brownish-black. *H. panduriformis* seeds are shaggy, small, and deep brown. The oil contents in the seeds of both the species are rather low (13.4 and 15.4%). The oils can therefore be recovered economically only by solvent extraction. The protein contents were appreciable (23.0 and 22.2%) but fiber contents were high (21.1 and 27.3%), which would have to be reduced for use in feeds.

The responses to the turbidity (3) and picric acid (4) tests on the oils were negative, indicating the absence of hydroxy and epoxy fatty acids. TLC of the oils and the derived methyl esters confirmed their absence. The Halphen test (5) gave a positive response showing the presence of cyclopropene fatty acids. The IR and UV specta showed no *trans* or conjugated unsaturation, respectively. The GLC analysis showed that the predominant acid in both the seed oils was linoleic (60.7 and 74.3%). On the basis of fatty acid composition, *A. pannosum* and *H. panduriformis* seed oils can be classified, respectively, as semidrying and drying (7). As these seeds belong to Malvaceae family, the presence of trace-to-significant quantities (2.2%) of cyclopropene fatty acids is not surprising. *A. pannosum* seed oil contained dihydrosterculic acid (1.3%), a suggested intermediate in the biosynthesis of sterculic and malvalic acids in seedlings of some species of Malvaceae family (8,9). In view of the potential for use of the oils in surface coatings, short crop period and ease of seed collection, cultivation of *A. pannosum* and *H. panduriformis* may be considered.

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Triacylglycerol Structure of an African Peanut Oil

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ABSTRACT

Triacylglycerols were isolated from an African peanut oil, then fractionated by unsaturation into classes, and the triacylglycerol structure was determined on these classes using pancreatic lipase hydrolysis. Fatty acid analysis of monoacylglycerols and, in some cases, of 1 or 2 classes of diacylglycerols, allowed the proportions of 84 isomers to be calculated. The oil had a high oleic acid content (60.3%) and contained nearly 25% of trioleoylglycerol, the major triacylglycerol. The 4 most abundant isomers together represented more than one-half of the total triacylglycerols. In 30 isomers, the 2-position was occupied by linoleic acid, and in 39 isomers, by oleic acid. The very long-chain saturated fatty acids (20:0, 22:0, 24:0) that formed 5.1% of the fatty acid content of the oil, were not found in the 2-position. In most cases, each was associated with 2 molecules of an unsaturated fatty acid. The placement of fatty acids, respectively, at the 1,3-position and the 2-position was relatively close to a 1,3-random-2-random distribution, except for trioleoylglycerol (24.7% instead of 21.7% by the random hypothesis).

INTRODUCTION

The study of the triacylglycerol structure of peanut oil from *Arachis hypogoea*, initiated by Crawford and Hilditch (1) in 1950, was then developed, using modern techniques (2), by several authors (3-6).

Interest for such studies was renewed recently, following observations that peanut oil presented atherogenic effects in several species (7-13). This atherogenicity has been attributed to the triacylglycerol structure of peanut oil (14-16), because treatment of the oil with a base to bring about randomization reduced the atherogenicity to that of corn oil (17).

The mechanism by which randomization of peanut oil leads to a reduced atherogenicity is not evident. However, the specificity of pancreatic lipase and of lipoprotein lipases for the 1- and 3-positions of the triacylglycerol molecules (18,19) can make the fatty acid in the 2-position less available metabolically, and, if this fatty acid is linoleic acid, can make the oil more saturated (15).

For this reason, it was of great interest to determine the precise triacylglyercol structure of peanut oil (20-22), especially the fatty acid esterified in the 2-position. In 1977, Myher et al. (15) determined the proportions of 18 molecular species of triacylglycerols. Recently, a more complete study was published by Manganaro et al. (16) for 3 varieties of peanut oil comprising an African oil. They have proposed the proportions of 37 molecular species of triacylglycerols.

This work proposes another detailed study of the triacylglycerol structure of an African peanut oil, leading to a precise determination of the proportion of 84 triacylglycerols, of which the 3 component fatty acids and the fatty acid in the 2-position are known.

MATERIALS AND METHODS

The materials and methods used have been detailed in 2 previous publications (23,24).

To summarize, the peanut oil studied was a crude oil from Upper Volta (Africa) prepared by pressing the ground seeds. The triacylglycerol fraction was isolated by silicic acid column chromatography (25) and its purity checked

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by thin layer chromatography (TLC) (26).

The triacylglycerols were separated according to their degree of unsaturation by argentation-TLC (3) into 10 classes (23). They were eluted from the silica and an aliquot was analyzed by gas liquid chromatography (GLC) for fatty acid (27) and triacylglycerol composition (28) and for the proportion of the different classes after heptadecanoic acid (17:0) was added as an internal standard.

The triacylglycerols of each class were hydrolyzed by pancreatic lipase (24). The mono- and diacylglycerols formed were isolated by TLC and their fatty acids were analyzed by GLC.

The diacylglycerols were acetylated (29), fractionated into classes according to their degree of unsaturation (3), and the fatty acids of each class were analyzed by GLC after heptadecanoic acid was added.

RESULTS AND DISCUSSION

Fatty Acids in the 2-Position

The peanut oil used in this work was particularly rich (Table I, first line) in oleic acid (60.3%), but relatively poor in linoleic acid (18.0%). These 2 fatty acids, particularly linoleic acid, were preferentially esterified in the 2-position (Table I, second line), whereas the saturated fatty acids, from 20 to 24 carbon atoms, were completely absent from this position.

These data are in close agreement with those published very recently (16) for an African peanut oil.

This fatty acid distribution between the 2- and the 1,3-positions was also found in the different classes, especially when the unsaturated fatty acids were associated with the saturated. In the class 001 (0: saturated, 1: monounsaturated, 2: diunsaturated fatty acids) most of oleic acid was found in the 2-position (33.1% in triacylglycerols, 91.3% in monoacylglycerols) as was the case in the class 011 (97.1% in monoacylglycerols). This was also true for linoleic acid in the triacylglycerol molecules (classes 012, 112, 122), the linoleic acid was preferentially found in the 2-position, even in the class 112 for which 2 molecules of oleic acid were associated with one molecule of linoleic acid.

In Table I, the fatty acid composition of certain classes of diacylglycerols issued from lipolysis of the corresponding triacylglycerols are also reported, because these data will be taken into account for the calculation of the proportions of the different triacylglycerol isomers.

Determination of the Triacylglycerol Isomers

The triacylglycerol isomers are defined as molecules comprising the same 3 fatty acids but differing by the fatty acid esterified in the 2-position.

In a given class, all the possible isomers were listed from the constituent triacylglycerol types, of which the nature and the proportion were previously established (23), by permuting the fatty acid in the 2-positon. For example, the triacylglycerol type 16:0 18:1 18:2 (class 012) may comprise 3 isomers, i.e.: 16:0 - *18:1* - 18:2; 16:0 - *18:2* - 18:1; or 18:1 - *16:0* - 18:2, in which the 2-position is respectively occupied by 18:1, 18:2 and 16:0.

TABLE I

Fatty Acid Composition (mol %) of Peanut Oil Triacylglycerols and of Monoacylglycerols and Diacylglycerols Issued from Lipolysis

		16:0	18:0	20:0	22:0	24:0	16:1	18:1	20:1	22:1	18:2	18:3
Total TG[a]	TG	10.5	3.5	1.5	3.0	1.6	0.3	60.3	1.3	tr	18.0	tr
	MG	1.5	0.1	–	–	–	0.3	66.2	–	–	31.9	tr
Class 001[b] (5.8%)	TG	36.2	13.2	4.9	8.0	4.4	0.2	33.1	–	–	–	–
	MG	6.9	1.0	–	–	–	0.8	91.3	–	–	–	–
	DG 00[b]	66.8	17.4	4.4	7.7	3.7	–	–	–	–	–	–
	DG 01	27.5	10.4	3.7	5.6	3.2	0.3	49.2	–	–	–	–
Class 001 (22.9%)	TG	18.0	7.2	2.3	4.0	2.3	0.2	65.1	0.8	0.1	–	–
	MG	2.4	0.4	–	–	–	0.1	97.1	–	–	–	–
	DG 01	24.4	9.9	4.6	7.0	3.7	0.3	49.9	0.2	–	–	–
	DG 11	–	–	–	–	–	0.4	97.3	2.2	tr	–	–
Class 002 (2.9%)	TG	36.3	10.4	3.6	7.0	3.2	0.5	8.8	–	–	30.2	–
	MG	9.2	2.6	–	–	–	–	–	–	–	88.2	–
	DG 02	32.0	9.8	3.5	5.6	3.3	–	–	–	–	45.9	–
Class 111 (26.3%)	TG	–	–	–	–	–	0.3	97.8	1.9	–	–	–
	MG	–	–	–	–	–	0.2	99.8	–	–	–	–
	DG total (11)	–	–	–	–	–	0.2	98.4	1.4	–	–	–
Class 012 (14.1%)	TG	17.3	5.7	2.6	4.1	2.3	0.4	33.0	0.7	0.2	33.7	–
	MG	1.7	0.4	–	–	–	0.2	27.0	–	–	70.7	–
	DG 01	24.6	8.8	4.9	8.3	3.9	0.4	48.9	0.2	–	–	–
	DG 02	29.4	9.0	3.3	5.6	3.1	–	–	–	–	49.6	–
Class 112 (18.4%)	TG	0.6	0.1	–	–	–	0.3	64.0	1.9	–	33.1	–
	MG	–	–	–	–	–	0.4	43.5	–	–	56.1	–
	DG 11	–	–	–	–	–	0.8	97.1	2.1	–	–	–
	DG 12	–	–	–	–	–	0.4	48.5	1.3	–	49.8	–
Class 022 (3.0%)	TG	15.2	4.0	2.3	6.0	3.5	0.2	2.4	–	–	66.4	–
	MG	1.5	0.5	–	–	–	–	–	–	–	98.0	–
	DG 02	21.7	7.5	4.9	12.1	4.2	–	–	–	–	49.6	–
	DG 22	–	–	–	–	–	–	–	–	–	100.0	–
Class 122 (5.7%)	TG	1.6	0.2	–	–	–	0.2	30.2	1.1	–	66.7	–
	MG	–	–	–	–	–	0.1	11.5	–	–	88.4	–
	DG 12	–	–	–	–	–	0.6	48.2	1.7	–	49.5	–
	DG 22	–	–	–	–	–	–	–	–	–	100.0	–
Class 222[c] (0.8%)	TG	2.5	0.6	–	–	–	0.4	9.5	–	–	84.7	2.3
	MG	1.5	0.4	–	–	–	0.3	9.3	–	–	85.6	2.9

[a]TG, DG, MG: tri-, di- and monoacylglycerols.

[b]TG or DG of the same unsaturation (0: saturated, 1: mono- and 2: diunsaturated fatty acids). The percentage of each class of TG (23) is reported in parentheses.

[c]TG 222 represented the major part of this fraction but not the total.

The isomers for which the fatty acid in the 2-position was not found in the monoacylglycerols issued from lipolysis were dropped out.

For each class of triacylglycerols, a certain number of isomers was found for which the proportion can be calculated from the only fatty acid composition of the monoacylglycerols (classes 011, 111, 022 and 122) or from the monoacylglycerols plus one class of diacylglycerols (012 and 112), or plus 2 classes of diacylglycerols (001, 011 and 002). Two examples of increasing difficulty will be given next.

Class 122. In this class (Table II), 3 triacylglycerol types (23) exist, the second of which contains one molecule of oleic acid and 2 of linoleic acid, and is in very high proportion (95.9%). To each type correspond 2 possible isomers, except for the third one in which eicosenoic acid (20:1) was not found in the monoacylglycerols.

The proportion of the 5 isomers can be easily determined from the fatty acid composition of the monoacylglycerols. Only one isomer exists which has palmitoleic acid (16:1) in the 2-position and, thus, its proportion is the one of this acid in the monoacylglycerols, i.e., 0.1%. The second isomer of this triacylglycerol type, for which the proportion in the class was 0.6%, thus represents 0.5%. The same argument can be followed for the next 2 isomers: 11.5% of the second (as much as oleic acid in the monoacylglycerols); the rest, that is: 95.9 - 11.5 = 84.4%, represents the proportion of the first. The third triacylglycerol type is composed of only one isomer for which the proportion is that of the type, i.e., 3.5%.

It is also possible to calculate this composition in isomers starting from the fatty acid composition of the diacylglycerols 12, according to the method described later. The values so found for the main 2 isomers, respectively, 83.7 and 11.6%, were very close to those just calculated, indicating that the data from the diacylglycerol classes can be used for calculating the composition in isomers as will be done in the next example.

Class 112. This class contains (Table III) 3 triacylglycerol types (23), of which the second represents the major part (93.5%). As eicosenoic acid was not found in the monoacylglycerols, only 7 isomers can be present. Their percentages in the class are a, b, c, d, e, f, g. In this case, calculation of these 7 values from the only fatty acid composition of monoacylglycerols is impossible even when the first 3 isomers (0.9%) were discarded. The fatty acid composition of one class of diacylglycerols has to be taken into account —the class 11, e.g.

We can write a first series of equations from the fatty acid composition of the monoacylglycerols (Table IV), which expresses that the summed percentage of the isomers comprising a given fatty acid (16:1 or 18:1 or 18:2) in the 2-position is equal to the percentage of this fatty acid found in the monoacylglycerols. As only one isomer has palmitoleic acid in the internal position, its percentage is 0.4% (that of the acid in the monoacylglycerols). But this is not true for oleic and linoleic acids, which are each found in the 2-position in 3 isomers.

A second series of equations can be derived from the fatty acid composition of the diacylglycerols 11. It is first necessary to determine the proportion the class should have if hydrolysis were not preferential, because several authors (30-32) have shown that unsaturated fatty acids were hydrolyzed from the 1,3-positions more rapidly than the saturated ones. In the triacylglycerols 112, because no saturated fatty acids were present, the experimentally determined fatty acid composition of the total diacylglycerols was very close to the one calculated when assuming a nonspecific lipolysis (Table V). This also shows that linoleic acid was not hydrolyzed more rapidly than oleic acid in the external positions.

Nevertheless, the theoretical proportion of the class 11 diacylglycerols can be calculated from the fatty acid composition of the monoacylglycerols in the following manner

TABLE II

Determination of the Composition (mol %) in Isomers[a] of the Class 122 (5.7%) Triacylglycerols from Peanut Oil

TG types[b]			Mol %	Isomers[a]	Mol %	MG-FA[c]	Mol %	Solutions[d]
16:1	18:2	18:2	0.6	16:1 - 18:2 - 18:2	a			a = 0.5
				18:2 - 16:1 - 18:2	b	16:1	0.1	b = 0.1
18:1	18:2	18:2	95.9	18:1 - 18:2 - 18:2	c			c = 84.4
				18:2 - 18:1 - 18:2	d	18:1	11.5	d = 11.5
20:1	18:2	18:2	3.5	20:1 - 18:2 - 18:2	e			e = 3.5

[a]The 3 component fatty acids and the fatty acid in the 2-position are known.

[b]The 3 component fatty acids are known but not their positioning in the molecules. Their composition was previously determined (23).

[c]Monoacylglycerol fatty acids (18:2, 88.4%).

[d]See text.

TABLE III

Determination of the Composition (mol %) in Isomers[a] of the Class 112 (18.4%) Triacylglycerols from Peanut Oil

TG types[b]			Mol %	Isomers[a]	Mol %	Solutions[c]
				16:1 - 18:1 - 18:2	a	0.3
16:1	18:1	18:2	0.9	16:1 - 18:2 - 18:1	b	0.2
				18:1 - 16:1 - 18:2	c	0.4
				18:1 - 18:1 - 18:2	d	41.5
18:1	18:1	18:2	93.5	18:1 - 18:2 - 18:1	e	52.0
				20:1 - 18:1 - 18:2	f	1.8
18:1	20:1	18:2	5.6	20:1 - 18:2 - 18:1	g	3.8

[a-c]See footnotes to Table II.

TABLE IV

Equations Derived from the Fatty Acid Composition of the Monoacylglycerols Formed during Lipolysis of the Class 112 Triacylglycerols from Peanut Oil

Monoacylglycerols		
Fatty acids	Mol %	Equations[a]
16:1	0.4	c = 0.4
18:1	43.5	a + d + f = 43.5
18:2	56.1	b + e + g = 56.1

[a]These equations express that the summed percentages of the isomers comprising each fatty acid in the 2-position (see Table III) was equal to the percentage of this fatty acid in monoacylglycerols.

(Table VI). The isomers 1-1-2 (the fatty acid in the 2-position is monounsaturated) are the only triacylglycerols to give monoacylglycerols composed of monounsaturated fatty acids. These monoacylglycerols accounted for 43.9%. Assuming a nonpreferential hydrolysis, the 2 classes of diacylglycerols 11 and 12 will be formed in the same proportion, i.e., 21.95%. The same is true for the isomers 1-2-1, so that the theoretical percentage of the class 11 is 22.0 and that of the class 12 is 78.0. The percentages experimentally determined were, respectively, 23.0 and 77.0, and thus very close to the theoretical ones. This confirms the nonspecificity of the enzymic hydrolysis for these 112 triacylglycerols. The same is true for classes 001 and 122. But some differences were observed in classes 011, 012 and especially in class 022. Despite this non-specific hydrolysis, which originated a nonrepresentative proportion of the diacylglycerol classes, the component fatty acids of these classes were representative, as was previously shown (24); only these will be considered in the equations.

Equations were derived as follows. Let us consider oleic acid in the diacylglycerols 11. Out of the 7 possible isomers of the class 112 triacylglycerols (Table III), those which generated a diacylglycerol 11 containing oleic acid after hydrolysis of one external fatty acid were summed. They were the isomers a, c, d, f (Table III). Assuming a nonspecific hydrolysis, these 4 isomers will give (a + c + d + f) mol of diacylglycerols, of which only one-half, i.e., 1/2 (a + c + d + f), will be diacylglycerols 11; the other half would be diacylglycerols 12. Three (a, c, f) of these diacylglycerol molecules 11 contain one molecule of oleic acid; the other (d) contains 2 molecules. The number of molecules of oleic acid will thus be: 1/2 (a + c + 2d + f).

Assuming a nonspecific hydrolysis, the diacylglycerols 11 will represent 22.0% (Table VI). These 22 molecules of diacylglycerols comprise 22 × 2 = 44 molecules of fatty acids, with 97.1% (Table V) of oleic acid, i.e., 42.7 molecules. Therefore:

$$1/2\ (a + c + 2d + f) = 42.7,$$
$$\text{or, } a + c + 2d + f = 85.4,$$

which is the second equation reported in Table V. The other 2 equations were similarly derived from palmitoleic and eicosenoic acids, respectively; the second directly represents the percentage (1.8%) of the seventh isomer.

A third series of equations was easily derived from the triacylglycerol types because the sum of the percentages of

TABLE V

Fatty Acid Composition (mol %) of the Diacylglycerols Formed during Lipolysis of the 112 Triacylglycerols and Equations Derived from the Fatty Acid Composition of the 11 Diacylglycerols

	Diacylglycerols				
	Total				
Fatty acids	Experimental	Calcd[a]	Class 12	Class 11	Equations[b]
16:1	0.2	0.3	0.4	0.8	a + c = 0.7
18:1	59.5	59.2	48.5	97.1	a + c + 2d + f = 85.4
20:1	1.4	1.4	1.3	2.1	f = 1.8
18:2	38.8	39.1	49.8		

[a]Fatty acid composition of total diacylglycerols calculated from the fatty acid composition of monoacylglycerols and that of original triacylglycerols (32).
[b]See text.

TABLE VI

Calculation of the Amount of the 2 Classes of Diacylglycerols Formed during Lipolysis of the 112 Triacylglycerols, from the Composition of Monoacylglycerols, Assuming a Nonspecific Hydrolysis

Monoacylglycerols				Diacylglycerols			
Fatty acids	Mol %[a]		Isomers[b]	Formed[c]	Mol %	Classes	Mol %
16:1	0.4	43.9	1-1-2	11	21.95	11	22.0
18:1	43.5			12	21.95	12	78.0
18:2	56.1		1-2-1	12	56.1		

[a]See Table I, the 112 triacylglycerols.
[b]Only 2 isomers can exist, the first containing a monounsaturated fatty acid (1) in the 2-position, the second a diunsaturated fatty acid (2).
[c]After a total nonpreferential lipolysis, the first isomer will give the same amount of the 2 diacylglycerols 11 and 12, i.e., 1/2 × 43.9 = 21.95 (ca. 22.0%). The second isomer will give only one type of diacylglycerol 12 in the same amount (56.1%), which will add to the same diacylglycerol 12 (21.95%) issued from the first isomer. This will give ca. 78.0% total.

the component isomers was equal to the percentage of the corresponding triacylglycerol type in the class.

Starting from these 3 series of equations, calculation of the percentages (a, b, c, d, e, f, g) of the 7 triacylglycerol isomers was easily achieved. The values thus obtained are shown in the last column of Table III.

Instead of the diacylglycerols 11, those of the class 12 (fatty acid composition in Table V) could also be used. The figures so calculated for the major 2 isomers (respectively, 41.9 and 51.6%) were very close to those reported in Table III (41.5 and 52.0%).

For the other classes (001, 011, 002) it was necessary to take into account 2 classes of diacylglycerols at the same time. Only one class could be used if slight approximations were made for isomers present in very low amounts. These approximations do not, in fact, introduce a higher error than do the analyses.

Overall results. Using the above calculation methods, the percentages of 84 isomers (Table VII) were determined in the peanut oil analyzed. Only 17 isomers were present in amounts of at least 1%. The first 3 together represented 43.5% of the total and the first 4 more than 50%. The major triacylglycerol was trioleoylglycerol, accounting for ca. 25% of the oil.

Next, 14 isomers from 0.5 to 1%, 25 from 0.1 to 0.5% and at least 28 in amount lower than 0.1% were found. The isomers that represented less than 0.01% were not considered.

In 69 isomers, especially in the first 42, the fatty acid esterified in the 2-position was found to be unsaturated, either linoleic acid (18.0% in the oil) in 30 isomers, or oleic acid (60.3% in the oil) in 39 isomers. However 15 triacylglycerols had a saturated fatty acid in central position, but the major one accounted only for 0.5%. Palmitic acid was present in 11 isomers, stearic acid in only 4 and the very long-chain fatty acids (20:0, 22:0, 24:0) were never found in internal position.

In the triacylglycerols with one very long-chain saturated fatty acid, either 2 molecules of oleic acid, one of linoleic (in 2-position) and one oleic acid, or 2 molecules of linoleic acid were combined. In trace amounts, 2 very long-chain fatty acids were present together in external positions, with an unsaturated fatty acid, mainly linoleic acid, in the 2-position.

These data can be compared to those published by Manganaro et al. (16), after adding, in most cases, the proportions of the 2 isomers they have determined, which correspond to only one isomer in our work. In spite of very similar fatty acid compositions of the 2 oils, certain triacylglycerols have proportions slightly different in each work. We have found 24.7% of trioleoylglycerol, as compared to 21.9% by Manganaro et al., for the same proportion of oleic acid in the 2 oils (60.3 and 60.4%, respectively). We have also found 7.6% of the isomer 18:1-18:1-18:2 instead of 11.0% by these authors, and 11.2% of the isomer 16:0-18:1-18:1 instead of 9.9%. These last 2 differences can this time be explained by a lower proportion of linoleic acid in the oil we analyzed and a higher proportion of palmitic acid.

In Table VII, the percentages calculated according to a 1,3-random-2-random distribution (34,35) are also reported. This hypothesis assumes 2 separate fatty acid pools, one for the 1- and 3-positions, the other for the 2-position. It can be seen that, for the main triacylglycerols, these

TABLE VII

Component Isomers (mol %) of Triacylglycerols of Peanut Oil

Isomers[a]	Mol %		Isomers	Mol %		Isomers	Mol %	
	Experimental	Random[b]		Experimental	Random		Experimental	Random
Percentage > 1						0.1 > Percentage > 0.01		
18:1-18:1-18:1	24.7	21.7	16:0-18:1-20:0	0.56	0.45	16:0-18:1-18:1	0.09	0.04
16:0-18:1-18:1	11.2	11.3	16:0-18:1-24:0	0.53	0.47	22:0-16:0-18:1	0.09	0.08
18:1-18:2-18:1	9.5	10.5	18:1-16:0-18:1	0.53	0.48	18:1-16:1-18:2	0.09	0.03
18:1-18:1-18:2	7.6	8.4	0.5 > Percentage > 0.1			20:0-18:1-22:0	0.07	0.14
16:0-18:2-18:1	5.2	5.5				16:0-18:0-18:2	0.07	tr
18:1-18:2-18:2	4.8	4.1	16:0-18:2-22:0	0.45	0.43	16:0-18:0-18:1	0.06	0.02
18:0-18:1-18:1	4.7	4.0	20:0-18:1-18:2	0.43	0.34	18:0-18:2-22:0	0.05	0.15
22:0-18:1-18:1	2.5	3.4	18:0-18:2-18:2	0.37	0.37	18:1-16:1-18:1	0.05	0.08
18:0-18:2-18:1	1.8	1.9	24:0-18:1-18:2	0.36	0.35	18:1-18:0-18:2	0.05	0.02
20:0-18:1-18:1	1.7	1.8	16:0-18:1-20:1	0.34	0.40	22:0-18:1-20:1	0.05	0.12
16:0-18:1-18:2	1.7	2.2	24:0-18:2-18:2	0.34	0.17	18:0-16:0-18:1	0.05	0.09
20:1-18:1-18:1	1.5	1.5	20:1-18:1-18:2	0.33	0.29	18:2-16:0-18:2	0.05	0.02
16:0-18:2-18:2	1.4	1.1	16:0-18:2-20:1	0.30	0.19	24:0-16:0-18:1	0.04	0.04
24:0-18:1-18:1	1.4	1.8	16:0-18:2-20:0	0.29	0.22	16:1-18:1-18:2	0.04	0.04
16:0-18:1-16:0	1.2	1.5	18:0-18:1-22:0	0.28	0.31	16:1-18:2-18:1	0.04	0.10
16:0-18:1-18:0	1.1	1.0	16:0-18:2-24:0	0.28	0.23	16:0-16:1-16:0	0.03	0.01
22:0-18:2-18:1	1.0	1.6	18:1-16:0-18:2	0.24	0.18	20:0-16:0-18:1	0.03	0.04
1 > Percentage > 0.5			18:0-18:1-18:0	0.24	0.18	16:0-16:1-18:2	0.03	tr
			20:0-18:2-18:2	0.23	0.16	16:1-18:2-18:2	0.03	0.02
16:0-18:1-22:0	0.92	0.89	20:1-18:2-18:2	0.20	0.14	16:0-16:1-18:1	0.02	0.04
18:2-18:2-18:2	0.73	0.39	16:0-16:0-18:1	0.19	0.25	20:0-16:0-18:2	0.02	0.01
20:0-18:2-18:1	0.72	0.84	18:0-18:1-20:0	0.18	0.16	18:0-18:2-24:0	0.02	0.08
16:0-18:2-18:0	0.72	0.50	18:0-18:1-24:0	0.17	0.17	20:0-18:2-22:0	0.02	0.07
18:1-18:2-20:1	0.69	0.73	22:0-18:1-22:1	0.16	tr	18:2-18:0-18:2	0.02	tr
22:0-18:1-18:2	0.69	0.66	22:0-16:0-18:2	0.15	0.01	20:0-18:1-24:0	0.01	0.07
18:0-18:1-18:2	0.66	0.77	18:0-18:1-20:1	0.14	0.14	22:0-18:1-22:0	0.01	0.13
24:0-18:2-18:1	0.65	0.88	16:0-18:2-16:1	0.14	0.03	18:0-18:2-20:0	0.01	0.08
18:2-18:1-18:2	0.65	0.81	16:1-18:1-18:1	0.13	0.20	18:2-16:1-18:2	0.01	tr
16:0-18:2-16:0	0.64	0.71	22:0-18:2-22:1	0.13	tr			
22:0-18:2-18:2	0.58	0.32	16:0-16:0-18:2	0.10	0.05			

[a]The 3 component fatty acids and the fatty acid in the 2-position are known.

[b]Composition calculated according to a 1,3-random-2-random distribution (33,34).

values are close to the experimental ones. For trioleoylglycerol, the relative difference is only 12% and it is still lower for the others.

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Mechanism of Palm Oil Bleaching by Montmorillonite Clay Activated at Various Acid Concentrations

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ABSTRACT

The mechanism of bleaching by a nonswelling montmorillonite clay activated at various acid concentrations was studied in the bleaching of palm oil. Montmorillonite clay was activated by 2 parts of H_2SO_4 at concentrations of 10-40%. Chemical composition, bleaching ability, specific surface area and phosphorus content were studied. The study showed that an initial increase in bleaching ability by clay activated by an increasing addition of H_2SO_4 was due to acid leaching of organic matter and impurities in the clay. The consequence of acid leaching in this case tends to expose active sites for adsorption. Acid leaching also removed Al^{3+}, causing charge deficiency in the clay lattice and, hence, promoting the adsorption properties of the clay. A drop in bleaching efficiency at higher additions of H_2SO_4 was observed. This was due to excessive acid leaching of Al^{3+}, causing collapse of the clay lattice structure.

INTRODUCTION

Bleaching clays are produced by activating montmorillonite clay with either sulfuric or hydrochloric acid to increase its adsorbent properties.

The bleaching process, as commonly understood, is the removal of color bodies. In the case of plam oil, its objective is to change the oil from a red to pale yellow color. In contrast to the original oil, bleached oil is also more stable.

It is now recognized that bleaching clay performs not only color removal, but also the removal of trace metals, adsorbtion of phospholipids, soaps and decomposition of oxidation products such as peroxides (1). As a result, bleached oil is lighter in color and more stable.

It has been suggested that the activation process results in the replacement of aluminium by Mg and Fe ion (2). Its bleaching mechanism involves physical adsorption and chemisorption (1).

Results obtained by Zchau (1) showed that oil treated by bleaching clay tends to give a lower phosphorus content and anisidine value. Shaw and Tribe (2) reported that bleaching clay removes a portion of the trace metals in vegetable oil, in particular copper and iron, that are known to have deleterious effects on their oxidative stability and flavor. It is known that the red color in palm oil is mainly due to the presence of carotenoid compounds. Khoo et al. (3) suggested that the chemisorption of β-carotene occurs on aluminosilicate surfaces with some of the exchangeable cations acting as active sites.

The purpose of this study is to elucidate the physicochemical mechanism of bleaching by montmorillonite clay activated at various acid concentrations. The study is conducted with special reference to palm oil, which currently has the most rapid growth rates of the world export of oils and fats (4).

ACTIVATION OF CLAY

The clay used for bleaching is a nonswelling montmoril-