366 nm ultraviolet light. The corresponding bands of triterpene alcohols (4,4-dimethylsterols), 4-monomethyl sterols and sterols (4-demethyl sterols) were scraped off and extracted with dichloromethane. Acetylations of components were made using the NFT 60-232 Norm (15). An OV-17 glass capillary column (30 m, 0.36 mm i.d., 0.15 μm df) was used to separate the acetates of the triterpene alcohols, 4-methyl sterols and sterols (temperatures were injector, 270 C; detector, 280 C; column, 260 C). Relative retention times (RRT) were expressed against cholesterol-acetate.

Analysis of Sterols by GLC-Mass Spectrometry (MS)

Identification of sterols was made using authentic commercial specimens of cholesterol, β-sitosterol, campesterol and stigmasterol. Analyses were also performed on a Girdel-Ribermag R 10-10 B GLC-MS (Ribermag, France). The Girdel 30 chromatograph was fitted with a 25 m silica capillary column (0.33 mm i.d.) coated with OV 1701 (0.1 μm df). Operating conditions were: column, 250 C; inlet, 270 C; ion source, 250 C; helium as carrier gas, 0.5 bar; ionizing voltage, 70 eV. A Sidar system was used for the data computation.

RESULTS AND DISCUSSION

The kernels from 16 different mango *(Mangifera indica)* varieties were examined. The kernel content of the mango fruits ranges from 2% to 14%. The kernel moisture contents vary from 22% to 54% and the fats range from 27% to 38% (dry weight basis). The fats extracted from mango kernels were yellow solids at ambient temperature. The unsaponifiable matter ranges from 0.9% to 2.8% (Table I).

The fatty acid composition of the crude fat is reported in Table II. The data given correspond to mean content encountered in the 16 varieties investigated. Maximum and minimum values, standard deviations and data found in the literature are also indicated. Note that Malagasy samples contain less stearic acid and more linoleic acid than mango fats studied previously (1,4-8). The main fatty acids are palmitic (7-12%), stearic (22-40%), oleic (41-48%) and linoleic (7-17%) acids. The results show a high variation, depending on variety, for the main fatty acids. Such a large range in fatty acid composition was also observed for Asiatic mango varieties by Lakshminarayana (17) and for African varieties by Van Pee et al. (1). There was a relationship between these main fatty acids. Plots of stearic, oleic and linoleic acid contents vs palmitic, stearic and oleic acid contents were linear. Regression coefficients of the straight-line and coefficient of correlations r are given in Table III. Significant correlations were obtained for stearic, oleic and linoleic acids vs palmitic, stearic and oleic acids. We have also obtained a good correlation by computing the data given by Van Pee et al. (1) for different mango variety fats of the Republic of Zaire (Table III).

Among the compound families contained in the unsaponifiable matter, we have studied the sterol, the 4-methyl sterol and the triterpene alcohol fractions. Seven sterols were investigated using an OV17 glass capillary column. The RRT were expressed against cholesterol acetate and the composition of sterol fraction of 15 mango

TABLE II

Fatty Acid Composition of Different Mango Kernel Fat Varieties

Fatty acid[a]	Range				Literature references				
	Min.	Mean	Max.	SD[b]	4	5	6	1[c]	8
12 : 0	tr	tr	0.2						
13 : 0	tr	0.3	0.9						
14 : 0	tr	0.2	0.3						
15 : 0	tr	0.1	0.1						
16 : 0	7.1	9.1	11.9	3.4	8.6	8.2	8.4	7.9	8.4
16 : 1 ω 9	0.1	0.2	0.2			0.2			
16 : 1 ω 7	tr	0.1	0.2						
17 : 0	0.2	0.4	1.0	0.2					
18 : 0	22.4	32.3	40.0	4.6	42.2	42.0	42.2	31.6	42.2
18 : 1 ω 9	40.7	43.6	48.4	2.3	45.8	43.0	42.4	49.3	42.4
18 : 2 ω 6	6.9	10.6	16.6	2.9	3.4	3.5	4.7	4.9	4.7
18 : 3 ω 3	0.5	0.8	1.3	0.3				0.5	
19 : 0	tr	0.1	0.2						
20 : 0	1.2	2.0	2.8	0.4				1.2	2.3
20 : 1 ω 9	tr	0.3	0.5	0.1					

[a]Percentage of area.
[b]Standard deviations determined on the 16 varieties investigated.
[c]Calculated values from fatty acid composition of 13 varieties.

TABLE III

Correlation Among the Different Fatty Acids Contained in Mango Kernel Fats[a] (linear regression equations: Y = aX + b)

Fatty acids (% by wt)		Regression coefficient		Correlation coefficient
Y	X	a	b	r
Stearic	Palmitic	−2.07	51.1	>0.98
Oleic	Stearic	−0.366	55.5	>0.99
Linoleic	Oleic	0.558	−13.8	>0.95
Oleic[b]	Stearic[b]	−0.779	74.5	>0.99

[a]Determined for 16 varieties.
[b]Correlation determined from the fatty acid composition of 13 varieties given by Van Pee et al. (1).

TABLE IV

Composition of the Acetylated Sterol Fractions of Mango Kernel Fats

RRT[a]	Compound	Composition (%)[b]			
		Min.	Mean	Max.	SD
1.00	Cholesterol	1.0	3.1	9.3	2.5
1.31	Campesterol	6.8	9.4	11.5	1.6
1.43	Stigmasterol	11.5	16.1	22.7	3.3
1.64	β-Sitosterol	46.7	67.4	76.0	6.8
1.81	Δ5-Avenasterol	0.2	3.4	8.5	2.3
2.05	Δ7-Stigmastenol[c]	0.0	0.3	2.3	0.6
2.15	Δ7-Avenasterol[d]	0.0	0.4	4.2	1.1
	Stigmasterol/campesterol	1.2	1.7	2.3	0.3

[a]RRT (relative retention time) of sterol acetate is expressed against cholesterol acetate on an OV-17 glass capillary column at 260 C.
[b]Area percentage determined from 15 mango varieties.
[c]Not detected in 2 mango varieties.
[d]Detected in only 3 mango varieties.

varieties investigated are given in Table IV. Identification was made using mixtures of known sterols as standards and GLC-MS of the sterol acetates. The configuration at C24 of the sterols possessing an asymetric carbon atom at the 24 position (campesterol, stigmasterol and β-sitosterol) was not determined. The more important were β-sitosterol (46.7-76.0%), stigmasterol (11.5-22.7%) and campesterol (6.8-11.5%). Cholesterol (1.0-9.3%) and Δ5-avenasterol were detected in lower amounts in all samples. Two sterols (Δ7-stigmastenol and Δ7-avenasterol) were not detected in all samples. The sterol composition of mango kernel fat is quite similar to that of cocoa butter (18), although stigmasterol is higher (24.0-28.5%) in cocoa butter (18) than in mango kernel fats as shown in Table IV. The stigmasterol/campesterol ratio has been used to detect adulteration of cocoa butter (19). The ratio is ca. 2.8-3.0 in pure cocoa butter. In the case of mango kernel fat, the stigmasterol/campesterol ratio is lower (1.7 ± 0.3), as indicated in

TABLE V

Composition of the Acetylated 4-Methyl Sterol Fractions of Mango Kernel Fats

RRT[a]	Compound	Composition (%)[b] Min.	Mean	Max.	SD
1.14	Unidentified[c]	0.0	3.4	11.8	4.7
1.33	Lophenol	6.2	13.5	30.8	9.5
1.49	Obtusifoliol	1.3	10.4	17.4	6.1
1.79	Gramisterol	22.1	43.0	66.7	6.6
1.86	Unidentified	0.0	4.23	8.2	3.9
1.90	Unidentified[c]	0.0	3.0	11.5	1.7
2.41	Citrostadienol	0.0	3.6	8.6	3.1
2.52	Unidentified[c]	0.0	4.7	11.9	5.2
2.85	Unidentified	2.2	8.2	21.5	6.4
3.45	Unidentified	0.0	2.7	8.6	3.2

[a]RRT (relative retention time) of 4-methyl sterol acetate is expressed against cholesterol acetate on an OV-17 glass capillary column at 260 C.

[b]Area percentage determined from 6 mango varieties.

[c]Detected in only 3 mango varieties.

TABLE VI

Composition of the Acetylated Triterpene Alcohol Fractions of Mango Kernel Fats

RRT[a]	Compound	Composition (%)[b] Min.	Mean	Max.	SD
1.18	Unidentified	9.8	16.4	36.5	7.5
1.47	Unidentified[c]	0.0	1.8	8.3	2.9
1.65	β-Amyrin, dammaradienol, germanicol	12.8	21.7	25.2	3.8
1.86	Cycloartenol, α-amyrin[d]	0.0	8.8	19.9	7.6
1.92	Lupeol	6.0	14.4	30.7	6.2
2.00	Unidentified	6.8	16.6	32.9	9.1
2.07	24-Methylene cycloartanol,[d] cyclosadol[d]	0.0	10.1	18.6	7.6
2.47	Unidentified	0.0	3.6	12.5	4.2
2.50	Cyclobranol	0.0	4.4	10.0	3.4
2.68	Friedelinol[c]	0.0	1.4	6.4	2.3

[a]RRT (relative retention time) of triterpene alcohol acetates is expressed against cholesterol acetate on an OV-17 glass capillary column at 260 C.

[b]Area percentage determined from 10 mango varieties.

[c]Detected in only 3 mango varieties.

[d]Not detected in 3 mango varieties.

Table IV. This characteristic might be used to distinguish adulteration of cocoa butter by mango kernel fats. The 10 compounds detected by GLC in the 4-methyl sterol fraction of 6 mango kernel fat varieties are given in Table V. Among them, 4 were tentatively identified by comparing their RRT expressed against cholesterol acetate with those given by Itoh et al. (20). Gramisterol (22-67%) was the prominent component of this fraction. Lophenol (6-31%), obtusifoliol (1-17%) and citrostadienol (0-9%) are commonly encountered in seed oils (21,22). These results are quite different from those given by Itoh et al. (21) for cocoa butter because these authors have found 16% obtusifoliol, 12% gramisterol and 29% citrostadienol. Table VI shows the composition of triterpene alcohol (and 4,4-dimethyl sterol) fractions from 10 mango varieties. Tentative identification was based on the comparison of their RRT expressed against cholesterol acetate with those found in the literature (20). However, many triterpene alcohol acetates have the same RRT on an OV17 column, i.e., β-amyrin, dammaradienol and germanicol (1.65); cycloartenol and α-amyrin (1.86); 24-methylene cycloartanol and cyclosadol (2.07). Quantification between each of the overlapped peak components is possible using argentation TLC (23). Lupeol was soon detected in the leaves of *M. indica* (13). Cycloartenol, α- and β-amyrins and friedelinol were also characterized in the root-bark of *M. indica* (14). The range of these components is large between the species (Table VI) and using them for the characterization of mango kernel fats seems difficult.

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Rapeseed Oil Transesterification By Heterogeneous Catalysis

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ABSTRACT

Methyl fatty esters derived from vegetable oils are a promising fuel for direct injection diesel engines. This study's purpose was to identify a heterogeneous catalyst to selectively produce methyl fatty esters from low erucic rapeseed oil. Most experiments were at atmospheric pressure and approximately the corresponding boiling point temperature of the mixture, 60-63 C. However, the catalytic activity of an anion exchange resin was tested at 200 C and 68 atm (1000 psig) and at 91 C and 9.2 atm (135 psig). All samples were analyzed by thin layer chromatography with samples from the elevated temperature and pressure experiments also analyzed by mass spectroscopy. The most promising catalyst examined was CaO•MgO. The activities of the catalysts CaO and ZnO appear to be enhanced with the addition of MgO, therefore the transesterification reaction mechanism may be, in this instance, bifunctional. The anion exchange resin catalyst at 200 C and 68 atm generated substantial amounts of both methyl fatty esters and straight-chain hydrocarbons, even though these reactions did not go to completion. At 91 C and 9.2 atm the cracking also occurred but at a substantially reduced rate, and no transesterification was noted.

INTRODUCTION

Vegetable oils have long been considered a potential diesel fuel, although their use has been hindered by economic and technical difficulties. High viscosity and other physical properties of neat vegetable oils promote incomplete combustion in conventional direct injection diesel engines (1). Recently, considerable research has been conducted on identifying and solving these problems to provide a viable diesel fuel.

Vegetable oil transesterification via alcoholysis into methyl or ethyl esters is one approach to a viable vegetable oil-based diesel fuel. Transesterification significantly reduces vegetable oil viscosity, thereby improving fuel atomization and consequently fuel combustion characteristics (2). Short- and long-term engine testing indicates that fatty ester fuels may perform well in both indirect (3) and direct injection diesel engines (2,4,5,6).

A number of excellent homogeneous catalysts exist for transesterification. Freedman and Pryde (7) and Kusy (8) report 95% fatty ester yields in one hr using sodium hydroxide, sodium methoxide and sodium ethoxide catalysts. Fuls and Hugo (9) also report good methyl ester yields using sulfuric acid and para-toluene sulfonic acid homogeneous catalysts. An interesting variation on the transesterification scheme by homogeneous catalysis is the successful attempt of Nye et al. (10) to produce methyl fatty esters from used frying oil. Homogeneous catalysts cause one primary problem; they must be neutralized and removed from the reaction products. A heterogeneous catalyst would greatly simplify and economize the catalyst removal step. This study's purpose was to identify a heterogeneous catalyst to selectively produce methyl esters from rapeseed oil.

MATERIALS AND METHODS

The quantities of reactants used in all experiments were 0.25 gmoles of crude low erucic rapeseed oil and 1.5 gmoles of methanol. The literature (7,11) demonstrates that the optimal molar ratio of alcohol to triglycerides is 6:1, i.e., twice the stoichiometric. The catalyst concentration suggested is 1 molar per cent (7) or 0.3-0.5% based on the weight of the vegetable oil (8). These concentrations reduce to approximately 0.02 gmoles at the reactant quantities used in this research. The actual catalyst amount used in each batch varied from 0.0055 to 0.82 gmoles.

The allotted reaction time was arbitrarily set at 12 hr for each batch with samples collected at the 6-, 9- and 12-hr marks. Freedman and Pryde (7) report that equilibrium was essentially reached in one hr with sodium hydroxide and sodium methoxide catalysts. The 12-hr reaction time was chosen to accommodate potential catalysts that might have been limited by slow reaction kinetics and to minimize the effects of any potential mass transfer resistance.

The reaction vessel was a 500 ml glass batch reactor with a water-cooled condenser and thermometer. The reactor temperature was generally maintained at 60-63 C, slightly under the mixture's boiling point. With an excellent catalyst, the reaction can proceed at room temperature (11). Groggins (12) states as a rule of thumb that the kinetics of a transesterification reaction approximately double with every 10 C incremental rise in temperature. Although perhaps true in general, Sridharan and Mathai (13) state that alcoholysis with basic catalysts at temperatures above 16 C (60 F) causes various side reactions, particularly saponification, to predominate. The reaction mixture was kept as moisture-free as possible to minimize the hydrolysis of the fatty acids into the fatty acid salts. As little as 0.3% water causes some fatty acid salt formation.

Because transesterification rates are a strong function of temperature, the reaction was attempted at an elevated temperature and pressure with an anion exchange resin catalyst. The purpose of the elevated pressure was to maintain the reactants in the liquid phase at the elevated temperature. The reactants and catalyst were placed in a 500 ml stainless steel container. The air was flushed from the system and replaced with nitrogen to prevent oxidation. The container was placed in a mechanical rocker with heat-