The Peracid Oxidation of Linoleic Acid[1]

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This is a preliminary report on the peracetic and performic acid oxidations of α-linoleic acid. Two new oxidation products have been isolated and partially characterized. It has been established that the isomeric sativic acids derived from the oxidation of α-linoleic acid are readily separated through their methyl esters. This procedure eliminates the difficulties experienced with the separation of the free acids, which is caused by the formation of eutectic mixtures. The oily by-products from the oxidation of linoleic acid have been demonstrated to have relatively low acid equivalents of 300–400.

Although the peracid oxidations of oleic acid[3] with opening of the oxirane ring give excellent yields of 9,10-dihydroxystearic acid (m.p. 95°), the yields of the two isomeric γ- and δ-sativic acids[4] from the peracid oxidation of α-linoleic acid or methyl linoleate are low.[5] The present report presents the preliminary work on this problem of the peracid oxidation of α-linoleic acid.

The peracid oxidation of oleic acid was repeated to ensure that the available method,[3] when employed by the present authors, would give yields comparable with those reported in the literature. A crude yield of 94.8% of 9,10-dihydroxystearic acid was obtained, and this method employing peracetic acid or performic acid was then applied to the oxidation of α-linoleic acid. The peracetic acid oxidation of linoleic acid gave 10.2% of δ-sativic acid (m.p. 147–148°), 1.27% of γ-sativic acid (m.p. 125.5–126°), 5.74% of the compound which melts at 95.5–96°, and an oil. Green and Hilditch[5] also isolated a compound melting at 95° from the peracetic acid oxidation of linoleic acid. They assumed that it was impure azelaic acid, but this *Compound A* depresses the melting point of an authentic sample of azelaic acid (m.p. 105–106°), and its molecular weight and analytical values are in good agreement with the formula $C_{18}H_{34}O_5$. This same compound was obtained by refluxing the oil from the performic acid oxidation of α-linoleic acid with glacial acetic acid followed by saponification.

Compound A was recovered unchanged in 76% yield after lead tetraacetate oxidation indicating the absence of an α-glycol structure. It was also recovered unchanged after treatment with the acetic anhydride–zinc chloride reagent used in opening furan ring structures.[6–9] The absence of a ter-

tiary hydroxyl group was indicated also by its recovery unchanged from solution in concentrated hydrochloric acid. This preliminary work does not establish the structure of compound A but it shows that a new C_{18} oxidation product is present in the peracetic oxidation products from α-linoleic acid. One possible structure is

$$CH_3(CH_2)_4\overset{\lceil\ \ \ \ \ \ O\ \ \ \ \ \ \rceil}{CH}—CHOHCH_2CHOHCH(CH_2)_7COOH$$
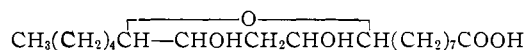
In the performic acid oxidation of α-linoleic acid, besides the known γ- and δ-sativic acids, a new *Compound B* (m.p. 90–91°) was obtained. Compound B depressed the melting point of compound A. It possesses an equivalent weight and analytical values in good agreement with the formula $C_{18}H_{34}O_4$. This compound gave a negative unsaturation test with tetranitromethane and it did not absorb bromine. It failed to form a semicarbazone but it appeared to form a diacetate. There was no evidence for the presence of the oxirane group. The methyl ester of this compound melted at 46–47° and had a mol. wt. of 341 ((Rast.); required for $C_{19}H_{36}O_4$, 328.

The infrared spectra of compound B and its methyl ester are shown in Figs. 1 and 2. The spectrum of the free acid, measured as a mull in Nujol, shows a broad absorption band between 3400 and 3200 cm.$^{-1}$ indicative of strong OH · · ·H bonding. Both the carbonyl band at 1703 cm.$^{-1}$ and the weak inflection at 2700 cm.$^{-1}$ indicate that the hydroxyl group of the carboxylic acid is tied up in the dimerized carboxylic acid structure and the bonded hydroxyl absorption at 3400—3200 cm.$^{-1}$ must therefore arise from hydroxyl groups in the chain. The spectrum of the methyl ester, which was measured in solution, confirms this, there being a typical bonded hydroxyl band with maximum at 3330 cm.$^{-1}$ and very weak indication of free hydroxyl absorption at 3600 cm.$^{-1}$.

In the spectrum of the ester there is a weak band at 3060 cm.$^{-1}$ which is suggestive of an unsaturated linkage. The spectrum fails to show any other evidence of unsaturation either in the region of the C=C stretching absorption (1675–1600 cm.$^{-1}$) or out-of-plane ethylenic C–H bending absorption below 1000 cm.$^{-1}$. A cyclopropyl group might provide an alternative explanation of the weak 3060 cm.$^{-1}$ band.

While this evidence is insufficient to establish an unequivocal structure for compound B, it does establish the presence of a third C_{18} oxidation compound in the products from the performic acid oxidation of α-linoleic acid.

When 90% hydrogen peroxide was used in the

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(2) Defence Research Chemical Laboratories, Ottawa, Ontario.

(3) D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, THIS JOURNAL, **67**, 1786 (1945).

(4) The term sativic acid is used for 9,10,12,13-tetrahydroxystearic acid throughout this paper. The use of the terms *cis* and *trans* (A. F. McKay and A. R. Bader, *J. Org. Chem.*, **13**, 75 (1948)) led to a misunderstanding concerning the implied spacial configuration of the α-glycols (*cf.* Swern, THIS JOURNAL, **70**, 1235 (1948)). This, however, was resolved by Bader (*ibid.*, **70**, 3938 (1948)) who pointed out that the conclusions of McKay and Bader and Swern as well as Wittcoff, *et al.*, (H. Wittcoff, O. A. Moe and M. H. Iwen, *ibid.*, **70**, 742 (1948)) were in agreement.

(5) T. G. Green and T. P. Hilditch, *Biochem. J.*, **29**, 1552 (1935). For additional references on the peracid oxidation of oleic and linoleic acids *cf.* D. Swern, "Organic Reactions," John Wiley and Sons, Inc., Vol. VII, New York, 1953, pp. 378–433.

(6) C. L. Wilson, *J. Chem. Soc.*, 48 (1945).

(7) R. Paul, *Compt. rend.*, **208**, 587 (1939).

(8) R. Paul, *ibid.*, **212**, 398 (1941).

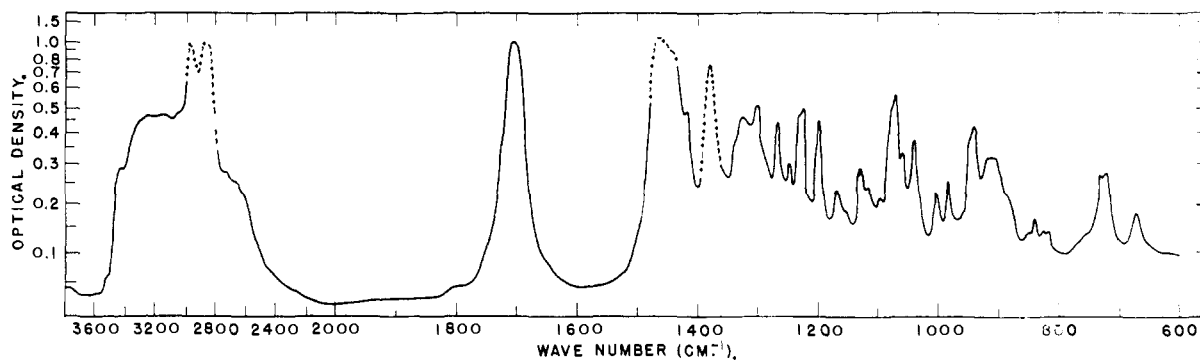(9) R. Paul, *Bull. soc. chim.*, **8**, 369 (1941).
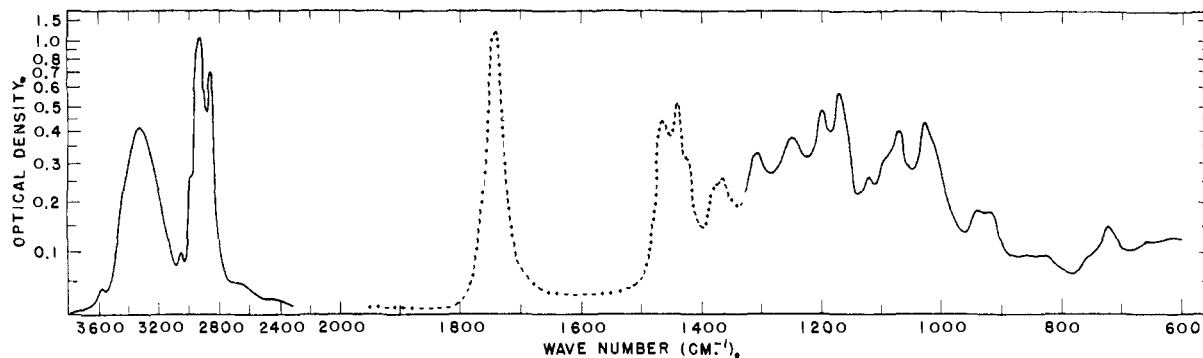
Fig. 1.—Infrared spectrum of compound B.

Fig. 2.—Infrared spectrum of compound B methyl ester: ————, carbon disulfide solution, 1 mm. cell, 10 mg. per ml.: — — — —, carbon tetrachloride solution, 1 mm. cell, 10 mg. per ml.
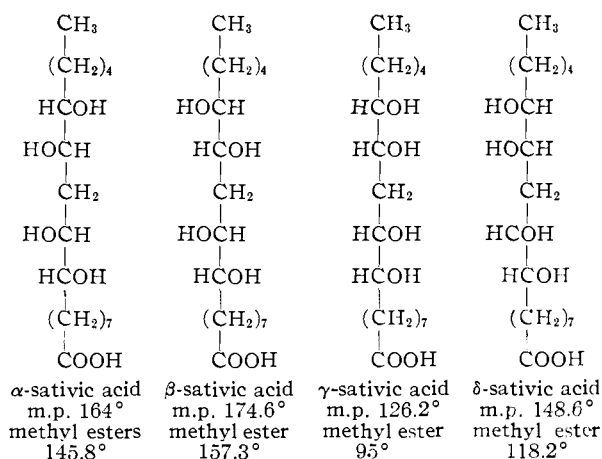
preparation of the performic acid, the yield of the crude mixture of γ- and δ-sativic acids was 15.2% while that of compound B was 5.7%. The use of 30% hydrogen peroxide decreased the yields of γ- and δ-sativic acids to 7–12% while the crude yields of compound B increased to as much as 25.8%. If sulfuric acid was employed as a catalyst in the performic acid oxidations, no compound B could be isolated from the oxidation products.

Since a considerable loss occurs in the separation of the isomeric γ- and δ-sativic acid mixtures obtained in the peracid oxidations, the separation of their methyl esters was attempted. It was found that this procedure eliminated the formation of eutectic mixtures so troublesome in the purification of the free acids. The methyl ester purification procedure gave high yields of the pure acids after saponification. Moreover, purification of the α-, β-, γ- and δ-sativic acids through their methyl esters and then saponification to the free acids has now confirmed the true melting points of these acids. These melting points along with the melting points of the esters are given below under their respective formulas.

Previously[10] the formulas for β- and δ-sativic acids were given incorrectly with respect to those of the other sativic acids, although the relative OH group positions were given correctly.

An attempt was made to separate the oily products from the performic and peracetic acid oxidation by chromatographing on silica gel. Practically all of the fractions remained as oils which possessed acid equivalents of 300–400. This precludes the formation of polymers through the partici-

pation of the carboxyl groups. Thus the polymer referred to by Green and Hilditch,[5] if present, must form from the oxido linkages during saponification.[11]

CH₃	CH₃	CH₃	CH₃
(CH₂)₄	(CH₂)₄	(CH₂)₄	(CH₂)₄
HCOH	HOCH	HCOH	HOCH
HOCH	HCOH	HCOH	HOCH
CH₂	CH₂	CH₂	CH₂
HOCH	HOCH	HCOH	HCOH
HCOH	HCOH	HCOH	HCOH
(CH₂)₇	(CH₂)₇	(CH₂)₇	(CH₂)₇
COOH	COOH	COOH	COOH
α-sativic acid	β-sativic acid	γ-sativic acid	δ-sativic acid
m.p. 164°	m.p. 174.6°	m.p. 126.2°	m.p. 148.6°
methyl esters	methyl ester	methyl ester	methyl ester
145.8°	157.3°	95°	118.2°

Experimental[12]

Linoleic Acid.—Linoleic acid was prepared from Mazola oil (corn oil) through the 9,10,12,13-tetrabromostearic acid (m.p. 115–115.5°) by the method of McCutcheon.[13] Debromination of the tetrabromostearic acid with zinc in methanol gave theoretical yields of linoleic acid, which was purified by distillation in vacuo. The final yield from tetrabromostearic acid was 93.5%, iodine number 181.0, calcu-

(10) A. F. McKay and A. R. Bader, J. Org. Chem., **13**, 75 (1948).

(11) D. Swern (private communication) has found that oxido formation in α-linoleic acid with peracid occurs normally in good yield.

(12) All melting points are corrected. Microanalyses by Oakwold Laboratories, Alexandria, Virginia, and Micro-Tech Laboratories, Skokie, Illinois.

(13) J. W. McCutcheon, Org. Syntheses, **22**, 75 (1942).

lated 181.0.[14] Ultraviolet absorption analysis gave a value of 87.0 for specific α at 2340 Å. while that reported[15] for pure linoleic acid is 87.1. There was no absorption maximum at 2680 Å. indicating the absence of conjugated trienoic acids. The purified linoleic acid without alkali isomerization gave a specific extinction coefficient (specific α) at 2340 Å. of 0.445. Since the specific α for pure conjugated linoleic acid is 119,[16] the amount of conjugation is approximately 0.37%. In addition several per cent. of the ethylenic linkages in linoleic acid prepared as above may exist in the *trans* form.[17]

Methyl Oleate.—A charge of 208.4 g. of methylated acids from Teaseed oil was fractionated in a Todd column packed with glass helices. The column was operated at 20 mm. pressure using a reflux ratio of 10:1. An intermediate fraction (b.p. 221.6–222° (20 mm.); iodine no. 83.8; weight 105.8 g.) was used for further purifications. It was dissolved in 1058 cc. of dry acetone and held at −36° for ten hours. The white crystals (4.2 g.) were removed by filtration and discarded. After the filtrate had remained at −60° for several hours, the second crop of crystals (56.6 g.) was redistilled *in vacuo* to give 37.5 g. of pure methyl oleate, b.p. 153–154° (0.09 mm.), iodine no. 85.6 (calcd. 85.6), setting point −20.2 ± 0.1°. Wheeler and Riemenschneider[18] report a melting point of −19.9°.

Peracetic Acid Oxidation of Methyl Oleate.—The procedures used for the peracid oxidations of methyl oleate and linoleic acid are essentially the same as described by Swern and co-workers.[3] Methyl oleate (8.1 g., 0.027 mole) was added to a solution of 1.2 g. of sulfuric acid (sp. gr. 1.84) and 3.17 g. (0.028 mole) of 30% hydrogen peroxide in 24.3 cc. of glacial acetic acid. This mechanically stirred solution was maintained at 38.5–41° for 2.75 hours. The oxidation was followed by titration[19] which indicated that the uptake of hydrogen peroxide ceased after 96.2% of the theoretical amount had been consumed. After the reaction mixture was drowned in 240 cc. of water, the oil was extracted with ether (3 × 50 cc.) and the ether washed with water (3 × 100 cc.). The residual oil from evaporation of the ether was heated on the steam-bath with 50 cc. of 3 N sodium hydroxide solution for 1.5 hours. On acidification and cooling to 4°, a white solid separated, yield 8.1 g. (94.8%). Crystallization from 95% ethanol raised the melting point from 89–90° to 94–95°. The reported melting point for this 9,10-dihydroxystearic acid[3] is 94–95°.

Peracetic Acid Oxidation of Linoleic Acid.—A solution of 12.6 g. (0.045 mole) of linoleic acid in 30 cc. of glacial acetic acid was poured into a mechanically stirred solution of 8.4 g. of sulfuric acid (sp. gr. 1.84) and 10.7 g. (0.097 mole) of 30.9% hydrogen peroxide in 70 cc. of glacial acetic acid. The temperature of this reaction mixture was maintained at 39–40.2° for three hours and twenty minutes. At the end of this period titration indicated that 97.3% of the theoretical amount of hydrogen peroxide had been consumed. The solution was then diluted with 900 cc. of water and the oil extracted with ether (2 × 105 cc.). After the ether solution was washed with water (3 × 105 cc.) and dried, evaporation gave 17 g. of an oily residue. This oil was saponified by heating on a steam-bath for 1.5 hours with 80 cc. of 3 N sodium hydroxide solution. The soap solution was added to 100 cc. of 3 N hydrochloric acid solution and the semi-solid oil recovered, yield 13.3 g. On treatment with ether (70 cc.), the oil dissolved leaving 1.6 g. (10.2%) of solid which melted at 144–145°. Crystallization from 50% aqueous ethanol raised the melting point to 147–148°. A mixed melting point determination with an authentic sample of δ-sativic acid (m.p. 147–148°) gave no depression.

The ethereal filtrate from the first crop of crystals on storage at −36° for two hours gave 0.2 g. (1.27%) of solid melting at 125–130°. Two crystallizations from 40% aqueous ethanol gave 85 mg. of material melting at 125.5–126°. A mixture melting point determination with an authentic sample of γ-sativic acid (m.p. 125–126°) showed no depression. The ether was evaporated from the filtrate of the second crop of crystals and the residual oil dissolved in ethyl acetate. After standing at −36° for several days, this ethyl acetate solution deposited 0.9 g. (5.74%) of crystals melting at 89–90°. Several crystallizations from ethyl acetate and aqueous ethanol gave 107 mg. of γ-sativic acid (m.p. 125–126°) and 87 mg. of needle-like crystals melting sharply at 95.5–96°. This compound on admixture with a sample of azelaic acid (m.p. 105–106°) melted at 76–86°.

Anal. Calcd. for $C_{18}H_{34}O_5$: C, 65.49; H, 10.39; equiv. wt., 330.2. Found: C, 65.42; H, 10.55; equiv. wt., 330.0, 336.1.

A portion (1.89 g.) of the oil remaining after evaporating of ethyl acetate from the final filtrate was dissolved in 40 cc. of benzene and poured into a column of 60 g. of silica gel (20 mm. in diameter and 300 mm. high). This column was developed with petroleum ether and it was eluted with benzene containing increasing amounts of acetone. Some 150 fractions were collected which remained as oils. The majority of these fractions were titrated and the equivalent weights (based on monobasic acids) found to vary between 288–768 with over 90% by weight of the fractions giving values of 311–356.

Several runs were made on the peracetic acid oxidation of linoleic acid. The yields of solid products varied from 10–16% and consisted of mixtures of γ- and δ-sativic acids along with the compound melting at 95.5–96°.

Performic Acid Oxidation of Linoleic Acid.—Three cc. (4.18 g., 0.111 mole) of 90% hydrogen peroxide in 20 cc. of formic acid was added dropwise to a stirred solution of 14.3 g. (0.051 mole) of linoleic acid in 64 cc. of formic acid (98%). The initial reaction was very exothermic and the temperature had to be maintained at 40 ± 2° by use of an ice–salt-bath. After 30 minutes the uptake of hydrogen peroxide had ceased. The reaction mixture became homogeneous a few minutes after the initial mixing. At the end of the 30-minute period, the reaction mixture was drowned in ten volumes of water and extracted with ether (3 × 50 cc.). After removal of the ether, saponification in the usual manner and re-extraction with ether, a mixture of γ- and δ-sativic acids (m.p. 135–141°) separated at the ether–water interface, yield 2.7 g. (15.2%). The ether was removed from the filtrate and the residual oil (17 g.) dissolved in 50 cc. of absolute ether. This ethereal solution, after standing one week at −78°, deposited 0.9 g. (5.7%) of solid melting at 64–69°. Crystallization of this solid from acetone and dilute alcohol raised the melting point to 90–91°.

Anal. Calcd. for $C_{18}H_{34}O_4$: C, 68.87; H, 10.92; equiv. wt., 314.3. Found: C, 68.97; H, 11.14; equiv. wt., 314.0, 322.2.

This compound on admixture with the compound melting at 95.5–96° from the peracetic acid oxidation of linoleic acid melted at 79–89°. The compound melting at 90–91° gave a negative test for unsaturation with tetranitromethane. Titration for oxirane oxygen by the method of Swern, *et al.*,[20] showed the absence of an oxirane ring. An attempt to form a semicarbazone of this compound gave a quantitative recovery of the starting material. When this compound, melting at 90–91° (105 mg.), was refluxed in 5 cc. of acetic anhydride in the presence of a few drops of pyridine and the reaction mixture worked up in the usual manner, 121 mg. (87% yield based on formation of diacetoxy derivative) of a colorless oil was obtained. This oil could not be induced to crystallize. On saponification in the usual manner this acetoxy derivative gave a nearly quantitative conversion back to the original compound (m.p. 89–91°). This was verified by a mixed melting point determination. Finally this compound (110 mg.) was converted to its methyl ester in the usual manner by ethereal diazomethane (prepared from methylnitrosonitroguanidine).[21],[22] Evaporation of the

(14) It was found that the method of Rosemund and Kuhnhenn (*Z. Untersuch. Nahrungs- u. Genussmittel*, **46**, 154 (1923)) gave low values for compounds having high iodine numbers. Thus the rapid Wijs method developed by H. D. Hoffman and C. E. Green (*Oil and Soap*, **16**, 236 (1939)) was used.

(15) J. H. Mitchell, Jr., H. R. Kraybill and F. P. Zscheile, *Ind. Eng. Chem. Anal. Ed.*, **15**, 1 (1943)).

(16) B. A. Brice and M. L. Swain, *J. Opt. Soc. Amer.*, **35**, 532 (1945).

(17) D. Swern, private communication, June 16, 1953.

(18) D. H. Wheeler and R. W. Riemenschneider, *Oil and Soap*, **16**, 207 (1939).

(19) D. H. Wheeler, *ibid.*, **9**, 89 (1932).

(20) D. Swern, T. W. Findley, G. N. Billen and J. T. Scanlan, *Ind. Eng. Chem., Anal. Ed.*, **18**, 414 (1947).

(21) A. F. McKay, THIS JOURNAL, **70**, 1974 (1948).

(22) A. F. McKay, W. L. Ott, G. W. Taylor, M. N. Buchanan and J. F. Crooker, *Can. J. Research*, **28B**, 683 (1950).

ether gave a quantitative yield of the methyl ester which melted at 45–47°. One crystallization from aqueous ethanol raised the melting point to 46–47°.

Anal. Calcd. for $C_{19}H_{36}O_4$: C, 69.41; H, 10.70. Found: C, 69.32; H, 10.54.

Into a column 4.8 cm. in diameter containing 182 g. of silica was poured 10.63 g. of oil (from the performic acid oxidation) dissolved in 100 cc. of benzene. This column was eluted with benzene–acetone mixtures (200 cc./washing). The oil was removed from the column in 190 fractions and the acid equivalent of each fraction was determined. The majority of the equivalent weights (based on monobasic acids) varied from 300–406. Fractions 18–27 (removed from the column with 3% acetone in benzene) gave 20 mg. of crystals (m.p. 87°). These crystals were identified as the compound (m.p. 90–91°) obtained above by a mixed melting point determination.

When 30% hydrogen peroxide was used in place of 90% hydrogen peroxide, the yields of mixed γ- and δ-sativic acids were lower (7–12%) while the crude yields of the compound melting at 90–91° increased to as much as 25.8%. The use of sulfuric acid catalyst in the performic acid oxidation of linoleic acid did not affect the yield of sativic acids, but none of the low melting compound (90–91°) could be isolated.

In one run, 1.5 g. of oil remaining after the removal of the compound melting at 90–91° was refluxed in 15 cc. of glacial acetic acid for four hours. At the end of this period, the solution was poured into 5 volumes of water and the oil extracted with ether. The washed ethereal solution was evaporated and the residual oil refluxed one hour and forty minutes in N sodium hydroxide solution. This solution on acidification gave 500 mg. of crystals melting at 84–85°. One crystallization from ethyl acetate (1 cc.) raised the melting point to 95.5°. This compound on admixture with the compound melting at 96–97° from the peracetic acid oxidation of linoleic acid gave no depression.

Separation of γ- and δ-Sativic Acids Through Their Methyl Esters.—The crude mixture (5.12 g., 0.0147 mole) of γ- and δ-sativic acids obtained from the performic acid oxidations of linoleic acid was dissolved in 100 cc. of 95% ethanol. To this solution, an ethereal solution of diazomethane was added until the yellow color persisted. The ether was allowed to evaporate spontaneously and the residual ethanolic solution poured into 300 cc. of water. A white precipitate formed, which was removed by filtration and washed with water, yield 3.9 g. (74.7%). Crystallization from 95% ethanol raised the melting point from 108–110° to a constant melting point of 117.8–118.2°. A portion (310 mg.) of this crystalline methyl ester was saponified in 8 cc. of 4% alcoholic potassium hydroxide solution. After working up in the usual manner 210 mg. of δ-sativic acid (m.p. 147–147.7°) was obtained. One crystallization from 95% ethanol raised the melting point to 148.2–148.6°. A sample of this acid did not depress the melting point of an authentic sample (m.p. 147–148°) of δ-sativic acid.

The filtrate from above gave a second crop of crystals (m.p. 82–91°), yield 430 mg. (8.1%). This latter crop of crystals, after several crystallizations from 50% ethanol, gave well formed rosettes of needle-like crystals with a constant melting point of 94.8–95°. Saponification of this methyl ester in the usual manner gave γ-sativic acid (m.p. 124.6–125.2°) which was identified by a mixed melting point determination. This acid was brought to a constant melting point of 125.4–126.2° by one crystallization from aqueous ethanol.

Attempted Lead Tetraacetate Oxidation of Compound A. —Compound A (287 mg.) was dissolved in 5 cc. of glacial acetic acid and 1.09 g. of red lead (Pb_3O_4) added. This mixture was heated at 60° for 25 minutes with constant

shaking. It was then drowned in 80 cc. of water and extracted with ether (2 × 30 cc.). The ether solution was washed with water (3 × 25 cc.), 1% sodium carbonate solution (3 × 20 cc.) and again with water (3 × 20 cc.). The neutral ether solution on evaporation left only a trace of oily residue which gave no derivative with phenylhydrazine reagent. When the sodium carbonate solution was acidified with concentrated hydrochloric acid solution, solid separated. This solid was extracted with ether (2 × 30 cc.) and the ether solution washed with water (3 × 20 cc.). Evaporation of the ether left 216 mg. (76%) of crystalline residue which melted at 95–96°. This material on admixture with original compound A (m.p. 95–96°) did not depress its melting point.

Treatment of Compound A with Concentrated Hydrochloric Acid.—Compound A (63 mg.) was dissolved in 5 cc. of concentrated hydrochloric acid. On dilution with ten volumes of water 62 mg. (98.4%) of solid (m.p. 96–97°) was recovered. This material on admixture with compound A (m.p. 96–97°) gave no depression in melting point.

Treatment of Compound A with Acetic Anhydride–Zinc Chloride.—Twenty milligrams of compound A was dissolved in 2 cc. of acetic anhydride to which a small crystal of zinc chloride was added. This solution was refluxed for 30 minutes and then added to 10 volumes of water. The oil was extracted with ether (1 × 15 cc.) and the ether washed with water. After evaporation of the ether, the residue was dissolved in 5 cc. of 3 N sodium hydroxide solution and heated on the steam-bath for two hours. This alkaline solution was poured into an excess of 3 N hydrochloric acid solution. The solid material, which separated, was filtered off and washed with water. It melted at 94–95.5° alone and on admixture with starting material. The recovery was almost quantitative.

In another experiment the reactants were heated in a closed tube at 160–190° for two hours. When the contents of the tube were worked up in the same manner as above practically quantitative recovery of unchanged compound A (m.p. 95–96°) was obtained.

Methyl Ester of α-Sativic Acid.—α-Sativic acid (194.8 mg.) was suspended in 40 cc. of absolute alcohol and treated with an excess of an ethereal solution of diazomethane. After standing overnight, the excess diazomethane was destroyed with dilute hydrochloric acid. The ether was removed by evaporation and the remaining alcoholic solution was diluted with water (400 cc.). The white solid (m.p. 145–146°) was removed by filtration and washed with water, yield 184.5 mg. After one crystallization from 95% ethanol the melting point was 145.6–145.8°. Saponification of this methyl ester of α-sativic acid with 4% alcoholic potassium hydroxide solution at room temperature gave a quantitative recovery of α-sativic acid melting at 163.6–164°.

Methylation of β-Sativic Acid.—β-Sativic acid (911 mg.) was methylated in the same manner as α-sativic acid to give an almost quantitative yield of methyl ester melting at 152.9–154.3°. One crystallization from 95% ethanol raised the melting point to a constant value of 157–157.3°. Saponification as above gave β-sativic acid melting at 174.2–174.6°.

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