Detection of Adulteration

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ABSTRACT

A program of work is in progress to establish the levels and ranges of fatty acids and other components present in the major edible vegetable oils. Authentic samples from the major producing areas for such oil have been obtained and analyzed. In the case of palm oil, ranges of the fatty acid composition and of the acids at the triglyceride 2-position, have been obtained for about 40 samples. These data were used to calculate enrichment factors, and triglyceride carbon number compositions, using a small computer program. Comparison with experimentally determined carbon number compositions were then made. Good correlations were found for whole unadulterated oils, but not for oil fractions. Unfortunately, these differences were insufficient to detect contamination of palm oil by 10 or 20% levels of other oils, or of palm fractions. Compositional ranges of sterols and tocopherols have also been determined on a selection from the original set of palm samples. Work on sunflower seed and groundnut oils has followed the same lines, particular attention having been paid to linolenic acid and, in the case of groundnut oil, also erucic acid, levels. Some groundnut kernels were found to have an oil with a component which cochromatographed with methyl erucate during fatty acid determination. This unknown constituent was studied by gas chromatography-mass spectrometry, and is thought to comprise a mixture of epoxy fatty acids. Analysis of the triglyceride fraction isolated from groundnut oil by thin layer chromatography removes this unknown constituent, and simplifies interpretation of the fatty acid composition of groundnut oil.

INTRODUCTION

Adulteration has been a problem in the oil and fat trade for a long time (1). It is sometimes deliberate, sometimes accidental. Indeed, accidental contamination is hard to avoid in modern bulk handling installations, where oils of different qualities must be pumped through common valves and pipelines. However, it is sometimes remarked that it is the expensive oil that usually gets contaminated with the cheaper one! For these reasons, tests were developed long ago for characterization of oils and fats. These include iodine value, to give a measure of an oil's unsaturation, and saponification value, which gives a measure of the average molecular weight of the constituent fatty acids. Some tests are so useful that they are widely used today, and are part of the common language of our nontechnical colleagues who buy, sell and trade the oils. We now have more sophisticated methods of analysis, but should not overlook the utility of some of the more traditional tests in detecting the presence of specific oils in suspected blends. The Halphen test (2,3), for instance, can detect as little as 0.1% of crude cottonseed oil, or stearine, in oil mixtures. Oils containing as little as 1% sesame oil will give a crimson color in the Boudouin (4) or modified Villavechia (5) test; while the Fitelson (or modified Lieberman-Burchard) test gives a positive indication in the presence of teaseed oil (6) or shea butter (7). Other traditional tests may be laborious and no longer of value, or even misleading, especially when determination of a fatty acid composition is required. The Reichert-Polenske-Kirchner test (8) gives a measure of (a) the water-soluble volatile acid content, (b) the water-insoluble fatty acid content, and (c) the butyric and valeric acid contents. It has, however, largely been replaced by determination of the fatty acid composition of a fat by gas liquid chromatography (GLC) of the derived methyl esters. The Evers (9) and modified Renard (10) tests claim to be able to detect as little as 5-10% groundnut oil in a mixture, and are used as a criterion of purity for groundnut oil itself (11). Together with the Bellier index (12,13) they rely on the crystallization characteristics of arachidic, behenic and lignoceric acids, and are of limited reliability due to the fact that the fractional crystallization of arachidic acid from a mixture of other solid acids is probably affected by the amount and type of the other acids present (14). Another complicating factor with these tests is that newer agricultural strains have different levels of both saturated and unsaturated fatty acids. Perhaps for this reason, the AOCS does not list these three tests in their Official and Tentative Methods (3). In any case, a far more reliable method for the determination of arachidic and lignorceric acids is by GLC analysis of their methyl esters.

A balance should be kept between the need to update and improve analytical techniques, and the need to retain those traditional tests which still have a useful function.

More recent work on oil authenticity has concentrated on the determination of fatty acid composition by GLC. Many papers have appeared on this topic, and the Codex Committee on Fats and Oils which was established by the joint FAO/WHO Codex Alimentarius Commission published (15) fatty acid composition ranges for typical commercial samples of bona fide fats and oils. However, it was recognized that these ranges were not definitive, and work continued on this topic. Spencer, Kwolck and Princen devised (16) a simple graphical procedure for the interpretation of fatty acid composition data of unmodified oils. They also calculated the saponification value, iodine value, and refractive index of each oil examined, and showed that, in all cases except one, the calculated values lie within the appropriate Codex ranges. Other workers (17,18) have studied the influence of seed maturity on fatty acid composition. As oils and fats are natural products, their compositions lie within ranges, and even when these ranges are positively identified, it is nevertheless possible for an oil to be adulterated or contaminated with another, and yet have a composition within the specified range.

Adulteration is, of course, increasingly more difficult to detect when the contaminant has a composition approaching that of the original oil. Various additional tests have therefore been devised, and many workers (19-21) have determined oil sterol compositions. This is an attractive approach as it helps resolve many issues where a fatty acid composition is indecisive. The Codex Committee on Fats and Oils discussed (22) at its tenth session a list of sterol ranges for 15 oils determined with each of two different types of stationary phase in the GLC stage of the analysis (OV17, versus SE30, JXR or SE52). Nevertheless, it is claimed (23) that sterol levels can be lowered by a variety of processes such as solvent crystallization, bleaching, and deodorization, thus reducing the reliability of sterol analysis for the detection of adulteration. In order to overcome the difficulties, Padley and Timms (23) developed a sensitive method for detection of foreign fats in cocoa butter, or chocolate, which relies on the analysis of the triglycerides according to their carbon number (molecular weight) classification by high temperature GLC. This method is partic-

ularly useful with cocoa butter as it has a composition comprising three main triglycerides (POP, POS and SOS). Although the technique can be applied to the analysis of other oils, it is likely to be less searching. Many of the liquid oils, for instance, differ from one another mainly on the basis of unsaturation, rather than the chain length of fatty acids.

More recent work (24) has drawn attention to the analysis of tocopherols and tocotrienols, collectively known as tocols. These were traditionally estimated by saponification of the oil, recovery of the unsaponifiable material, and analysis of this by GLC, or by paper and thin layer chromatography techniques (24). However, these procedures often involved losses of the tocols, e.g., by oxidation, and much early data is of insufficient reliability as a result. High pressure liquid chromatography (HPLC) coupled with fluorescence detection enables rapid analysis of the whole oil sample, there being no need for any sample pretreatment or work-up. As there are eight different tocol compounds, and as the relative proportions of these vary considerably from oil to oil, tocol determination by HPLC and fluorescence detection provides another useful tool for detection of adulteration or contamination.

A variety of methods, therefore, exist for the analysis of oils and fats, and for the detection of adulteration. Unfortunately, the different techniques have been carried out on different samples and in different laboratories. No collection of data on a single set of samples has been published. The present project, jointly funded by the UK Ministry of Agriculture, Fisheries and Foods, by the Federation of Oils, Seeds, and Fats Associations Ltd., and by the Leatherhead Food Research Association, was established with the object of collecting such a set of data. Nine oils are to be analyzed, by whatever tests are appropriate in each case, but concentrating on quantitative chemical, rather than physical, tests, as these vary directly in relationship to the proportions of oils in a blend.

At the present stage of the work, three oils (namely palm oil, sunflower seed oil, and groundnut oil) have been studied. The main problem with palm oil is detection of the presence of stearine (or oleine) byproduct which may be bled off into the oil, while the main problem with sunflower and groundnut is detection of contamination of groundnut oil with sunflower, and of either of these with cheaper oils such as soy or rape.

EXPERIMENTAL

Materials

Palm oil samples were obtained as far as possible from plantation mill managers. These were certified authentic by the suppliers.

Sunflower seed and groundnut kernels were obtained through FOSFA, supplemented by samples obtained from Food RA contacts. Sunflower seed origins were Argentina, Australia, Bulgaria, Canada, France, Hungary, South Africa, Turkey, and USA; while groundnut kernel origins were Argentina, Bangladesh, Brazil, China, Egypt, Guinea Bissau, India, Indonesia, Malawi, Paraguay, Sudan and the USA. Oil was quantiatively extracted with petroleum ether (bp 40-60 C) by a method technically similar to ISO 659. Samples of the oils were immediately analyzed. When a delay was anticipated, oils were stored at subambient temperatures.

Methyl esters were prepared from the oil by the method in ISO 5509, and analyzed on a Perkin Elmer F17 or Sigma 2 instrument fitted with a 2m × 2 mm id column packed with 6% Silar 5CP on 100/200 mesh Chromasorb W HP using nitrogen carrier gas at 20 mL/min and an oven temperature of 200 C. Peak integration was via a Spectra-Physics SP 4000. Reported fatty acid compositions are as a percentage of the total peak area. The apparatus was regularly calibrated with standard methyl ester mixtures.

Compositions of the fatty acids at the glycerol 2-position were determined by the IUPAC method (25) except that harder fats were incubated at 42 C for 5 min prior to lipase addition. This removed the need for hexane addition in most cases. We found that hexane addition, to dissolve high melting fats, gave results of lower reproducibility.

Carbon number triglyceride compositions were determined by direct injection of 12% (m/v) solutions of the sample in chloroform on to a Pye Unicam GCD gas chromatograph fitted with a 0.6m × 3 mm id glass column packed with 3% OV1 on 100/200 mesh Gas Chrom Q. Nitrogen carrier gas was used at a flow rate of 55 mL/minute. The column temperature was programmed at 300 C for 4 min, thereafter rising to 355 C at 4 C/min.

Tocol analysis was essentially by the HPLC and fluorescence detection method of Thompson and Hatina (26), using a Spectra-Physics SP 8100 HPLC instrument coupled to a Perkin Elmer LS3 fluorescence detector with an excitation wavelength of 290 nm and emmission of 330 nm. A 250 × 49 mm column packed with Partisil 5 (5μ), fitted with a 50 × 50 mm guard column, separated the tocols when eluted with a solvent comprising 49.55 dry heptane: 49.55 damp heptane:0.9 isopropanol solvent, at a flow rate of 1 mL/min. Peak integration was by Spectra-Physics SP 4100. Calibration was with pure samples of α-tocopherol, α-tocotrienol and δ-tocopherol supplied by Roche Products. Values for other tocols were obtained on experimental samples (RRT), and by reference to the literature (24,26). Calibration data are shown in Table I.

TABLE I

HPLC – Fluorescence Calibration Data

Tocol[a]	Relative retention times	Relative fluorescence peak areas
αT	1.0	100
βT	1.5[b]	100[c]
γT	1.8[b]	100[c]
δT	2.7	146
αT3	1.1	96
βT3	ca. 1.7[b]	100[c]
γT3	1.95[b]	100[c]
δT3	3.2[b]	146[c]

[a]T = tocopherols; T3 = tocotrienols.

[b]Values obtained on experimental samples after reference to literature.

[c]Values estimated on basis of our calibration and literature data (24, 26).

Sterols were determined according to ISO DIS 6799 using a 2m × 2mm packed column of 3% OV-17 on 80-100 mesh Gas Chrom Q and a temperature of 270 C on a Perkin Elmer F17 for the chromatography stage. An internal standard comprising 5-α-cholestane was added immediately prior to the derivatization step. Every fifth sample was analyzed in duplicate to confirm overall repeatability.

RESULTS AND DISCUSSION

Palm Oil

Forty-seven samples of whole palm oil, from a variety of geographic origins, were analyzed for fatty acid composition.

The ranges obtained are shown in Table II, alongside those of the Codex Committee on Fats and Oils (15) and the Malaysian Standard (27). Our results are broadly in line with these, but show narrower ranges, especially in comparison with the Codex ranges. The influence of geographic origin is shown to be minimal except in the case of the samples from Sumatra, where the high palmitic acid, and low oleic acid content, in comparison to our results on other origins, is believed to be due to the older mixed plantations of Tenera trees grown there (28). This difference should, therefore, become less as plantations are restocked with newer hybrid trees.

Table III shows ranges of fatty acids at the glycerol 2-position. Here again the Sumatran samples stand out as having the highest level of palmitic acid at the 2-position, and the lowest level of oleic.

Fatty acid composition data, and results of analysis of fatty acids at the glycerol 2-position for Malaysian stearines and oleines are also given in Tables II and III. The fatty acid ranges of the stearines are not sufficiently different to detect small levels of stearine in palm oil, especially if the origin of the palm oil is unknown.

The 1,3-random-2-random distribution law proposed almost simultaneously by Van der Waal (29) and by Coleman and Fulton (30) enables convenient and reasonably accurate estimations of the triglyceride compositions of most natural fats. However, it is not applicable to fat fractions (31). An attempt was, therefore, made to exploit this feature by calculating the carbon number triglyceride composition of the fat from the 1,3-random-2-random theory, and comparing these with experimental values. Overall fatty acid compositions, and 2-position results, were fed into a computer, converted to mole fractions, and the mole fraction carbon number composition calculated in each case. These results were converted back to a weight percent basis, and for convenience shown in the printout alongside the experimental values. Some comparisons are shown in Table IV. While the basis of the approach is borne out by the much better comparisons obtained on the whole oils than on the fractions, the differences are not sufficiently large to pinpoint oil batches adulterated with small amounts of stearine.

Table IV also shows enrichment factors (EF) for palmitic acid, defined as the ratio of the percent palmitic at the 2-position to the overall percentage (32). Here there is a much larger difference between the properties of whole oils and stearines. The EF ranges from 0.278 to 0.357 for Malaysian oils, and 0.274 to 0.415 when the other oils (especially Sumatran) are included, but is 0.430 to 0.869 for the stearines. This difference would be sufficient to detect some cases of adulteration of oil with stearine, but would not work with batches of whole oil having an initial EF at the bottom of the range.

Sterol and tocol compositions were also determined, on 20 of the original set of samples in the case of the sterols. The values obtained are shown in Tables V and VI. The sterol results are generally in line with the ranges previously discussed (22) by Codex following a review of literature data, although our range is somewhat narrower, the main difference being in the lower values we found for β-sitosterol.

The tocol compositions in Table VI show the predominance of tocotrienols in palm oil. Our results are in line with those reported (33) on Malaysian palm oils, although we did find some lower values. This is probably due to the age of the oils, as we knew some of them to be old samples, especially those from the Ivory Coast. The loss of tocols

TABLE II

Ranges of Fatty Acid Compositions – Palm Oil

Origin/no. of samples	wt % C12	% C14	% C16	% C18	% C18.1	% C18.2	% C18.3	% C20
Malaysia (21)	0.0-0.1	0.9-1.1	43.0-45.4	4.0-4.8	38.4-40.8	9.4-10.8	0.1-0.4	0.1-0.4
Ivory Coast (8)	0.1-0.2	0.8-1.0	43.4-45.2	4.9-5.5	37.1-39.9	9.6-10.9	0.2-0.4	0.2-0.4
Sumatra (6)	0.0-0.2	1.1-1.3	44.5-47.0	4.1-4.6	36.6-38.6	9.6-11.5	0.2-0.3	0.2-0.4
Papua New Guinea (3)	0.0-0.1	0.9-1.0	43.3-45.4	4.4-4.6	37.5-39.4	11.0-11.1	0.3[a]	0.2-0.4
Solomon Isles (4)	0.0-0.1	1.0-1.1	44.3-44.7	4.4-4.8	37.6-38.7	10.2-11.0	0.3-0.4	0.4[a]
New Britain (4)	0.1[a]	1.0-1.3	43.3-43.9	4.6-5.0	37.3-38.2	11.8-11.9	0.2-0.3	0.4[a]
Nigeria (1)	0.2	1.0	45.6	4.6	37.6	10.6	0.2	0.3
Overall (47)	0.0-0.2	0.8-1.3	43.0-47.0	4.0-5.5	36.6-40.8	9.4-11.9	0.1-0.4	0.1-0.4
Codex	0.0-1.2	0.5-5.9	32.0-59.0	1.5-8.0	27.0-52.0	5.0-14.0	0.0-1.5	0.0-1.0
Malaysian Standard	0.0-0.4	0.6-1.7	41.1-47.0	3.7-5.6	38.2-43.5	6.6-11.9	0.0-0.5	0.0-0.8
Stearines (8)	0.1-0.2	1.0-1.3	46.5-68.9	4.4-5.5	19.9-38.4	4.1-9.3	0.1-0.2	0.1-0.3
Oleines (5)	0.1-0.2	0.9-1.0	39.5-40.8	3.9-4.4	42.7-43.8	10.7-11.4	0.0-0.4	0.1-0.3

[a]All samples gave the same result within experimental error.

TABLE III

Ranges of Fatty Acids at the 2-Position – Palm Oil

Origin/no. of samples	% C14	% C16	% C18	% C18.1	% C18.2	% C18.3	% C20
Malaysia (17)	0.5-0.9	12.0-15.7	0.6-1.1	61.3-67.3	17.0-22.1	0.1-0.4	0.0-0.2
Ivory Coast (6)	0.4-0.7	13.7-15.4	0.5-1.4	62.8-66.5	17.0-20.3	0.2-0.3	0.0
Sumatra (6)	0.5-0.7	12.5-19.5	0.6-0.9	59.3-67.0	18.5-21.2	0.2-0.3	0.0-0.1
Papua New Guinea (3)	0.7-0.9	12.6-13.6	0.7-0.8	63.4-63.8	20.2-21.9	0.2	0.0
Solomon Isles (4)	0.5-0.6	12.8-14.5	0.8-1.2	63.5-63.9	20.1-21.7	0.0-0.3	0.0
New Britain (4)	0.4-0.7	12.7-13.2	0.6-0.9	62.6-63.6	21.9-22.8	0.1-0.3	0.0-0.1
Nigeria (1)	0.4	13.6	0.6	64.8	20.2	0.3	0.0
Overall (41)	0.4-0.9	12.0-19.5	0.6-1.4	59.3-67.3	18.5-22.8	0.0-0.4	0.0-0.2
Stearines (5)	0.6-1.6	20.1-59.9	1.3-2.1	28.9-61.2	7.4-18.2	0.0-0.2	0.0-0.1
Oleines (1)	0.5	11.6	0.9	66.1	20.5	0.1	0.0

TABLE IV

Comparisons of Calculated and Experimental Results

Origin	Result[a]	Carbon number compositions (wt %) C46	C48	C50	C52	C54	C56	EF[b]
Whole palm oils								
Malaysian IV 51.8	Calc	0.7	7.9	39.2	40.3	11.8	0.1	0.340
	Exp	0.7	7.8	39.6	40.5	10.8	0.6	
Malaysian IV 53.5	Calc	0.4	7.0	37.6	41.3	13.3	0.4	0.333
	Exp	0.6	7.5	38.3	41.3	11.9	0.5	
Ivory Coast IV 52.4	Calc	0.7	7.7	41.0	39.5	10.8	0.2	0.303
	Exp	0.6	7.9	40.7	39.7	10.4	0.7	
New Britain IV 53.3	Calc	0.7	7.6	39.2	40.0	12.0	0.3	0.295
	Exp	0.0	7.3	39.6	41.0	11.5	0.6	
Sumatra IV 51.3	Calc	0.7	7.6	39.2	40.0	12.0	0.3	0.274
	Exp	0.0	7.3	39.6	41.0	11.5	0.6	
Sumatra IV 51.0	Calc	0.7	9.4	40.5	38.4	10.8	0.2	0.384
	Exp	0.9	9.9	40.9	38.4	9.3	0.6	
Palm oil fractions								
Malaysian stearine IV 44	Calc	1.2	13.7	42.6	34.2	8.2	0.1	0.525
	Exp	1.2	15.1	40.3	33.9	9.0	0.6	
Malaysian stearine IV 24.4	Calc	2.3	35.7	42.6	16.8	2.3	0.0	0.869
	Exp	3.0	42.6	39.6	11.9	2.5	0.2	
Malaysian oleine IV 56.7	Calc	0.6	5.6	34.3	43.5	15.8	0.2	0.291
	Exp	0.3	2.7	37.7	45.6	12.8	0.8	

[a]Calc = value calculated according to 1,3-random-2-random theory. Exp=value obtained by high temperature GLC.
[b]EF = enrichment factor for palmitic acid.

TABLE V

Ranges of Sterol Compositions

	No. of samples								
	Palm oil			Groundnut oil			Sunflower seed oil		
	15		Codex	20		Codex	18		Codex
	Range	Mean	range	Range	Mean	range	Range	Mean	range
Cholesterol	2.2-6.7%	4.1%	1.0-8.0%	0.5-3.8%	1.5%	0-0.5%	0.3-1.3%	0.52%	0.0-0.4%
Brassicasterol	0.0	0.0	0.0	0.0-0.4	0.0	0.0	0.0-0.2	0.04	0.0
Campesterol	19.8-29.1	22.8	14.0-23.4	11.4-19.8	17.0	12.2-20.4	7.4-11.6	9.2	7.9-13.6
Stigmasterol	8.3-13.0	11.3	8.0-13.3	4.8-13.3	8.7	7.0-15.4	8.6-10.8	8.8	8.0-13.1
β-Sitosterol	50.2-62.1	57.5	58.1-70.4	47.6-64.8	58.5	54.3-74.6	56.2-62.9	59.8	59.2-69.5
Δ5-Avenasterol	0.0-2.8	1.5	0.0-2.0	8.3-19.0	12.3	0.0-15.6	1.8-5.2	3.35	0.9-7.0
Δ7-Stigmastenol	0.0-2.8	1.0	0.0-1.0	0.0-5.2	2.1	0.0-3.2	7.7-13.1	10.6	5.0-15.0
Δ7-Avenasterol	0.0-4.0	1.5	0.0-1.9	0.0-6.6	1.2	0.0-2.0	3.1-6.5	4.9	1.1-5.3
Total sterols (mg/kg)	326-627		–	901-2850		–	2750-4360		–

TABLE VI

Tocol Compositions (in mg/kg)

No. of samples	Palm oil 46		Sunflower seed oil 28		Groundnut oil 43	
	Range	Mean	Range	Mean	Range	Mean
αT	3-185	84.8	403-855	658	49-304	178
βT	traces	0	11-45	28.7	1-41	9.8
γT	4-36	17.7	0-34	11.0	99-389	220
αT-3	4-336	124.1				
γT-3	42-710	318				
δT-3	t-148	72				
Total	98-1330	617	176-556	415	447-900	699
Ratio α/γ	0.3-10.8	4.37	Over 16.8	219	0.35-1.2	0.82

T = tocopherol; T-3 = tocotrienol.

during storage, e.g., by oxidation, did not change the isomeric distribution pattern too much, as levels of all isomers fell. Tocol analysis is therefore a useful purity oriterion for crude oils.

The influence of both caustic and physical refining on the tocol compositions of Malaysian oils has been reported (33), and it appears that the changes are more dependent on the conditions used in the mill than on the choice of process. Some fully refined and deodorized products have tocopherol compositions quite close to those of the crude, while at other processing plants significant changes took place.

Sterol and tocol analyses are not suited to the detection of palm stearine in palm oil, but may be useful for the detection of palm products, e.g., palm oleine, in other oils.

Sunflower Seed and Groundnut Oils

Overall and 2-position fatty acid analysis ranges, for the geographical areas covered, are shown in Table VII. These ranges are broadly in line with those of the Codex (15), except that we found very low contents of C18:3 in both oils. This is a useful purity parameter, but does not identify adulteration of groundnut oil with sunflower, or vice versa. In this case the higher levels of long-chain saturated acids of groundnut oil are a useful parameter, and are of course the basis of the Evers, Renard, and Bellier tests (9-14). However, the ranges of 2.3-4.3 and 1.0-5.0 for C22:0 in the present work, and Codex (15), respectively, are sometimes too broad to be conclusive. Where confirmation is needed the C18:2 E.F., illustrated graphically in Figure 1, is useful.

The erucic acid content of groundnut oil is used as a measure of purity. Table VII shows an upper limit of 0.3% in comparison with 2.0% in the Codex range (15). A confusing factor with some samples is that a minor component coelutes with methyl erucate giving an apparently larger erucic acid level. This is illustrated in Figure 2. We believe that the compound is the same as that reported (18) by Sanders. It can be removed from the analytical sample by a TLC step to purify the normal triglycerides which are then analyzed separately. The unknown compound is found in the diglyceride band on the TLC plate. Although we have not yet identified it we think it may comprise several epoxy acid triglycerides.

Triglyceride carbon number analyses are shown in Table VIII. Here again the longer-chain saturated acids in groundnut oil are evident in the high levels of C60 and C62 glycerides. Attempts to verify authenticity of these liquid oils by a Padley-Timms type approach (23) have not been successful, mainly due to the very high levels of C18 acids in the liquid oils, their general similarity of carbon number com-

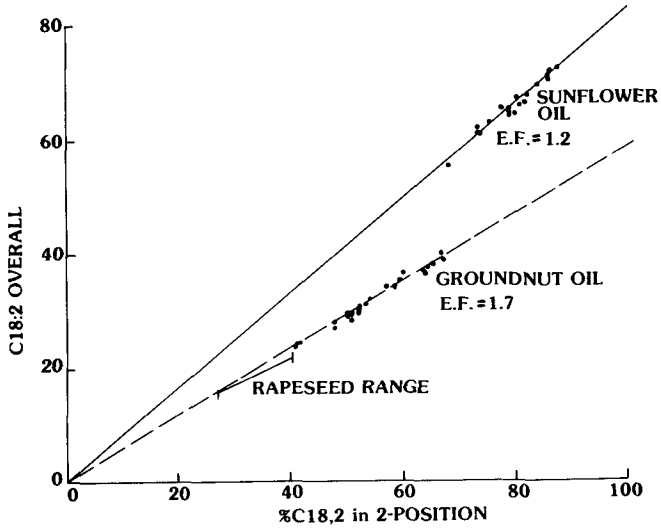

FIG. 1. Graphical representation of C18:2 enrichment factors for 3 liquid oils.

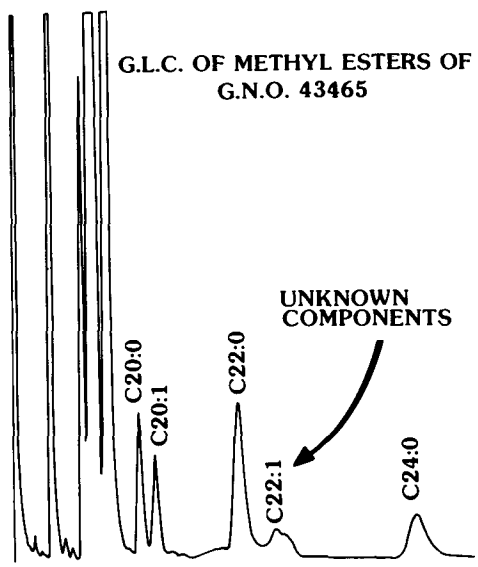

FIG. 2. Groundnut oil methyl ester analysis.

TABLE VII

Overall and 2-Position Fatty Acid Analyses

Acid	Sunflower seed oil		Groundnut oil	
	Overall	2-Position	Overall	2-Position
C16:0	5.7-6.9%	0.2-0.4%	9.2-13.9%	0.7-2.7%
C18:0	3.0-6.3	0.1-0.3	2.2-4.4	0.1-0.6
C18:1	14.0-34.4	12.1-31.3	36.5-64.7	31.5-71.5
C18:2	55.5-73.2	66.2-87.4	16.2-39.3	27.2-67.8
C18:3	<0.1	0	<0.1	0.0-0.07
C20:0	0.2-0.3	0	1.1-1.7	0.0-0.1
C20:1	0.1-0.2	0.05-0.1	0.8-1.7	0.0-0.1
C22:0	0.6-0.9	–	2.3-4.3	0
C22:1	0.0-0.15	0.0-0.1	trace-0.3	0.0-0.3
C24:0	0.2-0.3	–	1.2-2.2	–
No. of samples	29	19	51	23

TABLE VIII

Triglyceride Carbon Number Analyses

	Sunflower seed oil	Groundnut oil
C50	1.2-1.7%	2.6-5.5%
C52	16.4-18.5	22.7-30.4
C54	75.1-79.5	48.5-58.7
C56	1.2-3.0	6.2-10.4
C58	1.1-2.9	5.3-9.2
C60	0.3-0.7	2.3-4.7
C62	0	0.2-1.2
No. of samples	20	26

position, and the ranges of values encountered. Sterol compositions are shown in Table V, and are broadly in line with those previously discussed by Codex (22) following a review of literature data. The higher levels of Δ^5-avenasterol in groundnut oil, and of Δ^7-stigmasternol in sunflower seed oil are useful criteria. Several workers (34-36) have advocated the use of different sterol ratios to emphasize these differences.

Tocopherol compositions are shown in Table VI. These differ only slightly from the review of literature data published by Taylor and Barnes (24). Our results are in agreement with published data for sunflower seed oil, and show a lower level of α-tocopherol, and a higher level of γ-tocopherol in groundnut oil in comparison to sunflower seed oil. As a purity criteria, the ranges are quite wide, but the large differences between the two oils will show contamination of 10 or 25% in favorable cases. Again, it is easier to detect 10% groundnut oil in sunflower seed oil than vice versa. The ratio of α/γ tocopherol is useful, and ranges from 0.35 to 1.2 in groundnut oil, whereas in sunflower seed oil all values were over 16.8, the mean for the ratio being 219. This ratio will, therefore, be useful to identify contamination in some cases, but it is not as useful as at first thought, since the absolute values of tocopherol levels can vary over such wide limits. Thus use of a sunflower seed oil which itself has a low total tocopherol level will change the composition of a normal groundnut oil only slightly.

The main reason for the wide variation in tocopherol levels is, of course, that they are lost by oxidation, and although it appears that the relative proportions do not change too much, a low level ot total tocopherols in the contaminating oil will make it harder to detect by this means. It is known (37) that slight oxidation of linoleic acid in the presence of tocopherol leads to the formation of a tocopherol ether. This may be an additional reason for the low tocopherol levels found in some oils. These ethers can be decomposed, e.g., by bleaching earth, partial hydrogenation, or the application of heat, thus releasing the tocopherol. It may be worthwhile to study the influence of an ether decomposition step, prior to tocopherol determination, as this may help reduce the variability found in the results.

The program of work is continuing, and we are gradually building an extensive data bank, all obtained on a single set of samples. When complete it will be possible to crosslink parameters obtained from different tests, and produce derived functions and ratios. The use of these will make it progressively easier to detect adulteration or contamination, and in many cases enable us to estimate the level. An unsolved problem is the detection of small amounts of additional palm stearine in whole plam oil. This is perhaps an impossible analytical task, especially when the stearines have IV of over 40. However, the Malaysians are tackling this in another way. They have issued a Malaysian standard for palm oil (27) which takes into account natural variation. They are also preparing standards for palm oleine and palm stearine (38). The issue of such standards by the country of origin may become the basis of a form of guarantee, and is an approach with which the author is fully in favor, as it should help remove a lot of the disputes that arise over oil purity. It has advantages over the preparation of Codex standards, as only a single origin is involved, and natural variation is thereby reduced.

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