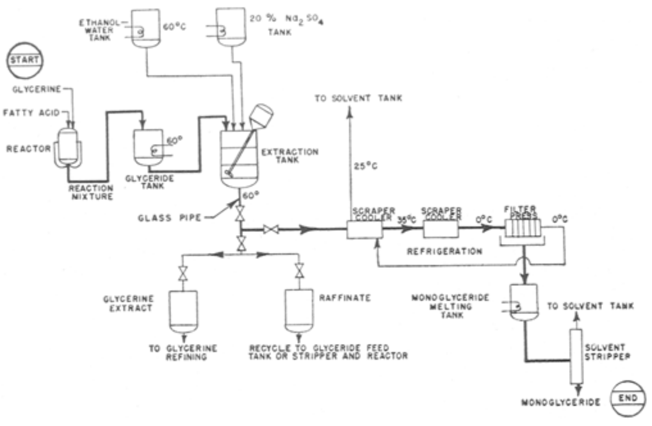

FIG. 7. Batch extraction process for monoglycerides.

tracts monoglyceride. This extract is then treated in the same manner as for the batch process. Solvent and raffinate are recycled, and final raffinate goes back into the monoglyceride reactor.

Both flowsheets indicate heat economy which can be obtained by recycling cooled and filtered extract countercurrently in the hot-extract heat exchanger.

Summary

Ternary-equilibrium data were obtained at 60°C. for mono- and dilaurin, and di- and trilaurin with aqueous alcohols. Distribution between phases and solvent selectivity are shown graphically. Variation of solvent polarity by water addition caused a shift in the phase boundary curve so that either Type 1 or Type 2 diagrams could be obtained.

Pure mono-, di-, and trilaurin mixtures, and commercial monoglycerides were studied as quaternary systems for monoglyceride distribution with 50 wt.-% aqueous ethanol. Pure and commercial systems showed similar distribution tendencies even with differences in molecular weight and degree of unsaturation.

Solvent selectivity data (β) for quaternary systems were predicted from ternary systems studied with a common solvent.

Aqueous ethanol will separate mixtures of mono-, di-, and triglycerides by selective liquid-liquid extraction; however the literature favors more complex systems based on two immiscible solvents.

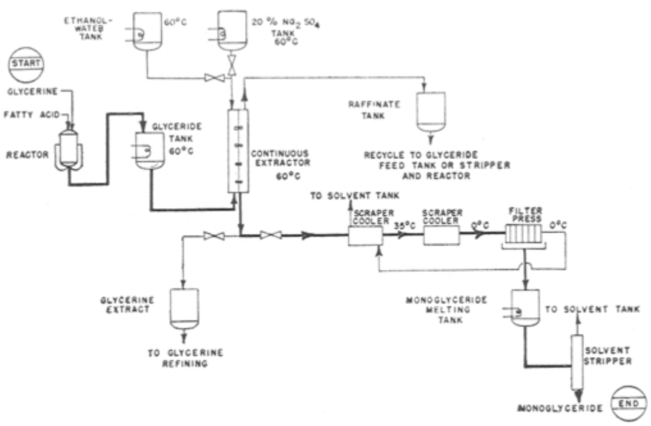

FIG. 8. Continuous countercurrent extraction for monoglycerides.

Continuous countercurrent extraction of commercial monoglycerides by 40% aqueous ethanol solution in a four-stage agitated column gave a 15% over-all stage efficiency. Cooling the extract to 0°C. precipitated 96.6% of the extract solids.

Flow diagrams were prepared for batch and continuous extraction processes.

REFERENCES

1. Averill, H. P., Roche, J. N., and King, C. G., J. Am. Chem. Soc., *51*, 866 (1929).
2. Ewell, R. H., Harrison, J. M., and Berg, L., Ind. Eng. Chem., *36*, 871 (1944).
3. Feuge, R. O., and Bailey, A. E., Oil and Soap, *23*, 259 (1946).
4. Feuge, R. O., and Gros, A. T., J. Am. Oil Chemists' Soc., *27*, 117 (1950).
5. Fischer, E., Bergmann, M., and Barwind, H., Ber., *53*, 1589 (1920).
6. Goldsmith, H. A., (Colgate-Palmolive-Peet Company), U. S. 2,651,646 (1953).
7. Grun, A. and Theimer, E., Ber., *40*, 1792 (1907).
8. Hilditch, T. P., and Rigg, J. C., J. Chem. Soc., 1774 (1935).
9. Kurt, N. H., Welch, E. A., and Kovarik, F. J., J. Am. Oil Chemists' Soc., *27*, 310 (1950).
10. Lawrence, E. A., Dr. Eng. Sc. Thesis, New York University, (1952).
11. Mattson, F. H., Baur, F. J., and Beck, L. W., J. Am. Oil Chemists' Soc., *28*, 386 (1951).
12. Monick, J. A., Dr. Eng. Sc. Thesis, New York University, (1955).
13. Pohle, W. D., Mehlenbacher, V. C., and Cook, J. H., Oil and Soap, *22*, 115 (1945).
14. Schlenker, E., and Gnaedinger, J., J. Am. Oil Chemists' Soc., *24*, 239 (1947).
15. Treybal, R. E., "Liquid Extraction," 1st ed., p. 20, New York, McGraw-Hill Book Company (1951).
16. *Ibid.*, p. 24.
17. *Ibid.*, p. 89.
18. Troy, A., and Bell, A. C., Proc. of T.G.A., *5*, May 17 (1946).
19. Zilch, K. T., and Dutton, H. J., Anal. Chem., *23*, 775 (1951).

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Molecular Distillation of Some Indian Vegetable Oils

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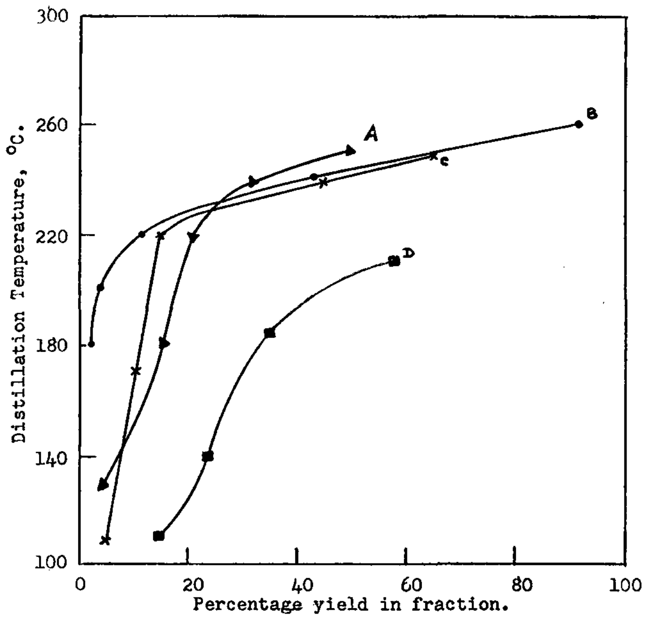
SEVERAL REPORTS indicate that fractionation of the triglyceride constituents of fatty oils by molecular distillation is poor compared to what is achieved by chromatography or low temperature crystallization. The advantage however of molecular distillation consists in the ease of separation of the unsaponifiable portion and free fatty acids from the bulk of the fatty material. These are found to be concentrated in the first few fractions. Oils molecularly distilled by previous investigators include those from fish (9), linseed (4), corn and soybean (13), cottonseed (14), menhaden (4), castor (4), sesame (6, 21), crude soybean (3), peanut (1), carrot (8), palm and fish liver (19), shark liver (10, 11), whale liver (15, 18), and rice (17, 22).

Rawlings (13), who carried out molecular distillation of soybean and corn oils, reported that the first two fractions were acidic, highly colored, and odoriferous while the major portion was pale and odorless. Riemenschneider *et al.* (14) also found that in the case of cottonseed oil most of the unsaponifiable matter was concentrated in the first fraction.

Patel and Sreenivasan (11) reported a thirty-fold concentration of vitamin A from Indian shark liver



(A) Undi oil; (B) Sesame oil; (C) Karanja oil; (D) Malkanguni oil.

FIG. 1. Elimination Curves.

oils. Sabashi (15) obtained molecularly distilled concentrate of vitamin A from whale liver oil. Bhat *et al.* (2) fractionated the antibacterial principle of undi oil (*Calophyllum inophyllum,* Linn), using a cyclic molecular still.

Several Indian inedible oils are characterized by dark color, strong odor, and high content of unsaponifiable matter and resist refining by conventional methods. Some of these are used in the indigenous (Ayurvedic) systems of medicine for their therapeutic properties which reside in their unsaponifiable portions. The effective separation of the latter and other impurities therefore becomes essential for the utilization of such oils. This report relates to the application of molecular distillation for obtaining unsaponifiable concentrates of certain inedible oils with a view to their analysis and identification.

The oils studied were karanja (*Pongamia glabra,* Vent), malkanguni (*Celastrus paniculatus,* Willd) and undi. Karanjin (16), the active principle responsible for curative action, and pongamol (12) were separated by crystallization from the first fraction of molecularly distilled karanja oil. Attempts to fractionate neem oil (*Azadirachta indica*) were not satisfactory since the distillate solidified on the condenser.

Sesamin, one of the components present in the unsaponifiable matter of sesame oil (*Sesamum indicum,* L) is claimed to possess high antitubercular activity (5) as well as marked synergistic activity with pyrethrins (6, 7). Therefore sesame oil, which is commonly used as an edible oil, was included in the present study.

Experimental

The oils were either authentic commercial samples or obtained by expression in a Carver hydraulic press. A cyclic falling film molecular still, type CMS-1000 (supplied by Distillation Products Inc.) was used. Distillations were carried out at a pressure of three microns. Fractions were collected at different ranges of temperature, and within each range residual oil was recycled four to six times to obtain good separation. All the cuts for a particular temperature were pooled together for analysis according to the methods of the American Oil Chemists' Society.

Results

The molecular distillation data and analytical values for the four oils are presented in Table I. The elimination curves (% yield in fraction *versus* distillation temperature °C.) are given in Figure 1.

Separation of Sesamin. The first semi-solid fraction rich in unsaponifiable matter obtained by molecular distillation of sesame oil was found to deposit, on holding, a solid portion which was removed from the rest of the liquid by decantation. The solid portion was washed with petroleum ether to remove the adhering fatty matter, dissolved in 95% ethyl alcohol, and crystallized. Recrystallization from 95% ethyl alcohol gave white needle-shaped crystals (m.p. 121° C.) of sesamin (reported m.p. 123°C.[20]).

Separation of Karanjin and Pongamol. The first fraction of molecularly distilled karanja oil, treated in a similar manner, gave white needle-shaped crystals (m.p. 158°C.) of karanjin which changed to orange-red in color on exposure to sunlight (reported m.p. 158°C.[16]).

Removal of alcohol from the filtrate after the separation of karanjin gave a residue, which on crystallization from ethyl ether yielded yellow rhombic prisms (m. p. 124° C.) that gave the characteristic tests of pongamol (reported m.p. 128–129° C. [12]).

Discussion

The first few fractions of the four oils were highly acidic. They were rich in unsaponifiable matter, except in the case of undi oil. The intermediate fractions were pale in color and had little odor while the first fractions and the residues were deep-colored. The odoriferous matter was also concentrated in the first fractions. The observations are in agreement with those reported by others. However, in the case of undi oil, while the free fatty acids had concentrated in the first three fractions, the unsaponifiable matter distilled off rather uniformly. Only malkanguni oil fractions showed considerable differences in saponification and iodine values, indicating some fractionation of its glycerides.

Sesame oil gave a small fraction (nearly 3.5%) which was volatile below 200°C. This was rich in free fatty acids and unsaponifiable matter. Sesamin could easily be separated from these concentrates. The first four fractions of sesame oil obtained up to 240°C. gave a positive Baudouin test; such a test was not obtained with the major fraction (nearly 50%) distilling between 240–260°C. or with the residue. In contrast to sesame oil a considerable portion (nearly 34%) of malkanguni oil was volatile below 185°C.

Summary

1. Karanja, malkanguni, undi, and sesame oils were molecularly distilled, and the fractions obtained were characterized for their physical and chemical constants.
2. Generally, the first few fractions were found to be rich in odor, free fatty acids, and unsaponifiable matter.

TABLE I

Physical and Chemical Characteristics of Oils and Their Molecularly Distilled Fractions

Fraction No.	Temperature range (°C.)	Weight % of original oil	Nature and color of the fraction	Acid value	Iodine value (Wijs)	Saponification value	Refractive index	Unsaponifiable matter (%)
1	2	3	4	5	6	7	8	9
Karanja oil (*Pongamia glabra*, Vent)								
1	Below 110	4.6	Semi-solid; lemon yellow	74.1	74.1	........[g]	....	46.1[e]
2	110–170	5.8	Solid; orange-yellow	36.7	56.6	........[g]	....	59.7[e]
3	170–220	4.9	Viscous; reddish orange	5.5	84.9	........[g]	1.4943[b]	9.8[e]
4	220–240	28.7	Liquid; yellow	0.5	90.9	193.6	1.4688[b]	1.9[e]
5	240–250	19.8	Liquid; pale yellow	0.3	93.3	194.6	1.4678[b]	0.4[e]
6[d]	....	36.2	Liquid; dark orange	0.3	90.6	191.5	1.4678[b]	0.3[e]
Karanja oil	....	......	Liquid; brownish orange	5.4	87.2	188.0	1.4803[b]	6.2
Malkanguni oil (*Celastrus paniculatus*, Willd)								
1	Below 110	14.0	Solid; whitish yellow	189.1	75.0	228.6	1.4482[c]	12.6[f]
2	110–140	9.2	Semi-solid; yellow	117.1	79.8	257.6	1.4582[c]	4.3[f]
3	140–185	10.7	Viscous liquid; orange-yellow	25.2	71.8	305.7	1.4728[c]	3.2[f]
4	185–210	23.2	Liquid; orange-yellow	3.9	105.9	264.6	1.4610[c]	2.4[f]
5[d]	....	42.9	Liquid; dark brown	3.9	100.8	227.8	1.4600[c]	1.9[f]
Malkaguni oil	....	......	Liquid; reddish brown	49.3	92.6	242.8	1.4601[c]	3.9[f]
Undi oil (*Calophyllum inophyllum*, Linn)								
1	Below 130	3.9	Solid mass, greenish yellow	183.2	91.6	199.2	1.4570[c]	1.0[f]
2	130–180	11.5	Jelly-like viscous; yellow	136.1	100.9	192.8	....	2.4[f]
3	180–220	4.9	Viscous liquid; orange-yellow	76.1	107.7	195.2	1.4947	2.6[f]
4	220–240	11.0	Liquid; dark yellow	7.3	86.1	194.6	1.4605[c]	1.3[f]
5	240–250	17.8	Liquid; pale yellow	1.3	86.4	193.2	1.4559[c]	0.2[f]
6[d]	....	50.9	Liquid; brownish black	0.6	86.6	191.5	1.4550[c]	1.4[f]
Undi oil	....	......	Liquid; dark green	27.6	92.3	197.1	1.4640[c]	1.3[f]
Sesame oil (*Sesamum indicum*, L.)								
1[a1]	Below 180	1.7	Semi-solid; orange-yellow	74.2	94.3	107.8	....	49.2[e]
2[a1]	180–200	1.8	Semi-solid; orange-yellow	10.3	104.2	142.3	....	30.2[e]
3[a1]	200–220	7.1	Liquid; pale yellow	0.6	107.4	193.5	1.4689[b]	2.3[e]
4[a1]	220–240	31.7	Liquid; pale yellow	0.2	109.8	200.7	1.4679[b]	1.4[e]
5[a2]	240–260	49.0	Liquid; pale yellow	0.1	111.2	200.4	1.4680[b]	0.2[e]
6[d, a2]	....	8.7	Liquid; blackish yellow	0.1	110.8	201.0	1.4699[b]	0.1[e]
Sesame oil	....	......	Liquid; yellow	1.6	109.4	193.7	1.4694[b]	1.2[e]

[a1] Baudouin test, positive. [a2] Baudouin test, negative. [b] At 30°C. [c] At 60°C. [d] Residual oil. [e] Ethyl ether. [f] Petroleum Ether. [g] Titration end-point could not be judged.

3. Sesamin could be isolated from the first fraction of molecularly distilled sesame oil by crystallization.
4. Karanjin and pongamol were similarly separated from the first fraction of molecularly distilled karanja oil.
5. With malkanguni oil there was some fractionation of the glycerides.
6. Elimination curves of karanja, malkanguni, undi, and sesame oils are given.

REFERENCES

1. Bailey, A. E., Oliver, G. D., Singleton, W. S., and Fisher, G. S., Oil and Soap, *20*, 251 (1943).
2. Bhat, S. G., Kane, J. G., and Sreenivasan, A., J. Am. Pharm. Assoc. (Sci. ed.), *43*, 543 (1954).
3. Detwiler, S. B. Jr., Bull, W. C., and Wheeler, D. H., Oil and Soap, *20*, 108 (1943).
4. Embree, N. D., Chem. Revs., *29*, 317 (1941).
5. Gangadharan, P. R. J., Natarajan, S., Wadhwani, T. K., Giri, K. V., Narayanamurty, N. L., and Iyer, B. H., J. Ind. Inst. Sci., *35*, 69 (1953).
6. Haller, H. L., McGovran, E. R., Goodhue, L. D., and Sullivan, W. N., J. Org. Chem., *7*, 183 (1942).
7. Haller, H. L., La Forge, F. B., and Sullivan, W. N., J. Econ. Entomol., *35*, 247 (1942).
8. Heftmann, E., J. Am. Oil Chemists' Soc., *24*, 404 (1947).
9. Hickman, K. C. D., Ind. Eng. Chem., *29*, 1107 (1937).
10. Komori, S., Kikuchi, S., Hachiya, K., Shinsugi, A., and Agawa, T., J. Chem. Soc., Japan, Ind. Chem. Sect., *54*, 225 (1951).
11. Patel, S. M., and Sreenivasan, A., J. Sci. & Ind. Res. (India), *9B*, 31 (1950).
12. Rangaswami, S., and Seshadri, T. R., Ind. J. Pharmacy, *3*, 3 (1941).
13. Rawlings, H. W., Oil and Soap, *16*, 231 (1939).
14. Riemenschneider, R. W., Swift, C. E., and Sando, C. E., Oil and Soap, *17*, 145 (1940).
15. Sabashi, K., Nakayama, A., and Hirao, S., Bull. Japan Soc. Sci. Fisheries, *16*, 46 (1950).
16. Subbarao, N. V., Veerabhadrarao, J., and Seshadri, T. R., Proc. Ind. Acad. Sci. (India), *10A*, 65 (1939).
17. Tetsujiro Obara and Keijiro Oka., J. Japan. Soc. Food Nutrition, *3*, 138 (1951).
18. Toshio Agawa, Suburo Komori, and Yoichi Nishimura, J. Oil Chemists' Soc., Japan, *1*, No. 1, 12 (1952).
19. Ueno, S., Komori, S., and Agawa, T., J. Chem. Soc., Japan, Ind. Chem. Sect., *52*, 67 (1949).
20. Villavecchia, V., and Fabris, G., Z. Angew. Chem., *17*, 505 (1893).
21. Wachs, W., Z. Lebensm-Untersuch. U. -Forsch, *96*, 168 (1953).
22. Yamakita, I., Araki, Y., and Shimamoto, S., Bull. Inst. Chem. Res., *24*, 81 (1951).

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Effect of Maleic Hydrazide Applied to the Cotton Plant on the Development of Free Fatty Acids in the Seed

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MALEIC HYDRAZIDE, a remarkably consistent plant growth inhibitor among many species, has been applied to cotton plants in concentrations of 0.5 to 1.0% (3) and 0.48% (8) as an inhibitor of secondary growth. It has been applied to cotton plants by many other investigators (5, 6, 7, 9, 10, 15, 16, 17), but in none of these studies have the effects of maleic hydrazide on the storage properties of the seed been reported. In a field experiment on cotton plants, considerably higher concentrations of maleic hydrazide than those hitherto reported were applied prior to and at defoliation to determine their effects on secondary growth. Seed harvested from these plants was made available to investigators at

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