

Component Fatty Acids and Composition of Some Oils and Fats

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Abstract

Nineteen different samples of oils and fats have been examined for their component acids and composition by gas-liquid chromatography. Under programmed-temperature operations, the temperatures at which different components start to elute bear a straight-line relationship with their respective carbon numbers. Chromatograms, under programmed-temperature conditions, of methyl esters from such oils as coconut, groundnut, mustard, etc., are used for identifying the components of an unknown oil by comparing its chromatogram taken under nearly identical conditions. For confirmatory identifications, such plots as logarithm of retention times versus carbon numbers for saturated acids (14:0 to 24:0), monoenoic acids (14:1 to 24:1), and dienoic acids (18:2 to 24:2), under isothermal conditions, have also been used. Some new fatty acids, noted for the first time in traditional oils, are 15:0 in cottonseed oil, 20:1 in sesame oil, 22:0 in soybean oil, and 24:2 in mustard oil. Odd-carbon chain acids from 11:0 to 23:0 have been observed in such vegetable oils as peanut germ, rice bran, and *Mesua ferrea*. Fatty acid composition by GLC for new samples like peanut lecithin, peanut germ oil, *Myristica attenuata*, *Myristica kanarica*, *Myristica magnifica*, *Mesua ferrea*, *Vateria indica*, *Schleichera trijuga*, and shark-liver stearine are presented. Industrial utilization of these new oils and fats is discussed.

Introduction

INDUSTRIAL UTILIZATION of an oil or fat is greatly enhanced by a knowledge of its fatty acid composition. Under a program of research some oils from seeds obtained from the jungles of Kerala were examined for their composition. Other oils such as coconut, cottonseed, groundnut, etc., which were regularly bought in ton lots, were also included in this study as the fatty acid composition of commercial samples was not readily available. All these were analyzed by gas-liquid chromatography (GLC) as this was the best available technique to reveal the component fatty acids both qualitatively and quantitatively.

Experimental Procedures

Raw Materials. Seed of *Myristica attenuata*, Chorapine (Malayalam); *Myristica kanarica*, Undapine (Malayalam); *Myristica magnifica*, Kothapine (Malayalam); *Mesua ferrea*, Nanku (Malayalam), Nahor (Hindi); *Schleichera trijuga*, Poovam (Malayalam), Kusum (Hindi); and *Vateria indica*, Vellapine (Malayalam), Dhupa (Hindi) were collected during June to August 1963, and generous quantities were made available for this study. These seeds were

crushed, dried where necessary, and extracted with commercial hexane (bp 65–67°C). The detailed analyses of these samples are recorded in Table I.

Groundnut lecithin was obtained as a sludge in the degumming of solvent-extracted groundnut peanut cake oil. It has the following analysis: moisture 28.1%, benzene insolubles 15.3%, acetone solubles 19.8%, acetone insolubles 36.8%; total phosphorus 1.7% and A.V. 25.7. This sludge was dried and extracted with hexane; the fatty matter thus obtained was converted into methyl esters according to a procedure described later. Yield of methyl ester 30%.

For groundnut germ oil the germs containing a small portion of groundnut kernel obtained from a groundnut flour plant were extracted with commercial hexane. The 45% of fatty matter was extractable and had the following analysis: S.V. 195.4, I.V. 73.6, A.V. 2.1, unsaponifiable matter 1.6%.

Shark-liver oil stearine was supplied by the Government Oil Factory, Calicut, Kerala, and had the characteristics: A.V. 38, S.V. 183.4, I.V. 127.5, unsaponifiable matter 3.9, glycerine 8.7% mp 37°C. Samples drawn from bulk lots from the plant were: coconut oil (A.V. 1.4, S.V. 253.1, I.V. 8.9), groundnut oil (A.V. 0.6, S.V. 194.1, I.V. 93.2), cottonseed oil (A.V. 0.3, S.V. 197.5, I.V. 107), palm oil (A.V. 5.6, S.V. 199, I.V. 55.1), sesame oil (A.V. 6.6, S.V. 190.1, I.V. 105.4), soybean oil (A.V. 1.0, S.V. 194.3, I.V. 132.8), rice bran oil (A.V. 91.3, S.V. 190.4, I.V. 80, unsaponifiable matter 4.0%), beef tallow (A.V. 21.0, S.V. 195, I.V. 58.4), and mutton tallow (A.V. 12.7, S.V. 202, I.V. 36.6). Mustard oil (S.V. 171.4, I.V. 102.9) was a market sample of edible quality.

Methyl Esters. About 3 g of oil or fat were refluxed with methanolic sodium hydroxide (40 g/liter) for one hour. After slight cooling the soaps were split in situ by the careful dropwise addition of concentrated sulfuric acid, with a gentle swirling of the flask. An excess of sulfuric acid to provide a concentration of 2% on the basis of alcohol (w/v) was then added, and the entire mass was allowed to simmer on a hot plate to ensure complete splitting of the soap. At this stage either the contents were allowed to simmer gently for two hours, or if the work was done toward the end of the day, they were left at room temperature overnight to permit esterification. Both the procedures gave identical results. After dilution with 100 ml of water, the esters were transferred to a separatory funnel with about 100 ml of ether.

After the ether extract was washed with water, it was washed once with 100 ml and twice with 50 ml each of 1% aqueous potassium hydroxide solution to remove any residual acidic matter. The ether layer was not allowed to be in contact with the alkaline layer for more than one hour, and the latter was withdrawn though slightly hazy. This precaution was necessary to avoid any saponification during the treatment. After the washing with water the esters were recovered in the usual manner and distilled under vacuum (0.2-mm pressure). Results obtained with a few samples by this method are recorded in Table II.

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TABLE I
Detailed Analysis of Some New Samples of Oils and Fats

| Name (local name) | Shape | On the Seed | | | | On the Oil | | | | | | | | |
|--|---|-------------------------|---------|----------|-------------------|---------------------|-------------------------------|-------------------------------|---------|------------|--------------|---------------------------|-----------------|------------|
| | | Length × diam. or width | Shell % | Kernel % | Moist. (kernel) % | Oil of dry kernel % | Protein content dry-extracted | Color ¼-in. cell Lovibond Y R | M.P. °C | Acid value | Sapon. value | Iodine value Wijs 30 min. | Unsap. matter % | Glycerin % |
| Myristica attenuata | Round | ¾ to 1 in. | 20.3 | 79.7 | 23.9 | 41.2 | 9.6 | 49 - 10.7 | 35 | 64.6 | 164.7 | 59.9 | 4.6 | 5.2 |
| Myristica kanarica | Oval | ½ in. | 18.5 | 81.5 | 11.5 | 58.1 | 16.4 | 10 - 1.0 | 38 | 14.6 | 195.4 | 51.3 | 1.7 | 9.1 |
| Myristica magnifica | Spherical | ¾ in. diam. | 21.0 | 79.0 | 19.6 | 27 ^a | 8.5 | 16 - 1.9 | 32.5 | | | | | |
| Mesua ferrea (resembles hood of cobra) | Cylindrical with round ends | 2 to 2 ¼ in. × 1 in. | 42.3 | 57.7 | 28 | 61.7 | 15.9 | 25 - 2.4 | 10 | 24.0 | 204.0 | 91.3 | 1.9 | 8.2 |
| Schleichera trijuga | Flat dish-shaped with ridge at center of concave side | ¾ in. diam. | 43.1 | 66.9 | 5.1 | 74.2 | 35.5 | 2.3 - 0.3 | 35 | 32 | 233.7 | 55.9 | 2.0 | 3.6 |
| Vateria indica | Big-sized peas | 1 ½ × 1 in. | 30.4 | 69.6 | 36.6 | 22.5 | 6.3 | 5.5 - 0.5 | 32.8 | 0.7 | 188.7 | 40.1 | 1.0 | 9.4 |

^a Benzene extract, highly viscous liquid darkens during saponification and interferes with the end-point. On methylation it yields about 21.1% methyl esters; these were analyzed for composition by G.L.C.

^b Cyanogen content of whole kernel (as HCN), 0.07%; extracted meal, .03%; and oil, nil.

TABLE II
Data on the Preparation of Methyl Esters^a

| Sample | Alkali-extractable matter % | % Yield of alkali-washed esters | % Yield of distilled esters |
|----------------------|-----------------------------|---------------------------------|-----------------------------|
| Myristica attenuata | 36.0 | 61 | 57 |
| Myristica kanarica | 16.9 | 78.4 | 74.3 |
| Schleichera trijuga | 3.0 | 96.6 | 93.1 |
| Mesua ferrea | 9.8 | 87.0 | 84.3 |
| Vateria indica | | 95.4 | 91.2 |
| Groundnut germ oil | | 97.3 | 93.7 |
| Coconut oil | 2.2 | 95.0 | 93.5 |
| Palm oil | | 96.6 | 93.6 |
| Cottonseed oil | | 96.6 | 93.1 |
| Soybean oil | | 97.2 | 94.6 |
| Sesame oil | | 96.8 | 93.8 |
| Mutton tallow | | 97.4 | 94.2 |
| Shark-Liver stearine | | 93.8 | 69.2 |

^a Handling loss averages to about 3% with all samples.

Gas-Liquid Chromatography. A Perkin-Elmer Model 800 gas chromatograph, equipped with a flame ionization detector and 2-meter × ⅛-in. I.D. stainless steel columns, packed with 8% butanediol succinate on 80-100 HMDS chromosorb W, was used. It was installed with a 50:50 split at the exit. Nitrogen at 50 lb of pressure and ambient flow rate of 53.6-55.6 ml/min was used as the carrier gas. The exit flows at the higher temperatures were 37.5 to 36.4 ml/min at 115C, and 25.5 to 24.2 ml/min at 215C. The injector temperature was varied from 250C (coconut esters) to 300C (shark-liver stearine esters). Sample size was about 0.1 μl. Samples were analyzed both under isothermal 215C and programmed-temperature (115-215C 10°/min) conditions. Peak areas were measured by triangulation.

Infrared spectrophotometry was done on a Perkin-

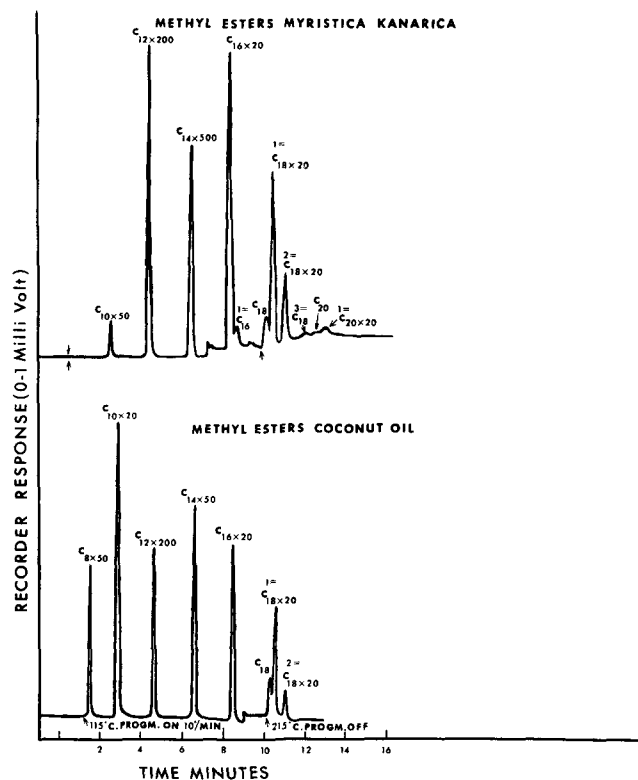


FIG. 1. Programmed-temperature chromatograms for *Myristica kanarica* and coconut oil methyl esters. The notation Cx of peak identification is chosen mainly to prevent confusion with attenuation figures (×100, etc.) given alongside of peaks. Where these are not given owing to lack of space, the attenuation for that peak is the same as the closest peak to the right or left of it.

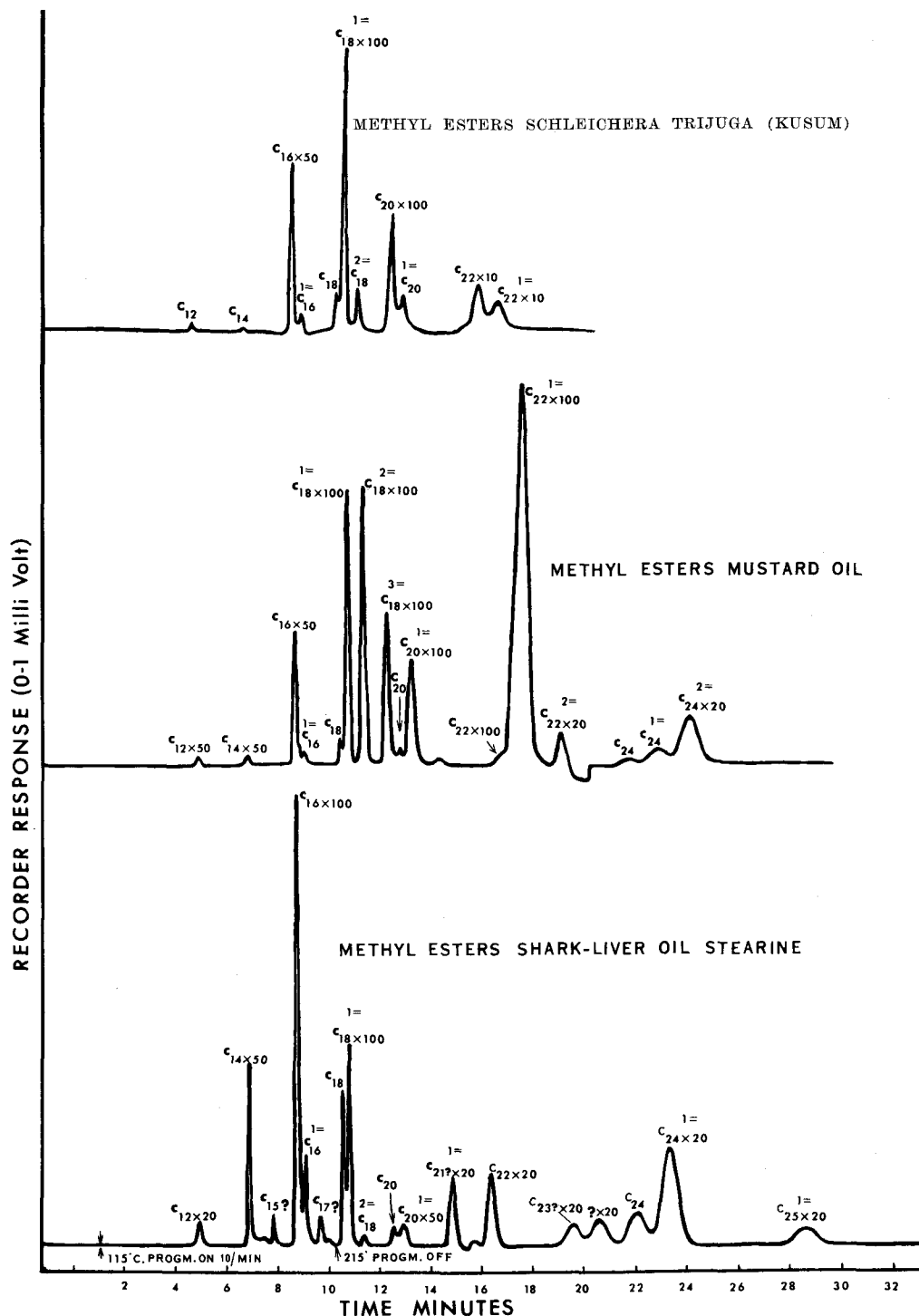


Fig. 2. Programmed-temperature chromatograms of *Schleichera trijuga* (Kusum), mustard, and shark-liver stearine methyl esters.

Elmer Model 21 spectrophotometer with sodium chloride optics, and measurements were made on carbon-disulfide solutions. AOCs Official and Tentative Methods were followed for all the routine analyses.

Results and Discussion

Preparation of Methyl Esters. Many reagents, such as diazomethane (1) and borontrifluoridemethanol (2), with fatty acids and such procedures as esterification in the presence of dimethoxy propane (3) to insure anhydrous conditions and methanolysis in the presence of basic and acidic catalysts (4-6) with oils and fats, have been used to prepare the respective esters. Comparative studies (7,8) of some of the

methods (methanol-hydrochloric acid or sulfuric acid, diazomethane, borontrifluoride-methanol) have been shown to yield identical results with most common oils and fats. Most of these methods are not suitable for unknown oils and fats which might contain resinous or phenolic materials (12-14). Side reactions with unsaturated fatty acids by borontrifluoride (10) and polymer formation with diazomethane (9) have been pointed out as drawbacks with these reagents.

In the method described in this paper the samples are subjected to hydrolysis both under alkaline (during saponification) and acidic (during esterification) conditions, thus ensuring that fatty acids attached to organic compounds other than glycerol are also split

from them and esterified. The alkaline wash will remove any acidic material (unesterified acids, resinic acids, phenols, etc.) but involves a small loss of material even with such oils as soybean, sesame, cottonseed, etc. (Table II). The washed material can be taken as representing the fatty portion of the parent material. Thus *Myristica attenuata*, *Myristica kanarica* and *Mesua ferrea* contain about 61%, 78.4%, and 87% respectively of fatty material; the rest is resinous or phenolic. Of these only *Myristica kanarica* gave a positive test for phenols (15). The vacuum distillation of all the esters took only about five minutes and was stopped soon after any coloring was noticed in the distillate drops. To avoid losses of low boiling esters, particularly with coconut oil and the *Myristica* series fats, an additional trap cooled in an ice-salt mixture was installed next to the distillate receiver. About 50 mg of material was recovered and added to the distilled esters with coconut oil, but no condensate was obtained with the others. The yield of alkaline-washed esters was about 96–98%, and this would have been more than 99% if the handling loss (likely to be only of esters) had been included. The present method was thus placed on a par with the other methods.

In the case of rice bran oil, methyl esters were prepared both by this method and the conventional method by using fatty acids, methanol, and sulfuric acid. The yields of distilled esters were 93.8% and 92.4% respectively. Both preparations gave identical gas chromatograms, suggesting that removal of unsaponifiable matter by extraction need not be done with most oils and fats. Since most of the unsaponifiable matter with the common vegetable oils or animal fats were sterols (16), these remained with the residue during the distillation step. The residue amounted to about 3% in common vegetable oils and fats. Shark-liver stearine gave a residue of about 25%.

Gas-Liquid Chromatography and Identification of Components. The oils and fats examined in the present study had fatty acids ranging from 8 to 24 carbon atoms, thus it was necessary to elute all of these in a reasonable time and not to alter the polyunsaturated components (17). Fig. 1 and 2 show that all components from C₈ to C₂₄ (this notation is preferred with Fig. 1 and 2 to avoid confusion with the attenuation values given on the peaks) are eluted in less than 30 min, and the programming temperatures (initial 115°C and final 215°C) and flow rates are such that good separations are obtained. Unsaturated components like linoleic, linolenic, erucic, etc., are exposed for about two to 15 min only to the highest temperature. Further, in the mustard oil esters chromatogram (Fig. 2), methyl linolenate and arachidate emerge as separate peaks.

For identification of components under programmed-temperature operation, chromatograms of such oils as coconut (for low-molecular-weight acids), groundnut and mustard (for acids from C₁₈ and above), the compositions of which are known (3,11,18,25), were taken under similar conditions and compared with those of the unknown. An advantage of this procedure is that authentic specimens of various fatty acids are not needed, and by just two runs, one for the sample and another for the standard, a wide spectrum of fatty acids can be identified.

Figs. 1 and 2 are self-explanatory. The peak coincidences are good up to 18:3, and some shifts are observed in the 20- and 22-carbon regions with *Schleichera trijuga* (Kusum) and mustard oil esters,

which are probably caused by slight changes in flow rates and do not vitiate identifications. The usefulness of this comparative chromatogram method is brought out in the shark-liver stearine esters, where there are numerous peaks to be identified and the chromatogram of mustard oil esters facilitates the identification of several of these and indicates probabilities with the others (15:0, 17:0, 23:0, etc.).

When the temperatures at which components start eluting are plotted against their number of carbon atoms, a straight line is obtained (Fig. 3, Graph 1). This provides a quick means of identifying a component during a run and greatly facilitates qualitative analysis, such as checking the purity of cuts in fatty acid distillation. The points on the graph represent the average temperatures ($\pm 1^\circ\text{C}$) of elution for the same components from at least 10 different samples of vegetable oils and fats.

Some investigators (26,27) have observed that, with programmed-temperature operations, a straight-line relationship exists between retention time and chain length of components. Graph 2, Fig. 3, confirms this, and arachidate (20:0) also falls on an extension of this line (dotted portion) though programming was off when stearate (18:0) started eluting. The temperature recorded is that of the oven, and though the oven temperatures are stabilized, the column is still being heated and attains isothermal equilibrium a few minutes after the programmed heating is off. Behenate (22:0) and lignocerate (24:0), which elute under isothermal equilibrium, fall on a curve.

To confirm the identification of components, especially in the range of 20:0 and above, the conventional plot of logarithm of retention time against carbon chain-length under isothermal conditions was constructed for saturated, monoene, and diene components from the average retention-time of the isothermal runs of several vegetable oils (groundnut, mustard, sesame, cottonseed, soybean, etc.). For the saturated series (Graph 3, Fig. 3) deviations occur from 12:0 down. Most of the others conform to the straight line remarkably well though the chromatograms of the various samples were taken on different days, some about three months apart, and there were slight variations in flow rates. The deviations of the low-molecular-

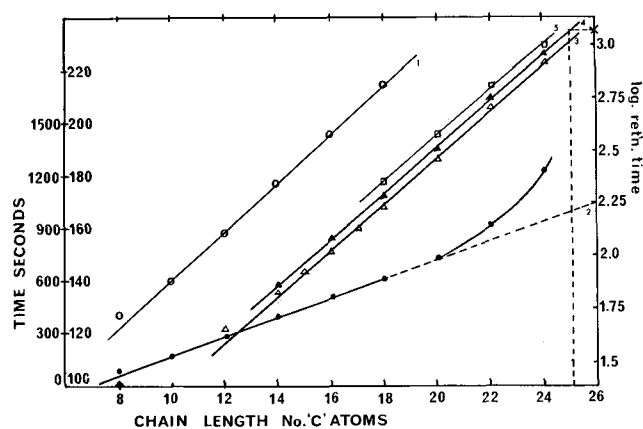


FIG. 3. Plots of retention time, temperature of elution, and log-retention time vs. carbon numbers. 1. Temperature of elution $^\circ\text{C}$ under programmed-temperature operation, versus carbon numbers. 2. Retention time in seconds under programmed-temperature operation, versus carbon numbers. 3. Logarithm of retention time versus carbon numbers, under isothermal conditions, for saturated acids. 4. Logarithm of retention time versus carbon numbers, under isothermal conditions, for monoenoic acids. 5. Logarithm of retention time versus carbon numbers, under isothermal conditions, for dienoic acids.

TABLE III
Fatty Acid Composition (%) of Oils and Fats

| Sample | 8:0 | 10:0 | 12:0 | 14:0 | 14:1 | 15:0 | 15:1 | 16:0 | 16:1 | 18:0 | 18:1 | 18:2 | 18:3 | 20:0 | 20:1 | 22:0 | 22:1 | 24:0 |
|-----------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Coconut oil | 7.1 | 7.3 | 54.0 | 17.4 | ... | ... | ... | 6.1 | 0.3 | 1.6 | 5.0 | 1.3 | 0.2 | 1.1 | ... | ... | ... | ... |
| Myristica attenuata | <0.1 | 1.2 | 0.3 | 66.0 | 0.6 | ... | ... | 8.3 | 0.1 | 1.9 | 20.6 | 1.3 | 0.2 | 1.1 | ... | ... | ... | ... |
| Myristica kanarica | ... | ... | 34.0 | 58.1 | ... | ... | ... | 2.7 | 0.2 | 0.3 | 2.1 | 0.6 | <0.1 | <0.1 | ... | ... | ... | ... |
| Myristica magnifica ^a | ... | ... | 0.7 | 54.2 | ... | ... | ... | 11.6 | 0.6 | 2.2 | 28.4 | 1.4 | <0.1 | 1.1 | ... | ... | ... | ... |
| Palm (Malayan) | 0.1 | <0.1 | 0.1 | 1.2 | ... | ... | ... | 42.1 | 0.6 | 4.3 | 43.0 | 8.6 | ... | ... | ... | ... | ... | ... |
| Vateria indica | ... | ... | 0.6 | 5.5 | ... | ... | ... | 16.2 | 0.2 | 46.5 | 34.6 | 1.7 | 0.1 | 0.7 | ... | ... | ... | ... |
| Mutton tallow ^b | ... | ... | 0.1 | 2.5 | ... | ... | ... | 25.8 | 1.5 | 30.3 | 30.0 | 1.4 | 0.2 | 0.2 | 0.1 | ... | ... | ... |
| Beef tallow ^c | ... | ... | 0.2 | 2.5 | ... | ... | ... | 22.8 | 0.5 | 30.3 | 30.0 | 1.4 | 0.2 | 0.2 | 0.1 | ... | ... | ... |
| Mesua ferrea ^d | 1.0 | <0.1 | 0.1 | 0.8 | ... | ... | ... | 16.3 | 0.3 | 15.2 | 57.4 | 6.5 | <0.1 | 0.8 | <0.1 | 0.2 | ... | <0.1 |
| Cottonseed oil | ... | ... | 0.4 | 0.8 | ... | ... | ... | 19.9 | 0.4 | 3.1 | 25.7 | 48.5 | 0.1 | ... | ... | ... | ... | ... |
| Rice bran oil ^e | ... | ... | 0.2 | 0.7 | ... | ... | ... | 27.6 | 0.5 | 4.1 | 47.5 | 16.1 | 0.2 | 0.8 | 0.3 | ... | ... | ... |
| Soybean oil | ... | ... | <0.1 | 0.3 | ... | ... | ... | 10.8 | 0.3 | 3.2 | 24.0 | 54.4 | 6.8 | 0.1 | 0.1 | 0.6 | ... | ... |
| Schleichera triluga (Kusum) | ... | ... | 0.4 | 0.2 | ... | ... | ... | 11.7 | 0.2 | 5.2 | 41.4 | 39.4 | 0.4 | 0.4 | 0.1 | 1.4 | 1.0 | ... |
| Schleichera oil | ... | ... | 0.3 | 0.2 | ... | ... | ... | 10.8 | 1.6 | 4.6 | 42.8 | 6.1 | ... | 22.0 | 9.2 | 1.4 | 1.0 | ... |
| Groundnut oil | 0.1 | 0.1 | 0.6 | 0.3 | ... | ... | ... | 13.3 | 0.3 | 2.1 | 47.8 | 29.2 | ... | 1.2 | 1.0 | 2.9 | 0.1 | 1.1 |
| Groundnut germ oil ^f | 0.1 | <0.1 | 0.2 | 0.1 | ... | ... | ... | 20.0 | 0.3 | 2.8 | 51.0 | 14.7 | ... | 1.5 | 1.6 | 3.4 | 0.2 | 1.6 |
| Groundnut leathings | ... | ... | 0.1 | 0.1 | ... | ... | ... | 24.6 | 0.3 | 2.4 | 54.1 | 16.8 | <0.1 | 0.1 | 0.7 | 0.1 | 0.1 | 0.1 |
| Groundnut oil ^g | ... | ... | 0.2 | 0.1 | ... | ... | ... | 2.6 | 0.2 | 1.1 | 12.9 | 13.8 | <0.1 | 0.7 | 7.3 | 1.0 | 48.7 | 0.1 |
| Muscard oil ^h | ... | ... | 0.2 | 6.4 | ... | ... | ... | 34.3 | 7.9 | 11.6 | 16.9 | 0.9 | ... | 1.0 | 1.5 | 2.4 | ... | ... |
| Shark-liver stearine ⁱ | ... | ... | 0.2 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |

^a 20:2-0.2, 16:2-0.6, 17:0-1.4, 17:1-0.2, 6.5% trans.

^b 13:2-0.1, 17:0-0.5, 17:1-0.2, 1.7% trans.

^c 16:2-0.1, 17:0-0.1, 12:1-0.1, 13:0-0.3 (12.8 ECL).

^d 11:0-0.2, 11:0-0.1, 12:1-0.1, 13:0-0.3 (12.8 ECL).

^e 11:0-0.2, 12:1-0.6, (12.7 ECL).

^f 11:0-0.1, 12:1-0.2, 13:0-0.6, 13:1-0.1, 13:2-0.2, 23:2-0.2.

^g 21:0-0.1, 21:1-0.2, 23:0-0.1, 23:1-0.4.

^h 16:2-0.2, 22:2-0.7, 24:1-0.3, 24:2-1.3.

ⁱ 17:0-2.1, 17:1-0.2, (16.8 ECL on monoene), 21:1-1.8 (20.8 ECL on monoene), 23:0-1.0, 23:1-1.3, 24:1-6.2, 25:1-0.8.

weight esters emphasize the inadequacy for these esters of the conventional plots and the importance of programmed-temperature operations (Graphs 1 and 2).

Similar plots of odd-carbon chain-length esters, 15:0, 17:0 obtained from isothermal runs of mutton tallow, beef tallow, groundnut germ oil, shark-liver stearine, etc., also conform to this line. Though the presence of odd-carbon chain-length acids are to be expected from lipids of animal and marine origin (29), pentadecanoic acid (15:0) is noted in quite a few vegetable oils (Table III), such as groundnut germ, rice bran, cottonseed, *Mesua ferrea*, etc. In fact, the presence of a number of these odd-carbon acids distinguishes groundnut germ oil from groundnut oil. Their occurrence in minor amounts in the oil from roasted groundnuts (24) has been reported but it is not stated whether the germs were removed from these.

Nonadecanoate (19:0) was not detected in any of the samples, presumably because it might have been eluted along with linoleate. Arachidate and behenate components of Kusum and mustard esters, when checked on this plot, had equivalent chain-lengths (ECL) (26,27), 19.9, 20.1, and 22, 22.2 respectively, thus confirming their identity by the comparative chromatogram technique. The variety of samples allowed the retention time of a number of monoenes in the range of 14-24 carbon atoms to be obtained for the first time. From their plot (Fig. 3, Graph 4) the evidence for the occurrence of eicosenoic acid in a number of oils such as sesame, rice bran, *Myristica kanarica*, Kusum, beef, and mutton tallows was obtained.

Docosenoic acid was noted in groundnut oil, its derivatives, and Kusum oil. Tetracosenoic (24:1) in mustard oil (21) has been confirmed. The last peak with shark-liver stearine was found to be pentacosenoic 25:1 (ECL25.1, Fig. 3). Odd-carbon monoenes were noted for the first time in groundnut, groundnut germ oil, beef, and mutton tallows, also with shark-liver stearine. For the identification of dienes most investigators (24) have used linoleate as the standard. Mustard and rapeseed oils were reported (21,25) to have C₂₀ and C₂₂ dienes (Graph 5, Fig. 3). The point corresponding to the logarithm of the retention time of the last peak with mustard oil was observed to fall on this line, thus was identified as a C₂₄ diene.

Peaks with all the new samples and some peaks in the other common oils and fats, which were examined, were checked with the various graphs of Fig. 3 for their identification and were recorded in Table III. Identities of two peaks with mutton tallow esters, eluting after myristate and having ECL 14.4 and 14.6 (Graph 2, Fig. 3), could not be ascertained.

Composition of Oils. All the values recorded in Table III are area percentages, which with the flame ionization detector, have been shown to be closest to the actual weight percentages of components (30-33). There is also a growing volume of evidence to indicate that the response of this detector is proportional to the combustible carbons in the chain (34-37). As the carboxyl group has no effect, corrections (33) have been suggested. These have a pronounced effect with low-molecular-weight fatty acids only where the ratio of carboxyl to the rest of the chain is high. Individual variations with different runs did not warrant corrections.

For each sample there was an average of at least two runs, and, in many cases, four to six runs were taken. Agreement between replicate runs was better

under programmed temperatures than under isothermal conditions. Comparative evaluations of compositions were restricted to oils and fats for which gas-liquid chromatographic analyses have been reported.

The laurate content of coconut oil which we analyzed was higher by about 6.0% than that reported by others (3,18), but caproate (10) content was lower by 3-5%. The rest of the components were in fair agreement though Mason and Walker (3) did not report any linoleic acid in their sample. They commented that this oil was the most difficult to analyze.

In the *Myristicaceae* species, *Myristica kanarica* differs from the others by having mostly saturated fatty acids, more than 90% of which are myristic and lauric. The unsaturated fatty acid content of this fat is less than 3%, and the chief component is oleic. *Myristica attenuata* and *Myristica magnifica* have more unsaturated fatty acids and are similar in their compositions with myristic, palmitic, and oleic as their major components. The former has more myristic and the latter, more oleic acids.

The Malayan palm oil of the present study agrees very well in its content of all components with that reported earlier (3,38). Sumatra (23) and Congo (39,40) palm oils have higher palmitic acid (46.8%, 46.5%, 44.4%) and lower oleic acid (37.6%, 38.9%, 38.6%) respectively as compared with the sample in this study. It thus appears that palm oils of different origins vary only to a small extent in their contents of palmitic, oleic, and linoleic acids and are composed of nearly the same number of component fatty acids. The major component fatty acids of *Vateria indica* fat are palmitic, stearic, and oleic, thus it is similar to cocoa butter and two tallows which are included in this study.

Tallow from different parts of beef cattle has been fairly well investigated (41-43). Compositions reported by Chacko et al. (43) are in great variance from those of the others (39,42) in the number of components, absence of odd-carbon chain acids, and distribution. Composition of beef tallow agrees well with that for the subcutaneous sample of Huston et al. (42) and Dahl (41) but has more stearic and oleic acids and less palmitic. Fat from different parts of the sheep have also been investigated by GLC (43,44) for their fatty acid composition. Mutton tallow comes close to that from the rib portion of Chacko et al. (43). Beef tallow is the more unsaturated of the two tallows and also contains lower *trans* acid, which is perhaps a reflection of the feed (45).

Mesua ferrea is an oleic acid-rich oil with stearic and palmitic acids as the other major components but is distinct from other vegetable oils for its small amounts of a number of odd-carbon chain acids.

Cottonseed oils from different parts of the world (3,22,23,46-48) have been analyzed for their fatty acid composition, most extensively by Bailey et al. (48). The commercial sample of this study agrees with these analyses in its number of components and major constituents but differs in the respective proportions. The higher linoleic acid content (54-61%) of the commercial American samples (3,22) is perhaps owing to winterization though some varieties of cottonseed have this acid in amounts of 52-57% (48). The Indian sample is lower in palmitic acid but higher in oleic acid content. Apart from these slight variations, it fits into the average composition of other samples (46,48,62).

Rice bran oils from different varieties (49) have

been analyzed for their composition, and only the presence of even-number carbon atoms (14 to 20) with fatty acids has been reported. In the commercial sample of the present study some low-molecular-weight, odd-carbon chain acids (11 to 15 carbon atoms) were observed. Soybean oil is an imported sample, and its composition agrees well with that reported by others (3,22,23,27,50). GLC confirmation of the presence (55) of a small amount of behenic acid (22:0) in this oil is presented for the first time. In a recent study of sesame oil (8) Kaufmann and Mankel reported the presence of 17:0 acid. Our study has indicated only even-number carbon atom acids from 8:0 to 22:0. In common with their studies, the presence of such unsaturated acids as palmitoleic, oleic, linoleic, and linolenic is confirmed. Eicosenoic and behenic acids are reported for the first time.

Kusum (*Schleichera trijuga*), though not a common oil, has been studied recently (51) for its composition, and a comparison of results shows that they have not reported evidence of lauric, myristic, behenic, and docosenoic acids though these taken together constitute about 3%. A feature of his oil is that, from palmitic acid on, every saturated acid is accompanied by one unsaturated acid and that the only polyenoic acid is linoleic acid. Groundnut or peanut is consumed as such or in the form of oil in large quantities throughout the world and thus has been extensively investigated for its fatty acid composition (3,11,19,20, 22,23,39,52). Several investigators (3,19,20,22,39,52) have mistakenly identified the arachidate peak for linolenate and eicosenate peak for arachidate because of the closeness of elution of these and thus have reported linolenic acid but no eicosenoic acid in their samples.

The absence of linolenic acid in groundnut (peanut), as observed in the present study, has been noted by others (11,24) though Jurriens et al. (23) report it to the extent of 0.3% along with arachidic (0.5%) and eicosenoic (0.7%) acids. Another discrepancy is that many (3,11,22,23,24) have reported high content for linoleic acid (36-47%), which Iverson et al. (24) suspect could be attributed to the winterization of samples. This finding is supported by the low content of linoleic acid (17-32%) in the laboratory-extracted oils from different varieties of peanut (19). In most respects the sample reported is similar to the Spanish variety noted by French (19) and in the number of components to that of Jurriens et al. (23). Caprylic (8:0) and capric (10:0) acids in small amounts are reported for the first time, and the presence of docosenoic acid (23) is confirmed.

Fatty acids of groundnut lecithin are richer in palmitic and oleic acids and poorer in linoleic acid; they are marked by high-molecular-weight acids in much smaller than and almost negligible proportions (total of 1.6%) than groundnut oil (total 6.3%). In contrast, groundnut germ oil contains these acids in about the same amounts as groundnut oil but is closer to lecithin in its content of oleic and linoleic acids. It is distinct from both because it contains numerous other acids, especially of odd-carbon chain length. An extensive study (21) of the *Cruciferae* species to which mustard belongs has brought out the presence of saturated even-number, carbon atom acids from 14:0 to 22:0 and such unsaturated acids as 16:1, 18:1, 18:2, 18:3, 20:1, 20:2, 22:1, 22:2, and 24:1, all of which find confirmation in the present study.

The presence of lignoceric (24:0) and tetracosadienoic 24:2 acids is observed for the first time. On

quantitative aspects our sample agrees in nearly all respects with that of *Brassica campestris* (field mustard 47% erucic) of Mikolajczak et al. (21) and that of Mattson and Volpenheim (20) (47% erucic acid) though Jakubowski et al. (53) have reported an average of 50% erucic acid for Russian samples. The shark-liver stearine, which is a solid deposited in the manufacture of medicinal grade shark-liver oils, is composed of a number of saturated and unsaturated fatty acids from 12:0 to 25:1. With the exception of linoleic acid, all the unsaturated acids have been identified as monoenes, as expected with a solid fraction. The dominant acid is palmitic, accompanied by oleic, stearic, palmitoleic, myristic, and tetracosenoic acids (24:1) in fairly large amounts. The odd-carbon chain acid (15:0, 15:1, 17:0, 17:1, 21:1, 23:0, 23:1) represents a total of 8%, which is also fairly large. The higher-molecular-weight acids 20:0 and above are present to the extent of 18% (total), also a characteristic of samples of marine origin.

Industrial Potential of Some New Oils and Fats. Of the myristica fats *Myristica kanarica* is the most promising as it is composed of 80% fatty matter and is wholly composed of saturated fatty acids. It is a good source of myristic and lauric acids. Presence of about 20% resinous and phenolic matter should not seriously affect its utilization for laundry soaps where rosin is included in the oil blends.

Myristica attenuata contains 40% resinous matter but can be similarly used as it is rich in myristic and palmitic acids. If such a method as liquid-liquid extraction can be developed to remove the resinous and other nonfatty materials, these two fats together will act as good sources for myristic acid, lauric acid (*M. kanarica*), and palmitic acids. *Myristica magnifica*, because of its high resin content (about 80%), will not be economical at all for commercial exploitation.

Mesua ferrea can serve as a good source of oleic acid, and if the resinous matter can be removed, it can be used for edible purposes also. *Schleichera trijuga* (Kusum) appears to be an excellent source for such acids as oleic, arachidic, and eicosenoic. If the cyanogenic material is removed, it can be substituted for liquid oils, such as groundnut oil in soap manufacture.

Vateria indica is the only fat which does not suffer from any of the drawbacks of these materials. Its light color, sharp melting-point, and similarity in component fatty acids to cocoa butter suggest that it can be used in blends with that fat or substitute for it in confectionery. Shark-liver stearine contains about 70% distillable fatty acids, of which palmitic acid is the major constituent. It thus can serve as a good source for this acid and hence for soap manufacture. As the total of 18 carbon fatty acids (stearic, oleic, and linoleic) is about 30%, it can be used for the manufacture of cosmetic-grade stearic acid (usually an eutectic of 55% palmitic and 45% stearic acid) after hydrogenation. Its fishy odor and the nonfatty

materials (about 30%) would have to be eliminated, of course.

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