Alkali-Isomerized Linoleic Acid*

D. E. TERRY and D. H. WHEELER
General Mills, Inc., Minneapolis, Minn.

ALKALI-INDUCED isomerization of polyene unsaturated fatty acids has become a subject of some interest in the last few years. It has become the basis of a method of analysis of mixtures of unsaturated fatty acids (1, 2, 3), and the possibility of commercial utilization of the isomerized acids is indicated by patents and publications on the subject (4, 5, 6, 7). An excellent review on "Ultraviolet Absorption Studies of Drying Oils" by Kass (8) summarizes the present knowledge concerning alkali-induced isomerization of unsaturated fatty acids and the diagnosis of the mixture of conjugated acids produced by this treatment. Kass points out that since all available pure conjugated octadecadienoic acids exhibit values of $K = 115$ at the peaks of their absorption curves (2340 Å), the development of a maximum specific absorption coefficient of 87.1 at 2340 Å in isomerized linoleic acid indicates approximately 75%, $\left(\frac{87.1}{115}\right)$, conversion to conjugated forms, among which the Δ 10,12 isomers predominate, whereas the Δ 9,11 acids are present in only small concentrations. The 25% of the acid remaining unconjugated is stated by Kass to be non-identical with the original linoleic acid, but is probably geometrically isomerized.

This 25% of altered linoleic acid is not due to polymerization of the conjugated linoleic acid since, as will be shown later, the isomerized acids can be distilled as methyl esters with a residue of not over 2 to 3%, under conditions which minimize prolonged or excessive heating. The nature of this 25% of altered linoleic acid has not been established. Kass states that it is probably geometrically isomerized acid. It is also possible that it is a form in which the double bonds have shifted to positions such that two or more CH_2 groups separate them or that a triple bond has been formed instead of the two double bonds. The conjugated linoleic acids produced have not been adequately characterized, and so their identities with known, pure Δ 9,11 or Δ 10,12 linoleic acids have not been established.

Kass, in an unpublished paper presented at the 103rd meeting of the American Chemical Society, reported that alkali isomerization of linoleic acid was found to result in three geometrically isomeric Δ 10,12 linoleic acids, melting at 57°, 45°, and 8°. The 57° melting acid was possibly identical with a 57° melting Δ 10,12 linoleic acid reported by Von Mikusch (14) from alkali-isomerized dehydrated castor oil acids.

Bradley (6) indicates that some degree of separation of the conjugated acids from the non-conjugated acids of isomerized soy and linseed acids can be obtained by fractional distillation. He showed that isomerized linseed acids containing 33.5% of dienoically conjugated acids and 5.5% of trienoically conjugated acids afforded a 26.1% fraction which contained 44.9% of dienoically conjugated acids and 8.7% of trienoically conjugated acids as well as a 2.2% fraction containing 33.6% and 17.5% respectively of di- and trienoically conjugated acids. Isomerized soy acids which contained 35.7% of di- and 1.45% of trienoically conjugated acids were also fractionally distilled by Bradley. He obtained a 35.0% fraction showing 42.4% and 2.12% of di- and trienoically conjugated acids and a 1.6% fraction containing 44.9% and 7.78% respectively of di- and trienoically conjugated acids. The degree of separation indicated by these data is significant, but not very striking, since the enrichment in conjugated acids was due in part to removal of shorter chained acids incapable of isomerization.

Anderson and Wheeler (9) fractionally distilled the methyl esters of tall oil fatty acids and observed that the conjugated linoleate present accumulated in a fraction above the esters of normal C_{18} acids and concluded that the conjugated linoleate was somewhat higher boiling.

In view of these indications of the possibility of separating the conjugated and unconjugated fatty acids in an alkali-isomerized fatty acid mixture by fractional distillation, the present study was made to determine the degree of separation possible by efficient fractionation of a mixture of conjugated and non-conjugated C_{18} fatty acids as methyl esters. A remarkably good separation was obtained. The methyl esters of alkali-isomerized C_{18} cottonseed oil acids were fractionally distilled. A composite of first fractions amounting to 29% was obtained with almost no conjugation and was apparently 90% or more methyl oleate. Intermediate fractions of about 19% had increasing conjugation. The main conjugation-rich fractions amounted to 48% and contained 75% conjugated methyl linoleate and about 95% total methyl linoleate.* Apparently the esters of altered linoleic acids as well as those of the conjugated linoleic acids produced by alkali isomerization boil higher than the esters of normal C_{18} acids. Fractional distillation of the methyl esters of alkali-isomerized pure linoleic acid confirmed these facts.

Experimental

Cottonseed oil was converted to methyl esters by alkali-catalyzed alcoholysis. The esters were fractionated through a Podbielniak Hyper-Cal fractionating column at 5 mm. head pressure, 26 mm. pressure drop, and 15:1 reflux setting. When the break between C_{16} and C_{18} acid ester was approached, the reflux setting was increased to 40:1. After complete removal of esters of acids shorter than C_{18} the residue of C_{18} esters was recovered and was alkali-isomerized by heating in an equal weight of diethylene glycol with a 10% excess of NaOH at 200° for 15 minutes. Bradley (6) has shown that these conditions produce maximum conjugation. The isomerized acids were recov-

---

* Paper No. 69, Journal Series, Research Department, General Mills, Inc. (Presented at the 19th Annual Fall Meeting of the American Oil Chemists' Society, Nov. 7-9, 1945, in Chicago, Ill.)

* Linoleic acid is used to designate any octadecadienoic acid. Suitable adjectives are used to designate the source or nature of specific materials.

ered and converted to methyl esters. Distillation of a small portion of the esters from a simple alembic flask without a column under a vacuum of less than 1 mm. afforded a residue of only 3%, indicating substantial absence of polymerized esters in this material.

A portion of the esters (approximately 200 gm.) was then subjected to careful fractional distillation in the same column under the same conditions as above with a reflux ratio of 40:1. The data on the various fractions are shown in Table I. The isomerized ester before fractionation contained 49.4% of conjugated methyl linoleate [calculated from the value of 115 for specific alpha of a pure △ 9,11 or △ 10,12 linoleic acid, according to Kass (8)]. The esters before isomerization contained about 62.4% of linoleate (calculated from specific alpha of the isomerized ester, using the constant of 86.8 found on the methyl ester of alkali-isomerized debromination linoleic acid under the same conditions).

TABLE I.

Fractional Distillation of Methyl Esters of Alkali-Isomerized C_{18} Cottonseed Acids.

Fraction	% Vol.	n_D^{25}	Specific alpha*	Iodine Number	
				Wijs rapid (10)	Woburn total (11)
Original	......	1.4649	54.1	......	116.3
1	4.8	1.4510	0.5	......	......
2	4.8	1.4508	......	90.5	91.3
3	4.8	1.4508	......	......	......
4	4.8	1.4508	0.5	......	......
5	4.8	1.4506	......	......	......
6	4.8	1.4508	7.1	......	......
7	4.8	1.4573	31.6	......	115.6
8	2.4	1.4641	61.0	......	......
9	2.4	1.4677	74.1	......	......
10	2.4	1.4694	79.9	......	......
11	2.4	1.4702	82.6	......	......
12	2.4	1.4711	84.0	......	182.5
13	40.7	1.4712	81.4	126.9	183.0
14 (res.)	13.6	1.4821	10.9	......	......

*At 2340 Å, 1 gm. per 1,000 c.c., alcohol solvent.

Fractions 1 through 12 were distilled as described. Since refractive index indicated that the main break in the distillation had been passed, the residual esters in the still were recovered and distilled in a simple flask without a column at less than 1 mm. pressure. Fraction 13 is the distillate from this operation and 14 is the undistilled residue consisting of polymerized linoleate. This procedure was followed to reduce the thermal polymerization which would have been caused by the longer heating involved in complete distillation through the column. Fractions 1 through 6 represent about a 29% yield of material which is very low in conjugated linoleate and has an iodine number and refractive index indicating rather pure methyl oleate. Fractions 7, 8, and 9 represent intermediate fractions of increasing conjugation content. Fractions 10 to 13 inclusive represent the conjugation-rich material. A composite of these fractions represents a 48% yield of material which is 75% conjugated methyl linoleate. The Woburn total iodine number is about 6% above theoretical (172.9). However, the same method applied to methyl esters of conjugated debromination linoleic acid also gave values 6 to 11% above theory (see data below). In view of these facts it is reasonable to conclude that these conjugated-rich fractions are at least 95% in total linoleate, with 75% of conjugated linoleate present. It is therefore evident that the methyl esters of altered linoleic acids as well as those of the conjugated linoleic acids produced by alkali isomerization boil higher than the normal C_{18} methyl esters such as oleic. It has been demonstrated by Norris and Terry (12) that separation of methyl oleate and normal methyl linoleate is quite incomplete by fractional distillation, even in a very efficient column (the same column used in the present work), and that the linoleate is concentrated in the lower boiling fractions—the opposite of what is observed in the present work with isomerized ester.

A comparison of the conjugate-rich fractions from the above fractionation with the methyl ester of alkali-isomerized pure linoleic acid was desired. A sample of debromination methyl linoleate was prepared from tetrabromostearic acid, m.p. 114-114.5; (from corn oil acids) by debromination with zinc in methanol followed by esterification with sulfuric acid catalyst. The esters were then washed free of mineral acid and vacuum distilled. Although Frankel and Brown (13) have shown that this procedure apparently produces a linoleic acid which contains approximately 12% of some acid isomeric with the normal acid, the esters were considered pure enough for the purpose. They were isomerized by the same procedure as described above, converted to methyl esters and distilled in a simple flask at less than 1 mm., with a residue of 2%. The distilled esters showed a specific alpha of 86.8, which, when calculated to free acid is 91.1 or about 5% higher than the value of 87.1 found by Mitchell (1) in his analytical method at 180° for 25 minutes. The methyl esters were fractionated in the same manner as described for the methyl esters of isomerized C_{18} cottonseed acids, with the results shown in Table II.

TABLE II.

Fractional Distillation of Methyl Ester of Alkali-Isomerized Debromination Linoleic Acid.

Fraction	% Vol.	n_D^{25}	Specific alpha	Iodine No., Woburn
1	7.6	1.4661	52.5	182.5
2	8.9	1.4696	76.4	185.9
3	6.6	1.4710	82.7	....
4	9.9	1.4713	85.5	184.9
5	10.0	1.4716	88.2	....
6	8.0	1.4716	88.7	184.3
7	38.2	....	87.8	192.1
8 (res.)	10.8	....	17.6	....

Fractions 1-6 inclusive were distilled as described. Fraction 7 was obtained by distillation of the residue after fraction 6 from a flask without a column, at less than 1 mm. pressure. The small amounts of fractions 1 and 2 and their relatively high values for specific alpha, and the fact that subsequent fractions have values of specific alpha within 1-2 units of the original ester indicate that the ester of the conjugated linoleate and of the altered linoleate are so close in boiling points that they are not separable to any appreciable extent by this method of fractionation. The Woburn iodine values are 6-11% above theory. No explanation of this discrepancy is offered at the present time. The similarity of fractions 3-7 in Table II to the conjugation-rich fractions in Table I is further evidence that the latter represent quite pure methyl linoleate, being a mixture of about 75% of conjugated linoleate and some 20% of altered linoleate.

The boiling points of fraction 7, Table II were determined at several pressures, in the apparatus previously described by one of us (12). Table III shows these results with those of the methyl esters of normal C_{18} acids for comparison.

TABLE III.
Boiling Points of Methyl Esters of C_{18} Acids.

Pressure mm.	Boiling Point °C. of Methyl Ester			
	Stearic	Oleic	Normal Linoleic	Isomerized Linoleic
2	170	166.5	163	175.5
5	189.5	186	182.5	193
10	204.5	201	198	210
20	222	218.5	215	223.5

It will be seen that the isomerized linoleate boils 5° to 9° above oleate, and 8.5° to 12.5° above normal linoleate.

The degree of separation which is reported above between oleic and isomerized linoleic esters requires quite efficient fractionation. The esters of alkali-isomerized C_{18} cottonseed acids were distilled under the same conditions, except that a reflux setting of 10-1 was used instead of 40-1, and the take-off rate was consequently about 4 times as great. In this case the first fractions contained about 15% of conjugated linoleate and the conjugate-rich fraction contained only about 63.5% of conjugated linoleate. When the free acids were similarly distilled at 10-1 reflux setting, the separation was quite similar, but the residue of polymerized linoleic acid was greater because of the higher pot temperature. When the free acids were fractionally distilled at 40-1 reflux setting, with the longer heating time and higher temperature involved, the polymerization of the conjugated linoleic acid was so extensive (36.5% residue) that the conjugation-rich fractions had only about the same content of conjugated linoleic acid as the original acids. The oleic-rich fraction had only 3.4% of conjugated linoleic acid in this case.

A pentaerythritol ester of the composite conjugate-rich fraction from Table I had a very high viscosity, owing to polymerization during esterification. (The specific alpha decreased from 82 to 59 during esterification.) It dried to a tack-free wrinkled film. With 0.01% Co and 0.01% Mn in a .003 in. film, it was set in 6 hours, compared to 12 hours for the pentaerythritol ester of cottonseed acids. It was dry in 8-9 hours while the cottonseed ester was tacky even after 96 hours.

Discussion

The data would indicate that for the most effective separation of conjugate-rich linoleic acid from other C_{18} acids, an efficient fractionating system would be required which would operate with minimum exposure of the mixture to high temperatures. A continuous feed column, operated at the lowest possible pressure and pressure-drop should permit the separation to be carried out on a commercial scale. Distillation as methyl esters rather than free acids would reduce the distillation temperature and loss by polymerization, but methyl esters might not be as acceptable in the present drying acid market as the free acids. Thorough evaluation of the usefulness of such a concentrated linoleic acid in synthetic drying oils and in drying alkyd resins would be necessary in order to determine whether the processing costs would justify commercial production.

The method of separation should be of interest in studying the structure of the alkali-isomerized linoleates, since it affords a means of separating them from the other C_{18} acids and avoids the necessity of preparing linoleic acid from the tetrabromide.

Summary

Alkali-isomerized linoleic acid and its methyl ester have been found to have boiling points higher than the corresponding normal C_{18} acids and esters.

By careful fractional distillation of methyl esters of alkali-isomerized C_{18} cottonseed acids, methyl linoleate of 95% or more purity is obtained consisting of 75% conjugated methyl linoleate and some 20% of methyl ester of an altered linoleic acid.

REFERENCES

1. Mitchell, J. H., Jr., Kraybill, H. R., and Zscheile, F. P., Ind. Eng. Chem. *15*, 1 (1943).
2. Beadle, B. W., and Kraybill, H. R., J. Am. Chem. Soc. *66*, 1232 (1944).
3. Burr, G. O., and Miller, E. S., Chem. Rev. *29*, 431-2 (1941).
4. Burr, G. O., U. S. Pat. 2,242,230 (1941).
5. Bradley, T. F., U. S. Pat. 2,350,583 (1944).
6. Bradley, T. F., and Richardson, D., Ind. Eng. Chem. *34*, 237 (1942).
7. Woburn Conjugated Fatty Acids. Woburn Bulletin No. 121. Woburn Degreasing Co. of N. J., 1941.
8. Kass, J. P., in Protective and Decorative Coatings, Matiello, John Wiley and Sons, Inc., N. Y., 1944, ch. 12.
9. Anderson, R. H., and Wheeler, D. H., Oil and Soap *22*, 137 (1945).
10. Hoffman, H. D., and Green, C. E., Oil and Soap *16*, 236 (1939).
11. Von Mikusch, J. D., and Frazier, C., Ind. Eng. Chem. Analyt. *13*, 789 (1941) Method A.
12. Norris, F. A., and Terry, D. E., Oil and Soap *22*, 41 (1945).
13. Frankel, J. S., and Brown, J. B., J. Am. Chem. Soc. *65*, 415 (1943).
14. Von Mikusch, J. D., J. Am. Chem. Soc. *64*, 1580 (1942).