

[CONTRIBUTION FROM THE DEPARTMENT OF BOTANY, UNIVERSITY OF MINNESOTA]

The Elaidinization of Linoleic Acid¹

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In contrast to the extensive investigation of the elaidinization of oleic acid,^{2,3} very little work appears to have been done on the similar isomerization of the biologically important linoleic acid.⁴ Green and Hilditch⁵ treated linoleic acid with Poutet's reagent for one hour and obtained on the partial oxidation of the resulting product, the iodine number of which had fallen to 137.5, a small quantity of a new sativic acid, m. p. 140–141°, in addition to the known α - and β -sativic acids corresponding to ordinary linoleic acid. Noller and Girvin⁶ stated that linoleic acid treated with this reagent loses its characteristic ability to form the ligroin-insoluble tetrabromide.

As a part of the larger study of the nutritive value of all fatty acids and their isomers, the elaidinization of linoleic acid was reinvestigated and the following isomers of this acid were prepared and described. Their nutritive value will be reported elsewhere.

Experimental

Elaidinization with Nitrogen Oxides.—Ten cc. of pure methyl linoleate⁷ in a glass-stoppered flask was mixed with 4 cc. of 1:1 nitric acid at 0°; 0.5 g. of finely powdered sodium nitrite was added gradually with rapid shaking. The flask was then immersed momentarily in a boiling water-bath and allowed to stand at room temperature overnight. The dark brown ester layer was extracted with ligroin, which precipitated much tarry material, the extract washed with water, dried over sodium sulfate, and the ligroin evaporated under partial vacuum. The residue was distilled at 150–160° at 3 mm.⁸ The distillate, a yellowish oil weighing 1 g., was saponified and the fatty acids isolated in the usual manner. The residue from the distillation, a dark red, viscous oil boiling above 200°, was discarded. The free acids readily set to a crystalline mass on cooling to 0°. The solid material was separated by rapid filtration on a cooled funnel, and after two crystallizations from methanol at –10° yielded 0.1 g. of white scales, m. p. 28–29°.

(1) This work was supported by grants from the Hormel Foundation and the Graduate School of the University of Minnesota.

(2) Griffiths and Hilditch, *J. Chem. Soc.*, 2315 (1932).

(3) Bertram, *Chem. Weekblad*, **33**, 3, 216 (1936).

(4) Burr and Burr, *J. Biol. Chem.*, **86**, 587 (1930).

(5) Green and Hilditch, *Biochem. J.*, **29**, 1552 (1935).

(6) Noller and Girvin, *THIS JOURNAL*, **59**, 606 (1937).

(7) Rollett, *Z. physiol. Chem.*, **62**, 410 (1909).

(8) All boiling ranges reported in this paper are only approximate. To minimize refluxing and decomposition, the distillations were performed in flasks with side-arms attached immediately above the bulbs and partly immersed in the heating-bath which was maintained at a temperature 20–30° higher than that of the distilling vapor.

On bromination in ligroin, this substance produced a white solid, m. p. 78°. The liquid residue from the crystallization formed on similar treatment a sirupy bromide which crystallized partially after twelve hours at ice-box temperatures. The liquid bromide readily dissolved on dilution with ligroin, while the solid precipitate melted at 76–78° after one crystallization from hexane.

The substitution of dilute sulfuric for nitric acid considerably improved the yield of recovered material. Ten cc. of methyl linoleate and 40 cc. of 1:3 sulfuric acid in a glass-stoppered flask were cooled to –20° and 1.5 g. of sodium nitrite was added slowly, the flask being shaken rapidly until the blue color of the aqueous layer was discharged between successive additions of the salt. The mixture finally was warmed at 60° for ten minutes and left at room temperature overnight. The marked discoloration noted with the nitric acid was absent, although the color of the ester became somewhat darker with time. The ester was taken up with ligroin, which in this case did not precipitate any tarry material, and the extract treated as before. The distillate weighed 4 g. and on saponification and solution in 15 cc. of ligroin at –18° deposited 0.6 g. of the crude crystalline substance. Bromination duplicated the previous results.

Still better yields of reaction products were obtained with Poutet's solution.² Twelve cc. of the ester was shaken with 1 cc. of the cooled reagent, and the glass-stoppered container then warmed on the steam-bath for several minutes. On standing at room temperature overnight, considerable discoloration and deposition of reduced mercury occurred. Distillation at 170–180° (6 mm.) of the ligroin extract (8 g.) yielded 6.3 g. of yellowish distillate. Droplets of mercury collected on the delivery tube and in the receiver during distillation. The distillate was saponified, the free acids washed thoroughly and re-esterified, and the methyl esters redistilled at 163° (4 mm.). The refractive index of the distillate was 1.4602, its iodine number 159.5. The iodine number of the free acids obtained on saponification of the distillate rose to 169.2. Bromination of 1.2949 g. of the mixed fatty acids in 25 cc. of ligroin at –10° produced the immediate precipitation of a solid and a sirupy bromide. After standing in the ice-box for twelve hours, the sirup was removed with three washings of cold ligroin, leaving 0.5951 g. of white solid. This corresponds to a yield of 21.47%, assuming the original parent substance to be linoleic acid. The melting point of the bromide after one crystallization from hexane, which dissolved all but a trace of sticky solid, was 75.5–78°. The remaining 4 g. of the mixed fatty acids was crystallized from methanol and 0.7 g. of the crude crystalline substance, melting at 28–29° after several recrystallizations, was obtained. Bromination of the solid and liquid fractions once again duplicated the previous results.

Slight warming is apparently necessary to induce the isomerization. When 10 g. of free linoleic acid and 1 cc. of Poutet's reagent were allowed to stand at room tempera-

ture for twelve hours with occasional shaking, 8.5 g. of ligroin extract was obtained. This did not crystallize on cooling and 1.039 g. of the undistilled acid produced 0.695 g. of ligroin insoluble bromide, m. p. 104–110°.

Elaidinization with Selenium.—The conditions described by Bertram⁸ for the elaidinization of oleic acid were applied to a pilot lot of 10 g. of methyl linoleate, which was heated under nitrogen with 0.05 g. of powdered selenium for six hours at 210°. Evolution of fumes began at about 160°. The product was decanted from the selenium and distilled at 156–165° (4 mm.). The dark red residue, boiling above 250°, was discarded and the distillate (8 g.) was saponified. The acids had an iodine number of 169, and 1.1851 g. yielded 0.2395 g. of bromide, m. p. 74–78°. From 5 g. of the remaining acids 0.8 g. of crude crystalline material was obtained (m. p. 28–29°, after two recrystallizations from ligroin). The behavior of the solid and liquid fractions toward bromine was identical with that of the similar fractions obtained with nitrous acid, 1.1362 g. of the liquid fraction producing the sirupy bromide from which 0.1236 g. of bromide, m. p. 72–76°, was centrifuged off after twelve hours in the ice-box. Repetition of the experiment with 50 g. of the ester produced 44 g. of distillate from which 6.6 g. of purified solid acid was obtained; 1.2626 g. of the liquid fraction, iodine number 165, precipitated on bromination only 0.1060 g. of a sticky orange semisolid substance insoluble in boiling hexane.

That six hours at 200–220° is the minimum time required for complete isomerization was indicated by brominating an aliquot part of a 100-g. lot of methyl linoleate that had been heated with 1 g. of selenium at 210° for only five hours. The 88 g. of distillate was saponified and the solid product removed as completely as possible by several crystallizations from ligroin cooled with a mixture of solid carbon dioxide and alcohol, followed by the removal of additional small crops from diminished volumes of ligroin at –18°; 2.7112 g. of the liquid fraction brominated in 30 cc. of ligroin with 0.9 cc. of dry bromine precipitated 0.5130 g. of a white bromide, m. p. 112–114°. This liquid fraction of the unsaturated acids was esterified and reheated with 1% its weight of selenium for another five hours and the product worked up as before. A total of 17.7 g. of purified solid was collected. The liquid portion had an iodine value of 160.3, a thiocyanogen value of 92.0, and 1.045 g. yielded 0.087 g. of bromide, m. p. 78–81°.

The nosterified acid isomerized with equal ease. Twenty-five grams of linoleic acid heated for six hours at 210° with 0.25 g. of selenium produced 19.8 g. of distillate, b. p. 200–208° (4 mm.). The residue was lighter in color than the isomerized ester residue, but it boiled above 300° at 4 mm. and was discarded; 2.640 g. of the distillate formed 0.382 g. of bromide, melting poorly at 74°. The remainder quickly deposited crystals on cooling, and 3.5 g. of crude solid was obtained from its ligroin solution after twelve hours at –18°.

Linolelaidic Acid.—The solid product of the isomerization crystallized readily from methanol or low-boiling ligroin and melted at 28–29° (uncorr.). Its iodine value (Wijs) was 178.3 (theory, 181.1); thiocyanogen value, 90.0 (theory, 90.6); neutralization equivalent 280 (theory, 280). Its lead salt was beautifully crystalline and in-

soluble in cold 95% ethanol. It was spectroscopically inactive, showing an $E_{1\text{cm}}^{1\%}$ of 4–5 at 2300–2350 Å.⁹

*Anal.*⁹ Calcd. for $C_{18}H_{32}O_2$: C, 77.06; H, 11.50. Found: C, 76.89; H, 11.25.

Bromination of Linolelaidic Acid.—1.5752 g. of the acid dissolved in 35 cc. of ligroin and cooled to –5° was slowly brominated with 0.5 cc. of dry bromine. After standing in the ice-box overnight, the mixture was centrifuged, the precipitate washed three times with 20-cc. portions of cold ligroin, and finally dried in the vacuum-oven at 60°; yield, 1.4104 g., or 42%. One crystallization from hexane produced feathery crystals, m. p. 78°.

Anal. Calcd. for $C_{18}H_{30}O_2Br_4$: C, 36.00; H, 5.37. Found: C, 35.68; H, 5.56.

Disruptive Oxidation of Linolelaidic Acid.¹⁰—4.25 g. of the solid acid was esterified with methanol and sulfuric acid. The colorless ester, b. p. 151–152° (2 mm.), was dissolved in 90 cc. of acetone and 45 g. of powdered potassium permanganate was added carefully to the solution. After refluxing for three hours, the acetone was evaporated and the residue was decolorized with 100 g. of sodium bisulfite and excess dilute sulfuric acid. A single extraction with ether and steam distillation of the ether residue produced 0.2 g. of a volatile acid, b. p. 66° (5 mm.), forming the water-insoluble zinc salt characteristic of caproic acid. The oily residue from the steam distillation was saponified, acidified, and thoroughly extracted with ether. Evaporation of the ether left 0.9 g. of a crystalline solid, m. p. 102–105°, after two recrystallizations from water. No depression was observed in the mixed melting point with authentic azelaic acid.

Partial Oxidation of Linolelaidic Acid.¹¹—A solution of 5.6 g. of linolelaidic acid and 5.6 g. of sodium hydroxide in 750 cc. of water was diluted to 4 liters and cooled to 0°; 10 g. of potassium permanganate in 750 cc. of water was added at once. After stirring for fifteen minutes, decolorization was effected with sulfur dioxide, and the solution acidified with 600 cc. of 20% sulfuric acid. The hydroxides, after filtration, washing, drying, and thorough extraction with ligroin, weighed 2.95 g. and melted at 121–136°. The ligroin extract, weighing 1.3 g., iodine number 175.5, proved to be the unoxidized acid. The hydroxides were extracted repeatedly with a total of 500 cc. of boiling ethyl acetate. The insoluble portion (0.5 g., m. p. 145–147°) was recrystallized from 50% methanol or from acetic acid as a fine white powder, melting sharply at 146°.

Anal. Calcd. for $C_{18}H_{36}O_6$: C, 62.07; H, 10.34. Found: C, 61.80; H, 9.70.

The cooled ethyl acetate solution deposited a voluminous and gelatinous precipitate which dried to a difficultly friable powder weighing 1.3 g., m. p. 121–126°. This was taken up in 500 cc. of boiling water. A slight insoluble residue melted at 146° after extraction with ethyl acetate. The water-soluble portion was fractionated from 50% methanol into three crops, 0.15 g., m. p. 130–141°; 0.18 g., m. p. 121–125°; 0.44 g., m. p. 123–126°, precipitated

(9) We wish to thank Dr. Elmer S. Miller of this department for the spectroscopic analyses, and Mr. J. W. Opie of the Department of Organic Chemistry for the micro-analytical combustion data herein reported.

(10) Armstrong and Hilditch, *J. Soc. Chem. Ind.*, **44**, 43T (1925).

(11) Lapworth and Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

from the mother liquor by dilution with water. The first fraction, m. p. 130–141°, was dissolved in 5 cc. of acetic acid, from which 50 mg., m. p. 145–147°, was obtained on cooling. Addition of 25 cc. of water precipitated the remainder, m. p. 124–134°. The second and third fractions were combined and crystallized from 40% acetic acid and from ethyl acetate, discarding the least soluble fractions in each case. After treatment with charcoal in boiling acetate, 0.19 g. of a more easily friable solid, m. p. 120–123°, was obtained. This was taken up in 10% methanol, a slight residue of poorly crystalline material, m. p. 119–124°, discarded, and the filtrate cooled. A flocculent precipitate, melting sharply at 122°, was obtained: neut. equiv., 356; calcd., 348.

Anal. Calcd. for $C_{18}H_{36}O_6$: C, 62.07; H, 10.34. Found: C, 62.51; H, 10.34.

The Liquid Linolelaidic Acid.—The precipitation from the liquid product of the isomerization of variable quantities of a bromide identical with linolelaidic acid tetrabromide made it apparent that this isomeric fraction is characterized by its ligroin-soluble liquid bromide and that the formation of the solid bromide probably depended upon the concentration of the dissolved linolelaidic acid, complete removal of which was successful in only one case, as indicated previously. The separation of the reaction products was therefore attempted through their lead salts.

The Lead-Salt Separation.¹²—To a 10% alcoholic solution of 7.5 g. of mixed isomerized acids, obtained from methyl linoleate that had been heated under nitrogen with 1% Se for twelve hours at 200–210°, was added an equal weight of lead acetate in 75 cc. of 95% ethanol. After two hours at 15°, the voluminous white precipitate was filtered with suction and washed with cold alcohol. The solution was diluted with water to incipient precipitation and acidified with 1:5 nitric acid. Ligroin extracted 4.2 g. of a yellowish oil, iodine number 159. This was converted to the methyl ester, which distilled as a practically colorless liquid. Saponification in the cold again produced the yellowish acid, equiv. 282 (calcd., 280); iodine number 170.5 (calcd., 181.1); thiocyanogen number 90.5 (calcd., 90.6); refractive index 1.4695; 0.5422 g. yielded 0.0543 g. of solid bromide, in addition to the soluble sirupy bromide. Spectroscopic examination indicated the presence of about 5% conjugation.

Partial Oxidation of the Liquid Isomer.—Three grams of the acid obtained from the soluble lead salt was converted to 1 g. of hydroxy acids by the method of Lapworth and Mottram¹¹ exactly as described above. These were resolved with ethyl acetate into an insoluble fraction (0.15 g.), and a soluble portion, m. p. 121–126°. The insoluble substance crystallized from ethyl acetate-acetic acid solution as a fine white powder, m. p. 156–158°.

Anal. Calcd. for $C_{18}H_{36}O_6$: C, 62.07; H, 10.34. Found: C, 61.78; H, 9.98.

Evaporation of the mother liquor left 10 mg. of solid, m. p. 134–138°.

The ethyl acetate-soluble portion was fractionated from small volumes of the same solvent into 0.11 g. of an easily soluble substance, m. p. 126–127°, and 0.05 g. of difficultly soluble solid, m. p. 130–133°.

Anal. of substance, m. p. 126–127°. Calcd. for $C_{18}H_{36}O_6$: C, 62.07; H, 10.34. Found: C, 61.90; H, 10.24.

The mixed melting point with the analogous soluble linolelaidic tetrahydroxy acid (m. p. 122°) was 116–121°. Evaporation of the original ethyl acetate mother liquor left 15 mg. of solid, m. p. 108–122°.

The two fractions, m. p. 134–138° and 130–133°, difficultly soluble in ethyl acetate, were combined (60 mg.) and fractionated from 10% methanol into a discarded 10 mg. of an insoluble, poorly crystalline solid melting indefinitely at 130–140°, and a well-crystallized portion, m. p. 131–135°. A mixed melting point with the fraction m. p. 126–127° was 126–130°.

Anal. Calcd. for $C_{18}H_{36}O_6$: C, 62.07; H, 10.34. Found: C, 61.77; H, 10.47.

Partial oxidation of the liquid isomer prepared by repeatedly freezing out the solid linolelaidic acid gave essentially identical results.

The Solid Lead Salt.—The precipitated lead salt was taken up in boiling 95% ethanol, which left undissolved a sirupy mass only partially soluble even in large volumes of the hot alcohol. This was extracted by decantation and finally acidified with 1:5 nitric acid under ligroin, yielding 1.5 g. of yellow acid, iodine number 116. Its behavior toward the Wijs and Hanus solutions was typical of the conjugated acids,¹³ and spectroscopic examination confirmed the assumption of such a structure. An attempt to prepare a larger quantity of this substance ended in failure when another lot of the sirupy lead salt reacted violently with the dilute nitric acid, evolution of nitric oxide fumes indicating rapid oxidation. We hope to reinvestigate this fraction at a later date.

The hot alcohol solution of the solid lead salt was cooled and the precipitate acidified to yield 1.51 g. of crude solid linolelaidic acid.

Discussion

The diethenoid structure of linoleic acid permits the existence of four geometric isomers, each capable of forming a pair of distinct racemic tetrabromo and tetrahydroxy acids. When, however, a given addendum may be introduced in two ways (*cis* and *trans*) without the simultaneous isomerization of the parent substance, the number of addition products from any one isomer is doubled. In the latter case, paired isomeric unsaturated acids will have the four derivatives in common; that is, the pair of *cis* addition products of one will correspond to the pair of *trans* addition products of the other. In the simpler instance of the monoethenoid oleic and elaidic acids, this is exemplified by the ability of each to form distinct racemic dibromo and dihydroxy acids, the latter being related in such a manner that the dihydroxy acid of oleic acid obtained through permanganate oxidation is identical with that formed from elaidic acid through oxidation with hydrogen

(12) Twitchell, *J. Ind. Eng. Chem.*, **13**, 806 (1921).

(13) Böeseken and Gelber, *Rec. trav. chim.*, **46**, 158 (1927).

peroxide, and *vice versa*.⁴ Ordinary linoleic acid yields four tetrahydroxy derivatives: with permanganate, the familiar α - and β -sativic acids, the melting points of which have been variously reported as 153 to 164° and 170 to 174°, respectively^{4,14,15}; and with hydrogen peroxide, two isomers, m. p. 126 and 146°.⁴ Nicolet and Cox¹⁵ also reported the preparation of two sativic acids, m. p. 135 and 144.5°, by way of the linoleic chlorohydrins. Green and Hilditch⁵ considered the higher melting product to be identical with theirs, while the wide discrepancy in the melting points of the other two substances pointed to a probable difference. In view of the probable identity of the two higher melting derivatives, the assumption of the similar identity of the lower melting products is imperative, since addition may take place either in the *trans* or *cis* manner, and thus no more than four sativic acids may conceivably be formed from any one linoleic acid. Consideration of the melting point ranges reported by Nicolet and Cox¹⁵ for the mixed γ - and δ -sativic acids presents the possibility that further purification may have lowered the melting point of the isomer in question below 135°. It is therefore to be expected that the hydrogen peroxide oxidation products of linoleic acid should correspond to the products of the permanganate oxidation of its "elaidic" form. This is undoubtedly borne out by the sativic acids of the solid linoleic acid, the melting points of which we have tentatively set at 122 and 146°. The solid isomer therefore bears the same relation to linoleic acid as elaidic does to oleic acid.

As in the case of ordinary linoleic acid,^{7,17,18} the yield of a new insoluble bromide from the solid linoleic acid approaches 50%. Since there is no question of the homogeneity of the crystalline isomer, it may be assumed safely that the analogous behavior of ordinary linoleic acid points to the individual nature of the latter, disposing of the possibility that it is a 1:1 mixture of two isomers, one of which gives complete precipitation of bromide and the other, none.

(14) Birose, *THIS JOURNAL*, **59**, 689 (1937).

(15) Nicolet and Cox, *ibid.*, **44**, 144 (1922).

(16) Nicolet and Cox termed their product, m. p. 144.5°, γ -sativic acid, and the more soluble, lower melting form, δ -sativic acid. Uniformity of nomenclature with the α - and β -sativic acids suggests the reverse, and we propose to give the lower melting, soluble isomer the lower designation, so that γ -sativic acid will refer to the isomer of m. p. 122°, and δ -sativic acid to the other member of the pair, m. p. 146°.

(17) Brown and Frankel, *THIS JOURNAL*, **60**, 54 (1938).

(18) McCutcheon, *Can. J. Research*, **16**, 158 (1938).

The elaidinization of only one of the two double bonds of linoleic acid would lead to the formation of only one new substance, while the inversion of both double bonds could produce two or all three of the expected isomers, their concentrations being determined by equilibrium constants or by their relative stabilities and ease of formation. If, therefore, the elaidinization of linoleic acid is similar to that of oleic acid, the product of the reaction may contain the original unchanged acid as well as the new isomers. Our data suggest that linoleic acid is either totally converted or is present in the reaction mixture in quantities too small for detection by bromination and partial oxidation procedures. The removal of the solid isomer and the conjugated by-products thus leaves a liquid fraction characterized by its ligroin-soluble bromide. This fraction, which we shall refer to as β -linoleic acid in agreement with the older literature, may obviously be either a distinct substance or a mixture of the two remaining isomers. Inoue and Suzuki¹⁹ have claimed the isolation from the fat of silkworm pupae of an isolinoleic acid giving no precipitable bromide. Smith and Chibnall²⁰ suggested the presence of a linoleic acid with similar characteristics in grass fats. Hilditch and Longenecker²¹ proposed the existence in butter and ox depot fats of another isomer characterized by an indefinite bromide, m. p. 170° d. However, partial oxidation of the grass and bovine fats produces ordinary α - and β -sativic acids, though in poorer yields than would be expected from the calculated concentrations of the octadecadienoic acid. Hilditch²² considers this property, in conjunction with the absence of appreciable quantities of the α -tetrabromide, m. p. 114°, in the products of bromination, as characteristic of the geometric isomers of linoleic acid in these fats. It is evident from our experimental data and the subsequent discussion that the formation of α - and β -sativic acids upon permanganate oxidation is possibly only from ordinary α -linoleic acid, unless permanganate be assumed to isomerize the isomeric linoleic acids in question during oxidation. Such a supposition appears extremely unlikely in view of the normal behavior of the other isomers described in this paper, and we must conclude that the sativic

(19) Inoue and Suzuki, *Proc. Imp. Acad. Tokyo*, **7**, 15 (1931).

(20) Smith and Chibnall, *Biochem. J.*, **26**, 228 (1932).

(21) Hilditch and Longenecker, *J. Biol. Chem.*, **122**, 497 (1938); *Biochem. J.*, **31**, 1805 (1937).

(22) Hilditch, *Analyst*, **62**, 250 (1937).

acids of these isomers, if the latter are actually present in the fats mentioned, have as yet not been prepared from natural products.

On the other hand, if the ligroin-insoluble bromide of butter fat (m. p. 170° d.) be assumed to characterize one of the isomers of linoleic acid, then the liquid linolelaidic acid is obviously a single substance. The results of the partial oxidation of this fraction are not sufficiently clear cut to permit a definite conclusion at present. While there is no doubt of the homogeneity of the ϵ - and ζ -sativic acids, m. p. 126 and 158°, respectively, the additional crystalline fraction, m. p. 131–135°, obtained from the β -linolelaidic acid, may be an ill-defined η -sativic acid, a mixture of the γ - and δ -sativic acids arising from the residual solid linolelaidic acid, or a mixture of the ϵ - and ζ -isomers, this last finding support in the failure of the doubtful fraction to depress the melting point of the ϵ -isomer, although the data of Nicolet and Cox¹⁵ and Birose¹⁶ make this criterion appear largely inapplicable. But if this fraction is the η -sativic acid, it should have been accompanied by the remaining possible θ -isomer. Our methods of separation did not reveal the formation of this substance and we may therefore conclude tentatively that the liquid fraction of

(23) Birose, *Natural and Applied Science Bulletin of the University of the Philippines*, **2**, 103 (1932).

the isomerization is, aside from the by-products, the individual β -linoleic acid. Ordinary linoleic acid thus appears to be elaidinized into only two of its isomers, as would follow from the assumption that the 9,10-double bond may elaidinize alone, but that the 12,13-bond cannot elaidinize without the previous or simultaneous isomerization of the 9,10-bond. The fourth possible member of the linoleic acid group consequently remains to be isolated.

The work on the problem of isomerism in the linoleic acid series is being continued and extended to the linolenic acids.

Summary

Linoleic acid was elaidinized with nitrogen oxides and with selenium.

A crystalline linoleic acid, m. p. 28–29°, a liquid isomer in an impure form, and conjugated by-products were isolated from the reaction mixture.

The crystalline linolelaidic acid yielded equal parts of a liquid and a solid tetrabromide, m. p. 78°. Partial oxidation produced two sativic acids, m. p. 122 and 146°.

The non-crystalline isomer formed only liquid bromides, and two sativic acids, m. p. 126–127° and 156–158°.

The isomerism of the linoleic acids is discussed.
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Fluorenones and Diphenic Acids. VII.^{1,2} Ring Cleavage of 1,8-, 1,6- and 3,6-Dichlorofluorenones with Potassium Hydroxide in Diphenyl Ether

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Previous work⁴ in this Laboratory has shown that when 3,3'-dichlorodiphenic acid (I) is heated with concentrated sulfuric acid it first yields 1,6-dichlorofluorenone-5-carboxylic acid (II) but that this material is isomerized on further heating with the sulfuric acid to yield 1,6-dichlorofluorenone-4-carboxylic acid (III).

(1) For Article VI of this series see Huntress and Seikel, *THIS JOURNAL*, **61**, 816 (1939).

(2) Presented before the Division of Organic Chemistry, Baltimore Meeting of the American Chemical Society, April, 1939.

(3) This paper is constructed from part of a dissertation submitted by Miss Seikel to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1938.

(4) Huntress and Atkinson, *THIS JOURNAL*, **58**, 1514–1518 (1936).

Possible Mechanism.—Since it is extremely unlikely that either the halogen atoms or the carboxyl group migrate as such under these conditions,⁵ and since by similar treatment both 1,8- (IV) and 1,6-dichlorofluorenone (V) also isomerize to 3,6-dichlorofluorenone (VI), it is conceivable that the observed results might be effected by fission of the ketonic linkage followed by subsequent reclosure in the opposite sense to yield the new products. Thus a possible mechanism which would account for all the facts could be represented as follows

(5) Cf. Moyle and Smith, *J. Org. Chem.*, **2**, 128 (1937).