Liquid C-18 Saturated Acids Derived from Linseed Oil[1]

J.P. FRIEDRICH, H.M. TEETER, J.C. COWAN, and G.E. McMANIS, Northern Regional Research Laboratory,[2] Peoria, Illinois

Liquid C-18 saturated monocarboxylic acids that fail to crystallize at −70°C. have been prepared from linseed oil, linolenic acid, and tung oil. Heating one part of linseed oil in three parts of glycol (weight-volume ratio) at 295°C. for 1 hr. with 25% excess sodium hydroxide, followed by distillation and hydrogenation of the resulting free fatty acid monomers and separation of the straight-chain components by low temperature crystallization from acetone, yielded these liquid acids.

The relative proportions of cyclic acids, straight-chain monomeric acids, and polymer varied with the type of starting material and with the conditions employed. Cyclic acids in excess of 30% yields were obtained from linseed oil. Some hydroxylation of the fatty acids apparently takes place during cyclization; the amount increases with ascending temperatures, as evidenced by a rise in polyester content of the polymer fraction.

Evidence indicates that the bulk of the unhydrogenated cyclic acids are vicinal disubstituted cyclohexadienes. Gas chromatography of the cyclic acids hydrogenated to an iodine value <1 shows that there are several components. These have not as yet been separated and positively identified.

SCHOLFIELD AND COWAN recently reported that prolonged alkali isomerization of linolenic acid in ethylene glycol leads to the production of cyclic monomeric acids in good yield along with smaller amounts of dimeric acids and other products. Aromatization of the cyclic monomeric acids, followed by oxidation of the side chains, yielded phthalic acid.

Previously cyclic compounds have been postulated to explain a liquid product produced by heat treatment of *alpha-* and *beta*-eleostearic acids (4,5,6,8). Rossmann (6) was among the first to report such a product and postulated a 5,6-disubstituted 1,3-cyclohexadiene structure; however, in studying this material further by alkaline permanganate oxidation, Sunderland (8) could not obtain the C_{16} tricarboxylic acid that should have been produced. He did obtain a polycarboxylic acid or mixture of acids of lower molecular weight, the presence of which he accounted for by suggesting that hydrogen migration within the molecule could result in a shifting of the relative positions of the double bonds. This idea was also suggested by Rivett (5).

Bradley and Richardson (1) showed that in the alkali isomerization of linseed oil in water, ethylene glycol or diethylene glycol, triene conjugation reaches a maximum and then decreases upon continued heating. Kass and Burr (2) showed that the triene formed in the alkaline isomerization of linseed oil is at least partly 10,12,14-octadecatrienoic acid. Since the disappearance of conjugated triene coincides with the formation of cyclic monomeric acids, it would appear that a trienoic acid of this type is an intermediate in the cyclization reaction. The exact chemical constitution of these cyclic acids and the mechanism by which they are formed have not as yet been elucidated.

TABLE I

Hydrogenation of Cyclic Acid with Palladium-Carbon Catalyst

Pressure (p.s.i.g.)	Temp. °C.	Time, hr.	Weight of sample, g.	Weight of 10% Pd catalyst, g.	Volume of HAc, ml.	Iodine value
29	Room	7	10	0.5	40	10
29	100	1½	10	0.5	40	16
29	100	7	10	0.5	40	10
500	100	4	10	0.5	40	< 1
500	150	4	10	0.1	None	3–4
1,000	200	4	10	0.02	None	< 1
1,100	150	4	10	0.1	None	< 2
1,600	Room	2	10	0.5	40	< 1
1,600	150	4	10	0.1	None	< 1
2,000	200	½	10	0.02	None	< 1

In this paper it will be shown that the monomeric acids produced by prolonged alkali isomerization of linseed and tung oil in ethylene glycol, followed by complete hydrogenation and careful separation of the straight-chain fatty acids, yield saturated C-18 monocarboxylic acids that have a very low pour-point (about −40°C.). These acids become a clear glass when cooled further but fail to crystallize at −70°C. In addition, the variables involved in the cyclization reaction have been studied to determine the most suitable conditions for producing these cyclic acids from linseed oil.

Experimental

Isomerization and Cyclization of Linseed Oil. A mixture of 250 g. of nonbreak linseed oil, 47 g. of 98% NaOH, 750 ml. of ethylene glycol, and 10 ml. of water was introduced into a 2,000-ml., stainless-steel medium-pressure stirred autoclave. The autoclave was thoroughly flushed with nitrogen and heated rapidly to 295°C. (about 1 hr.). The temperature was automatically controlled within ±3°C. and maintained for 1 hr. The reactor was then allowed to cool to 150°C. and subsequently quenched in water.

The reaction mixture was diluted with three volumes of distilled water, stirred vigorously, and acidified with dilute HCl. A small amount of ether was added to facilitate the phase separation. The acidified mixture was stirred for about 30 min. under nitrogen to ensure complete acidification. The two phases were separated; the water phase was extracted twice with ether, and these extracts were combined with the oil phase. The ether solution was then washed three times with water and dried over sodium sulfate.

After stripping off the solvent, the crude acids were distilled under vacuum through an 8-in. Vigreaux column. A low boiling forerun I (6.3 g.) was obtained b.p. 60°–150°C. at <0.1 mm., followed by the monomer fraction II (166.8 g.) b.p. 155°–170°C. and a dark residue III (63.4 g.).

Characterization of Fractions I, II, and III. The ultraviolet and infrared spectra of fractions I and II are shown in Figures 1 and 2, respectively.

The low boiling forerun I was quite mobile and contained acidic groups, as indicated by titration as well as by the infrared spectrum. An appreciable absorp-

---

[1] Presented at fall meeting, American Oil Chemists' Society, New York, N.Y., October 17–19, 1960.

[2] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

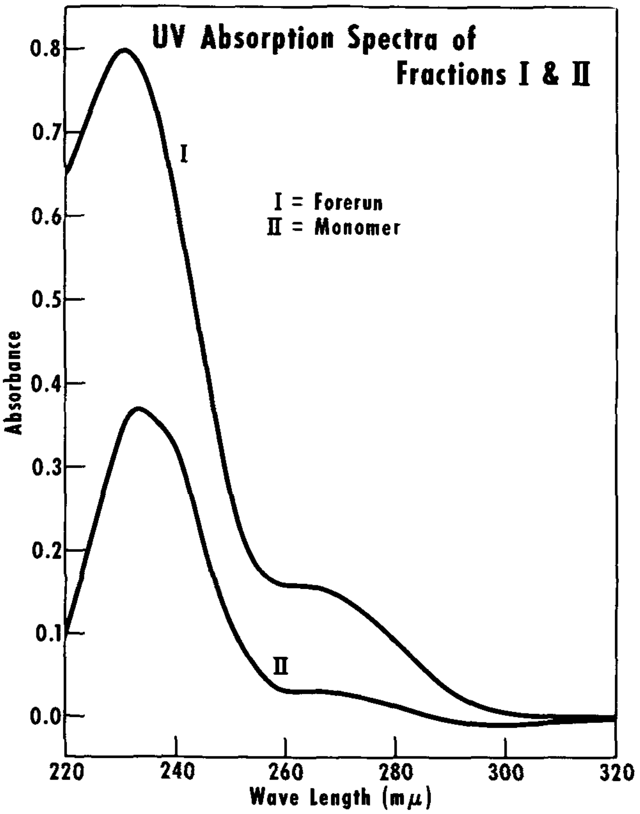

FIG. 1. Ultraviolet absorption spectra of isomerized linseed oil (distillable fractions): iso-octane solution, 1-cm. cell, I (forerun) C = 0.034 g./l.; II (monomer) C = 0.019 g./l.

tion at 230.6 mμ indicates the presence of straight-chain conjugated dienes. An aromatic structure in the forerun is indicated by the presence of a shoulder at 3.30 μ characteristic of the =C—H stretching vibration in aromatics and by bands at 6.22 μ, 6.29 μ, and 6.66 μ (in the spectrum of the pure sample), caused by aromatic C=C stretching. Indication that the aromatic ring is *ortho*-disubstituted is furnished by the presence of a band at 13.55 μ and 13.98 μ, caused by a C—H out of plane, in phase-bending vibration.

The monomer fraction II exhibits a strong band in the ultraviolet region at 231.8 mμ, caused by conjugated diene and corresponding to 26% of the sample. The wavelength of the absorption peak (231.5–231.8 mμ) indicates that the majority of the diene present exists in the *trans,trans* form (9); however the infrared peak at 10.17 μ accounts for only about 10% of the sample as the conjugated *trans,trans* isomer, and there is no conjugated *cis,trans* peak (10.56 μ) present. Dienes that have the ethylenic structure exocyclic to the ring system exhibit an absorption in the region (232–242 mμ); hemicyclic dienes, *i.e.*, a cyclic structure, in which one of the ethylenic linkages forms part of the hydro-aromatic ring system while the other remains exocyclic to the ring, absorb in the region (235–237 mμ). If these species were present, they would contribute to the total absorption in this region and could account for the additional 16% of the sample.

The absorption exhibited as a shoulder between 260 and 270 mμ is characteristic of conjugated cyclohexadienes (10). By using the absorption at the center of this shoulder (265 mμ) and a calculated absorptivity of 9.56, based on the ultraviolet curve of the purified cyclic material prepared by Scholfield (7), the monomer fraction was estimated to contain about 30% cyclohexadiene.

The polymer fraction III proved to be composed partly of polyester. The neutral equivalent of III was approximately 1,100; after saponification, the neutral equivalent dropped to 310 and, upon distillation, yielded an additional 22.4 g. of monomer and 41 g. of thermal polymer. The source of the hydroxyl groups has not as yet been established.

Hydrogenation of the Monomer Fraction. A 10-g. sample of II was hydrogenated under a pressure of 2,000 p.s.i. at 200°C., for 30 min. Twenty milligrams of 10% Pd on powdered charcoal were employed as the catalyst. The bomb was allowed to cool to room temperature before opening to the air to prevent darkening of the product. The contents (an oily solid)

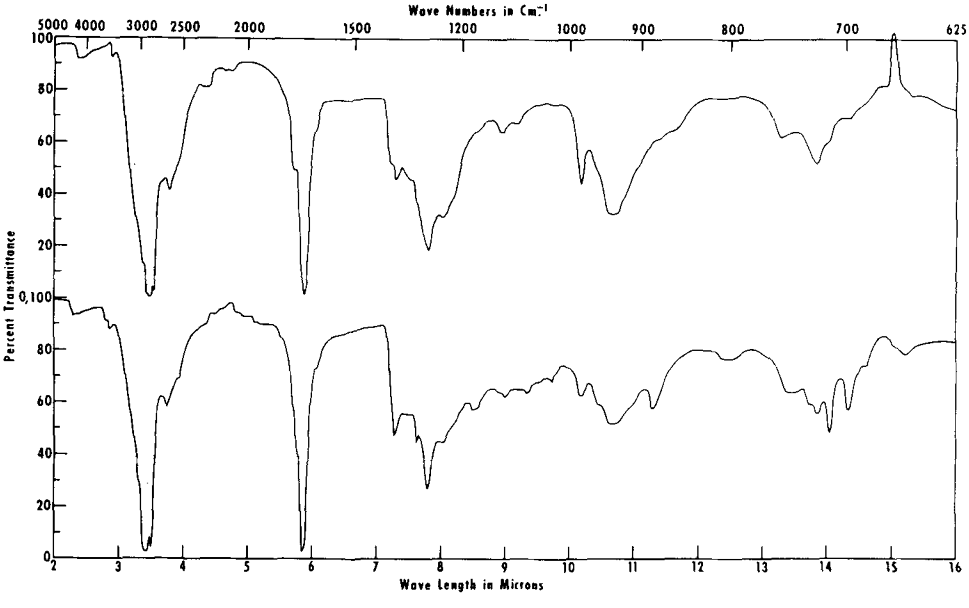

FIG. 2. Infrared absorption spectra of isomerized linseed oil (distillable fractions): carbon disulfide solution, 1-mm. cell, I (forerun) C = 17.86 g./l.; II (monomer) C = 17.72 g./l.

were dissolved in an ether acetone mixture, and the catalyst was filtered off. The stripped acids had an iodine value <1.

The hydrogenation may be carried out under less strenuous conditions (Table I). Data in Table II show that it is relatively easy to reduce the iodine value to from 10 to 20; considerably stronger conditions are necessary to reduce the iodine value to essentially zero.

Attempts to hydrogenate the monomer II with a suspended Ni catalyst under even the most strenuous conditions listed gave residual iodine values from 15 to 30.

Separation of Straight-Chain Saturates from Cyclic Acids. A 5-g. sample of the hydrogenated acids was dissolved in 50 ml. of acetone and cooled slowly to −40°C. with constant stirring.[3] The solid acids were removed by filtration and recrystallized once from acetone. The filtrates were combined, and the solvent was stripped off, leaving 2.3 g. of cyclic acids IV. This corresponds to a 46% yield, based on the monomer II or an over-all yield of about 31%, based on the linseed oil. The various physical constants determined for saturated cyclic acids and their methyl esters are given in Table II.

TABLE II
Physical Constants of Hydrogenated Cyclic Acids and Methyl Esters

Hydrogenated derivative	n_D^{25}	Specific gravity 25°C.	Iodine value	B.P. 0.075 mm. Hg., °C.	F.P. to −70°C.	Neut. equiv.
Cyclic acids[a]	1.4698	0.936	<1	159–166	No cryst.	286
Methyl esters of cyclic acids	1.4609	0.918	<1	125–131	No cryst.	......

[a] Because of the complex nature of this material and the purely empirical method of defining it, *i.e.*, the material which does not crystallize from 10 volumes of acetone at −40°C., these physical constants may vary within reasonable limits.

The ultraviolet spectrum of saturated cyclic acid fraction IV (Figure 3) shows adsorptions at 250, 255.9, 262.9, 267.4, and 271.2 mμ characteristic of *ortho*-disubstituted aromatics. The peak at 13.25 μ in the infrared spectrum of IV (Figure 4) is also characteristic of the *ortho*-disubstituted aromatic structure. These bands, although distinct, represent only a small portion of this material. This fact was shown further by an examination of the spectra of these acids after fractional distillation. After removal of an initial fraction (about 3%), the spectra of the remaining material was consistent with that expected for completely-saturated materials.

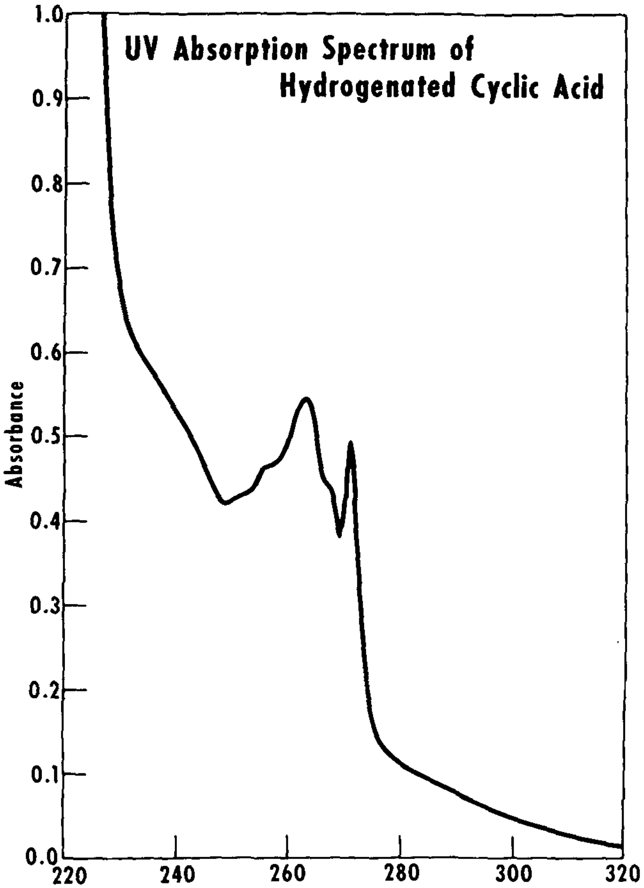

FIG. 3. Ultraviolet absorption spectrum of hydrogenated cyclic acid: iso-octane solution, 1-cm. cell, C = 2.988 g./l.

A gas chromatogram of the methyl esters of IV indicates the presence of at least 12 separate components in varying amounts.

Discussion

Liquid C-18 saturated monocarboxylic acids with an extremely low pour-point (about −40°C.) can be readily prepared in good yield by the technique described. This material has been prepared in satisfactory yields under a variety of conditions (Table III).

Glycerine appears unsuitable as a solvent since its use results in poor conversion under mild conditions and in large distillation residues under more vigorous conditions.

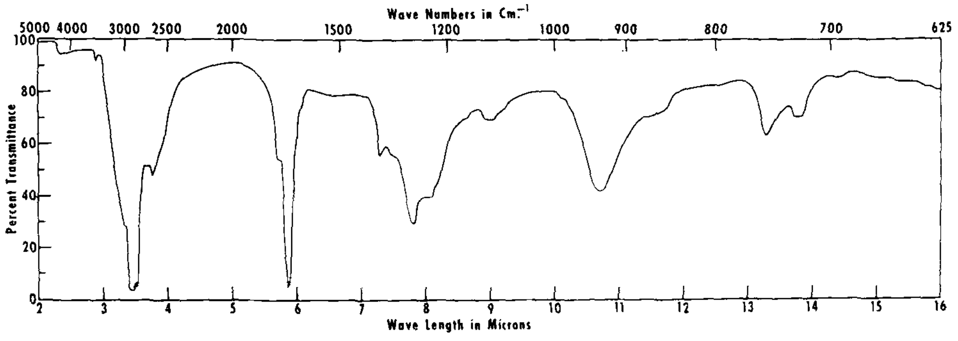

FIG. 4. Infrared absorption spectrum of hydrogenated cyclic acid: carbon disulfide solution, 1-mm. cell, C = 15.59 g./l.

---

[3] A low-temperature crystallization apparatus, particularly suited to semimicro quantitative work, has been designed at the laboratory and is the subject of a paper being prepared for publication.

TABLE III

Effect of Changing Various Conditions on the Production of Cyclic Acids from Linseed Oil

Fatty material	Type of base	Excess base %	Solvent 3:1 ratio	Temperature, °C.	Time, hrs.	% Based on recovered crude acids[a]			
						Forerun	Monomeric acids[b]		Polymer[c]
							Cyclic acids	Straight-chain acids	
Refined linseed oil	KOH	25	Glycol	225	6½				
				295	6½	2.7	29.6	39.7	28.0
Refined linseed oil	KOH	5	Glycerine	250	4	1.7	15.0	59.8	23.5
Refined linseed oil	KOH	5	Diethylene glycol	220	14	......	27.5	45.0	27.5
Nonbreak linseed oil	KOH	10	Glycerine	235	13	......	10.0	40.0	50.0
Nonbreak linseed oil	NaOH	10	Glycerine	225	12	......	11.0	69.0	20.0
Nonbreak linseed oil	KOH	50	Glycol	225	10	......	30.5	52.0	17.5
Nonbreak linseed oil	NaOH	25	Glycol	295	1	2.7	32.4	38.1	26.8
93% Linolenic acid	KOH	50	Glycol	225	6	......	64.0	16.6	19.4
Tung oil	KOH	100	Glycol	210	6	......	56.2	17.8	25.0
Tung oil	None	......	Glycol	210	11	......	6.0	49.0	45.0

[a] The percentages of forerun, monomeric, and polymeric acids were determined by vacuum distillation of the recovered crude acids.
[b] The percentages of cyclic and straight-chain acids were determined by hydrogenation of the monomeric acids and removal of the saturated straight-chain acids by low-temperature crystallization from acetone.
[c] In all cases the polymer is at least in part a polyester.

Diethylene glycol is a convenient solvent if the cyclization is run at atmospheric pressure since its reflux temperature is somewhat higher than that of glycol.

Glycol can be used at temperatures up to 295°C. (Table III), provided that pressure vessels are adequate. At 225°C. the reaction mixture produces a pressure of about 30 to 40 p.s.i.g. whereas at 295°C. the pressure is about 250 p.s.i.g., and it increases slowly but constantly as cyclization continues. This increase may be caused by slight decomposition of the linseed oil, as indicated by the presence of a low-boiling forerun or else by decomposition of the glycol itself.

Alkali is apparently a catalyst for the cyclization, also for the conjugation of the triene system, as indicated by the results with tung oil (Table III). The ultraviolet and infrared spectra, as well as the physical constants of the cyclic acids obtained from tung oil, agree very well with those found for the same materials derived from linseed oil. The best conversion reported for eleostearic acid to a cyclic product by a purely thermal means was about 25% (4) whereas alkali treatment of tung oil (about 80% eleostearic) resulted in about a 70% conversion based on the eleostearic acid present.

As previously stated, evidence indicates that cyclization of the conjugated system occurs with the formation of vicinal-disubstituted cyclohexadienes as the principal products. This material differs from the product prepared by MacDonald (3) by heat treatment of linseed oil in that our material exhibits pronounced absorption above 255 mμ in the ultraviolet characteristic of cyclohexadiene while MacDonald's product does not.

Evidently the reaction proceeds by a base-catalyzed ionic mechanism of some sort. Further speculation on the mechanism of formation of the varied products seems futile until a more detailed study of their structure is undertaken.

REFERENCES

1. Bradley, T.F., and Richardson, D., Ind. Eng. Chem., *34*, 237 (1942).
2. Kass, J.P., and Burr, G.O., J. Am. Chem. Soc., *61*, 3292 (1939).
3. MacDonald, J.A., J. Am. Oil Chemists' Soc., *33*, 394 (1956).
4. Paschke, R.F., and Wheeler, D.H., J. Am. Oil Chemists' Soc., *32*, 473 (1955).
5. Rivett, D.E.A., J. Am. Oil Chemists' Soc., *33*, 635 (1956).
6. Rossmann, E., Fettchem Umschau., *40*, 96 (1933); *via* C.A., *27*, 5057 (1933).
7. Scholfield, C.R., and Cowan, J.C., J. Am. Oil Chemists' Soc., *36*, 631 (1959).
8. Sunderland, E., Oil Colour Chemists' Assoc. J., *28*, 151 (1945).
9. Tolberg, W.E., and Wheeler, D.H., J. Am. Oil Chemists' Soc., *35*, 385 (1958).
10. Woodward, R.B., J. Am. Chem. Soc., *64*, 72 (1942).

[Received December 15, 1960]

Plant-Scale Operations for Degumming, Caustic-Refining, and Water-Washing Soybean Oil by a Two-Step Continuous Process[1]

H.R. KAISER [1] and C.A. HOFFMAN,[2] Podbielniak Inc., Division of Dresser Industries Inc., Chicago, Ill.

Operation of a four-tank-car-per-day plant, using a Duozon[3] and a Hydrazon[3] "in series" to perform continuous degumming, caustic refining, and water washing of soybean oil is described. A simplified flow sheet, illustrating the process, and a detailed functional description of the degummer and the caustic refiner-water washer are given. Typical plant-operating data for this versatile, low-cost plant are presented.

PODBIELNIAK INC. entered the vegetable oil refining field in 1955. During the ensuing years a number of technical papers have been published in the Journal of the American Oil Chemists' Society. Continuous water-degumming of soybean oil on a commercial scale by means of a centrifugal type of oil-gum separator, operating under pressure, was reported in 1956 (1). The use of a multistage, countercurrent centrifugal contactor, for efficient removal of dis-

---

[1] Presented at 34th fall meeting, American Oil Chemists' Society, New York, October 17–19, 1960.
[2] Present address: Iowa Soy Company, Redfield, Ia.
[3] Podbielniak Inc., Chicago, Ill.