chilled 2.03 or 5.28% mixtures at 33.6°C. for 30 minutes was sufficient to permit extensive transformation of the crystals to the high-melting form, as evidenced by the lack of any perceptible melting at 44.6°C. in the 5.28% mixture, whereas prior to this treatment the shock-chilled sample melted completely at this temperature. After tempering complete melting did not occur until a temperature of 52-53°C. was reached. The shock-chilled 2.03% mixture tempered in the same manner was capable of withstanding 38°C. without any oil separation.

As shown in Table I, the tempered mixtures range from translucent liquids to opaque rigid plastic substances, depending upon the hard fat content and the temperature. This is in harmony with the general behavior of such materials (2b). The 5.28% mixture however may resemble either a rigid, translucent, plastic fat, or a partially melted plastic fat. Agitation during or after tempering produces the latter condition, which however is unstable, requiring an undetermined period of time to reset. If the material is not worked, the former condition results. Evidently there is a range of concentrations in the neighborhood of 5% where this thixotropic behavior (1c) is possible. Those mixtures containing less than 2% hard fat were always semiplastic or viscous liquids, depending on the hard fat content, and never set up as rigid plastic fats. In none of the tempered mixtures above 2% was separation of clear oil observed at room temperature (25-30°C.) even when the mixture was centrifuged for 20 minutes at 400 times gravity.

This information indicates that it should be possible to stabilize such a mixture by tempering in this manner, possibly due to the predominance of the higher-melting modification in the tempered product. The product would be expected to retain the crystal fineness (2c) essential for improved palatability and yet would withstand ordinary storage without separation of the oil.

Slowly cooled mixtures. All the mixtures given in Table I when melted and gradually cooled show grainy characteristics in the solidified hard fat. This was especially apparent in those hard fat concentrations of 10% or less where the granules of fat crystals tended to settle, especially with centrifugation, to give a clear supernatant oil. At concentrations above 10% the quantity of hard fat separating is large enough to mask any liquid oil, even under centrifugation. Agitation during the cooling period caused no perceptible difference in this behavior.

Conclusions

Data obtained on the solubility of hydrogenated peanut oil in refined peanut oil and the behavior of the mixtures on cooling indicate that freedom from oil separation on storage is largely determined by the nature as well as the amount of solid crystals present in the oil. The results suggest that the best procedure for prevention of oil separation would involve shock-chilling the molten mixture to produce the finely divided metastable crystalline modification followed by tempering at such a temperature as to permit transformation of the crystals into the more desirable higher-melting form without changing the finely divided state necessary for improved palatability.

The data imply that under controlled conditions any amount of the high-melting modification of the hard fat incorporated in peanut oil above the solubility temperature in excess of 2% should produce a mixture free from oil separation under average storage conditions. The choice of the actual concentration of the hard fat, above the minimum amount, would depend upon the degree of plasticity desired. Ambient temperature to which the mixture is likely to be subjected will influence to a considerable extent the selection of the hard fat content. The information obtained is of fundamental importance in connection with the problem of oil separation in peanut butter.

REFERENCES

1. Bailey, A. E., "Industrial Oil and Fat Products," 2nd ed., Interscience Publishers Inc., New York, N. Y. (1951); a) pp. 210-216; b) pp. 215-216; c) p. 218; d) p. 277.
2. Bailey, A. E., "Melting and Solidification of Fats," Interscience Publishers Inc., New York, N. Y. (1950); a) pp. 22-23; b) p. 291; c) p. 305.
3. Freeman, A. F., and Singleton, W. S., Peanut Journal and Nut World, *31*, (4), 23 (1952).
4. Hofgaard, K., "Dilatometriske Fedtstof-Undersøgelser," Dissertation, Danmarks Tekniske Højskole, G. E. C. Gad Forlag, Copenhagen, 1938, Table 40.
5. Holman, George W., and Quimby, Oscar T. (to the Procter and Gamble Company), U. S. Patent 2,521,219 (September 5, 1950).
6. Magne, F. C., and Skau, E. L., J. Am. Chem. Soc., *74*, 2628 (1952).
7. Mitchell, P. J. Jr., U. S. Patent 2,562,630 (July 31, 1951).
8. Singleton, W. S., and Freeman, A. F., Food Research, *15*, 297 (1950).
9. Stockton, Frank Webb, U. S. Patent 1,395,934 (November 1, 1921).

[Received October 19, 1953]

The Eicosenoic Acid of Cameline Seed Oil

J. D. von MIKUSCH and URSULA DYLLA, F. Thörl's Vereinigte Harburger Oelfabriken A. G., Hamburg-Harburg, Germany

FROM a previous investigation (1) it was concluded that the seed oil of *Camelina sativa*, Crantz, contains little if any erucic acid. This result contradicts statements found in a number of textbooks on oils which have been traced back to de Negri and Fabris (2) and older literature. It is also exceptional with regard to the observation pointed out by Hilditch (3) that all *Cruciferae* seed fats previously investigated, with the exception of *Hesperis matronalis*, contain 40-50% erucic acid.

Instead cameline seed oil was found to contain a considerable proportion of an eicosenoic acid in addition to linolenic, linoleic, oleic, saturated, and a monounsaturated hydroxy acid, the monounsaturated acids totalling 42.8%, the polyunsaturated acids 48.3% with more than twice as much linolenic as linoleic acid, and the saturated acids 8.9%. In addition to eicosenoic acid there was evidence of the presence of some higher monounsaturated acids not giving however the characteristic derivatives of erucic acid. The presence of eicosenoic acid became apparent when the dioxy acid (acid value 160.1), formed upon oxidation of cameline fatty acids, was compared to that obtained upon similar treatment from rape seed oil and was verified by the isolation upon elaidination of an acid melting at 43.5°C. having an acid value of 180.7 and an iodine value of 77.3.

According to an almost simultaneous publication by Swedish workers (4), the acids of cameline seed or dodder oil were calculated to contain 13.8% eicosenoic and 3.2% erucic acid in addition to 33.4% linolenic, 14.5% linoleic, 23.9% oleic, 2.4% hexadecenoic, and various saturated fatty acids. Except for the absence of a hydroxy acid and the presence of a minor percentage of erucic acid their overall result agrees remarkably well with the author's since it adds up to 43.3% monounsaturated, 47.9% polyunsaturated, and 8.8% saturated acids.

Since eicosenoic acid is not a usual component of vegetable oils, a specimen of it was isolated and analyzed in the present investigation.

Isolating the Acid

Upon treating 400 g. of the fatty acids of cameline seed oil of German origin (1) in alcoholic solution with an excess of boiling lithium hydroxide and cooling to room temperature, lithium soaps were precipitated which, after one recrystallization from 50% ethyl alcohol, yielded approximately 50 g. of fatty acids, saponification value 180.2, iodine value 63.3. After removing some 20 g. of mainly saturated fatty acids (I. V. 17.5) by a lead salt precipitation, 22 g. of a concentrate of monounsaturated acids, iodine value 93.4, saponification value 166.2, $n_D^{25} = 1.4680$, containing 3% of saturated acids according to a modification of the Bertram method (5) resulted.

After the remaining saturated acids had been removed by treating with mercuric acetate according to Bertram (6), the liquid acids were esterified with methanol and fractionated by distillation *in vacuo*. About half of the ester distilled at 186 ± 1°C. at 2 mm. Hg. The fatty acid obtained from this distillate melted at 10°C. Repeated recrystallizations from acetone and petroleum ether (60-80°C.) raised the melting point to a constant value when determined on a Kofler micro hot plate (7).

Properties and Structure

The thus purified eicosenoic acid had:

melting point	21.5-22.5°C.
density 25°/4°	0.8826
refractive index n_D^{25}	1.4598
iodine value (Wijs)	80.8 (calc. 81.7)
acid value	181.2 (calc. 180.7)

From these data the specific refraction is found to be 96.3 or 0.7 units above the value calculated according to Eisenlohr.

Elaidination with nitrous oxide vapors gave a trans-acid of

melting point	42.8-43.5°C.
acid value	180.0 (calc. 180.7)

Mild oxidation with 1% aqueous $KMnO_4$ solution at 0° gave dioxy arachidic acid with

melting point	131-132°C.
acid value	162.5 (calc. 162.8)

Hydrogenation with Raney-nickel in hexane gave a saturated acid with

melting point	74.2-75°C.
acid value	178.0 (calc. 179.5)

and no melting point depression with arachidic acid.

Destructive oxidation with $KMnO_4$ in boiling acetone gave mainly undecanedioic acid, melting at 110° with an acid value of 520.5 (calc. 519.2).

From this there follows that the double bond is located between the eleventh and twelfth carbon in the chain counting from the carboxyl group. The acid therefore has the structure of normal Δ^{11}-eicosenoic acid-1 and is identical with the acid which has been found in jojoba wax by British and American authors (8, 9).

Summary

The eicosenoic acid previously discovered in cameline seed oil (1) was isolated and identified. It melts at 22.5°C. and yields an elaidinated acid melting at 43.5°C. and a dioxy derivative melting at 132°C. By its hydrogenation to arachidic acid and destructive oxidation to undecanedioic acid it was shown to be normal Δ^{11}-eicosenoic acid-1 like the acid in jojoba wax.

REFERENCES

1. von Mikusch, J. D., Farbe und Lack, *58*, 402-406 (1952); Chem. Abst. *46*, 11715-6 (1952).
2. de Negri, G., and Fabris, G., Zeitschr. f. analyt. Chem., *33*, 555 (*1894*).
3. Hilditch, T. P., "The Chemical Constitution of Natural Fats," 2nd ed., p. 183, London, 1947.
4. Holmberg, J., and Sellmann, G., Svensk Kem. Tid., *64*, 270-9 (1952); Chem. Abst. *47*, 2514 (1953).
5. Pelikan, K. A., and von Mikusch, J. D., Oil and Soap, *15*, 149-150 (1938).
6. Bertram, S. H., Rec. Trav. *chim.* Pays-Bas, *46*, 397 (1927).
7. Kofler, L., and Kofler, A., "Mikromethoden," Universitätsverlag Wagner G.m.b.H., Innsbruck, 1948.
8. McKinney, R. S., and Jamieson, R. S., Oil and Soap, *13*, 289 (1936).
9. Green, T. G., Hilditch, T. P., and Stainsby, W. J., J. Chem. Soc., *1936*, 1750.

[Received November 6, 1953]

Letter to the Editor

Kartha (1) has reported that fully saturated glycerides (F.S.G.) show on progressive dilutions with other glycerides (non-F.S.G.) an even series of decrements in melting point and solidifying point and that these decrements are independent of the degree of unsaturation of the non-F.S.G. portion of the mixture. These conclusions appear to us to be of such wide significance that they merit the fullest investigation, and we are therefore reporting work done in this laboratory on these lines.

TABLE I

Percentage of F. S. G.	Melting point	Solidifying point
	°*F.*	°*F.*
100	142.5	136.5
50	135	128.5
25	129	118.5
12.5	122	105.5
6.3	115	88.5
3.2	108	80.5

We have had no success in using the technique of Kartha, involving the use of a Thiele tube as a water bath, and therefore adopted the capillary tube (clear) melting point procedure (2) and a method of determining solidifying point similar to that used for determining solidifying point of fatty acids in the A.O.C.S. Titre Test method (3). The F.S.G. was a sample of hydrogenated tallow (I.V. 0.3), and for