decomposition would be observed; or when ring closure becomes slow, this may become the rate-determining step. Also, the possibility of having two rate-determining steps may explain the non-linearity of the rate of decomposition with temperature.

One of us, E. D. H., wishes to acknowledge a grant-in-aid from the Hynson, Westcott and Dunning Research Fund.

### Summary

1.  Two compounds, methyl 4-oxo-2-pentenoate and the 5-oxime of methyl 4,5-dioxo-2-pentenoate, were studied polarographically. The former compound showed a polarographic wave corresponding to a two-electron reduction, whereas the latter compound gave two waves equal to a four- and a two-electron change, respectively.

2.  The oxime was found to decompose in solution according to a first-order reaction. This decomposition was followed polarographically.

3.  A polarographic study of 3,5-diphenyl-4-isoxazolol was made.

4.  A mechanism for the decomposition of the oxime was proposed.
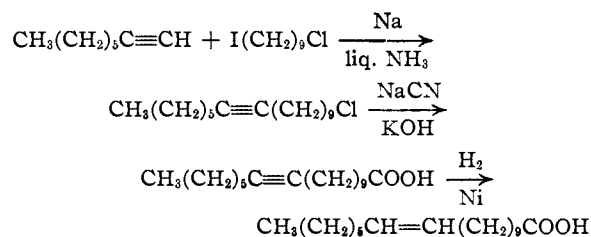
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# A Synthesis of *cis*-11-Octadecenoic and *trans*-11-Octadecenoic (Vaccenic) Acids[1]

BY KAMALUDDIN AHMAD, F. MERLIN BUMPUS AND F. M. STRONG

Vaccenic acid, *trans*-11-octadecenoic acid, was discovered in 1928 by Bertram,[2] who succeeded in isolating it from fats of animal origin and in establishing its structure. Interest in this substance was stimulated by the recent announcement of Boer, Jansen, Kentie and Knol[3] that vaccenic acid is one of the components of butter fat responsible for the superior nutritive value of butter as compared to vegetable fats when tested on certain diets.

Hart and co-workers in this laboratory[4] and Deuel, *et al.*,[5] have been unable to confirm this claim. In these studies solid mono-unsaturated fatty acid fractions obtained from butter and from hydrogenated vegetable fats by Bertram's method have been used as the source of vaccenic acid. In view of the well-known difficulty of isolating completely pure fatty acids from natural fats, it seemed possible that this discrepancy might be related to the quality of the vaccenic acid prep-

arations being tested. In order to obtain an authentic sample of the acid for further feeding experiments it has been synthesized by a suitable application of the method recently reported.[6]

$$CH_3(CH_2)_5C{\equiv}CH + I(CH_2)_9Cl \xrightarrow[\text{liq. NH}_3]{Na}$$

$$CH_3(CH_2)_5C{\equiv}C(CH_2)_9Cl \xrightarrow[KOH]{NaCN}$$

$$CH_3(CH_2)_5C{\equiv}C(CH_2)_9COOH \xrightarrow[Ni]{H_2}$$

$$CH_3(CH_2)_5CH{=}CH(CH_2)_9COOH$$

Each of the indicated reactions was found to give excellent yields and the desired product was obtained without difficulty.

In contrast to natural vaccenic acid which was reported to melt at 39° and was regarded by Bertram as the *trans* form,[2] the synthetic acid melted at 10.5–12° and is probably the *cis* isomer. The production of *cis* olefins by catalytic partial hydrogenation of alkyl acetylenes has been reported.[7]

*trans*-11-Octadecenoic (vaccenic) acid was obtained by isomerization of the *cis* acid with selenium at 180–200°, and was found to melt at 43–44°. Each form was converted to the correspond-

(1) Published with the approval of the Director of the Wisconsin Agricultural Experiment Station. Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

(2) Bertram, *Biochem. Z.*, **197**, 433 (1928).

(3) Boer, Jansen, Kentie and Knol, *J. Nutrition*, **33**, 356, 359 (1947).

(4) E. B. Hart, personal communication.

(5) Deuel, Greenberg, Straub, Jue, Gooding and Brown, *J. Nutrition*, **35**, 301 (1948).

(6) Ahmad and Strong, THIS JOURNAL, **70**, 1699 (1948).

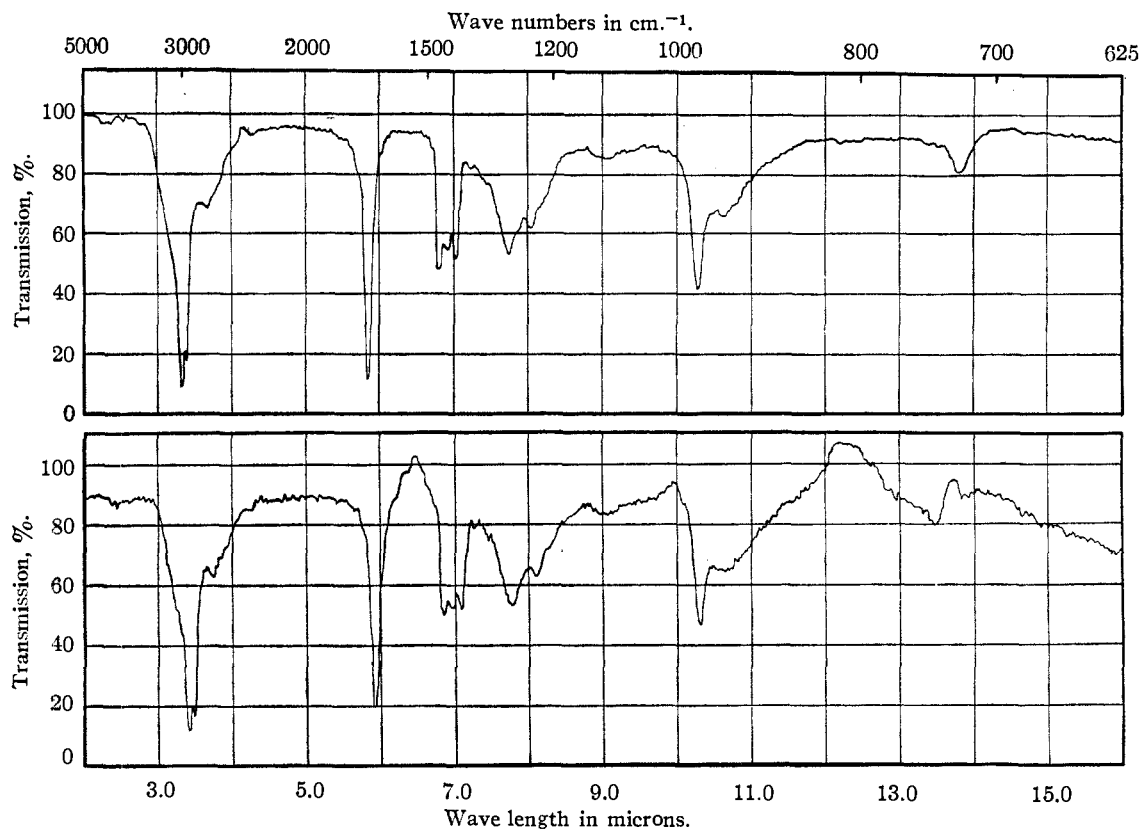(7) Campbell and Eby, *ibid.*, **63**, 216 (1941).

Wave numbers in cm.$^{-1}$.



Fig. 1.—Upper: infrared absorption curve for synthetic trans-11-octadecenoic (vaccenic) acid.
Fig. 2.—Lower: infrared absorption curve for natural vaccenic acid.

ing 11,12-dihydroxystearic acid by oxidation with alkaline potassium permanganate whereupon the cis form gave rise to a higher melting dihydroxy acid (m. p. 127–128°) while the trans form yielded a lower melting isomer (m. p. 93–94°). These results parallel the behavior of oleic and elaidic acids when oxidized under similar conditions.[8]

The position of the unsaturated bond in the cis and trans acids was verified by cleavage of the corresponding dihydroxystearic acids with lead tetraacetate, and periodic acid, respectively, which after further oxidation of the acidic fragment, resulted in the expected products, n-heptaldehyde and undecanedioic acid.

The isolation of a highly purified specimen of vaccenic acid from beef tallow has been reported recently by Rao and Daubert.[8a] A sample of the synthetic trans-11-octadecenoic acid was sent to Professor Daubert, who very kindly took a mixed melting point (42.0–42.5°) and arranged for running the infrared absorption curve shown in Fig. 1. Figure 2 is the corresponding curve for natural vaccenic acid. These curves were made as previously described.[8a] The significant minima are essentially identical in the two patterns. There is thus little doubt that the two

products are identical and that the configuration natural of vaccenic acid is trans.

## Experimental

1,9-Dichlorononane.—Commercial azelaic acid[9] was recrystallized from water, converted to the diethyl ester (b. p. 125–126° (1 mm.), sapon. equiv. calcd. 122.2, found 123.0), and hydrogenated over copper–chromium oxide catalyst at elevated temperature and pressure.[10] Saponification of the product, isolation of the neutral fraction, and distillation gave an 84% yield of 1,9-nonandiol, b. p. 147–149° (1 mm.) which solidified on cooling.

The diol (130 g., 0.812 mole) and pyridine (10 ml.) were placed in a three-necked flask immersed in an ice-bath and equipped with a stirrer, reflux condenser and dropping funnel. Thionyl chloride (371 g., 3.12 moles) was added dropwise with stirring at such a rate that the temperature remained in the neighborhood of 5–10°. The ice-bath was then removed, the mixture allowed to stand overnight, and refluxed for three hours. After cooling, ice water was cautiously added, and the organic layer was shaken out successively with concentrated sulfuric acid, dilute sodium bicarbonate solution, and water. Fractionation gave 149 g. (93.3%) of a colorless oil, b. p. 90–92° (0.1 mm.), $n^{20}$D 1.4591.

Anal. Calcd. for $C_9H_{18}Cl_2$: C, 54.82; H, 9.21. Found: C, 54.59; H, 9.12.

1-Chloro-9-iodononane.—A solution of 32.7 g. (0.218 mole) of sodium iodide in 250 ml. of acetone was added with constant stirring over a period of two hours, to a refluxing solution of 43 g. (0.218 mole) of 1,9-dichloro-

(8) Markley, "Fatty Acids," Interscience Publishers, New York, N. Y., 1947, p. 396.
(8a) Rao and Daubert, This Journal, 70, 1102 (1948).

(9) Obtained from Emery Industries, Inc., Cincinnati, Ohio.
(10) The assistance of Dr. Homer Adkins in carrying out this hydrogenation is gratefully acknowledged.

nonane in 100 ml. of acetone. After three additional hours of refluxing, the acetone was distilled off, the precipitated sodium chloride removed, and the organic layer washed with water and dried over anhydrous potassium carbonate. Fractional distillation through a Vigreux column gave 13.3 g. of unchanged dichloride, b. p. 95–105° (0.48 mm.) and 26.6 g. of the iodochloride, b. p. 120–123° (0.48 mm.), of 96.7% purity according to its iodine content. This represents a 59.3% yield based on the dichloride not recovered. In various runs the purity of this product ranged from 90 to 97%, which was satisfactory for the purpose at hand since the main contaminant appeared to be the dichloride. The substance was not sufficiently stable to permit distillation through a Fenske column.

A small sample was further purified by distillation through a micro spinning band column.[11] Considerable decomposition occurred, but a sample of distillate, b. p. 123–124° (2.8–2.9 mm.), $n^{25}$D 1.5060, was obtained.

*Anal.* Calcd. for $C_9H_{18}ClI$: I, 43.97; Found: I, 43.18.

**1-Chloro-10-heptadecyne.**—1-Octyne, b. p. 124–126°, was prepared in 65.4% yield from sodium acetylide and *n*-hexyl bromide.[12] Sodamide was prepared from 13.8 g. (0.6 gram atom) of sodium in 2000 ml. of liquid ammonia as previously described,[6] and 66.4 g. (0.6 mole) of 1-octyne was added to the mixture with continuous stirring over a period of one and one-half hours. After stirring one hour longer, 127.8 g. (0.44 mole) of 1-chloro-9-iodononane was added during two and one-half hours. Ammonia lost by evaporation was replenished at this point, and stirring was continued overnight. About 500 ml. of water was cautiously added, the organic layer collected in ether, and worked up in the usual manner. Fractional distillation gave a small forerun boiling up to 120°, followed by 111.7 g. (95.3%), b. p. 146–147° (0.48 mm.). This product, containing 0.21% iodine, was used without further purification.

For analysis a small sample was distilled through a micro spinning band column,[11] b. p. 121–122° (2.8 mm.), $n^{20}$D 1.4644.

*Anal.* Calcd. for $C_{17}H_{31}Cl$: Cl, 13.08. Found: Cl, 12.86.

**11-Octadecynoic Acid.**—A mixture of 33 g. (0.12 mole) of 1-chloro-10-heptadecyne, 15 g. (0.31 mole) of sodium cyanide, and 300 ml. of 95% ethanol was refluxed for ninety hours. Most of the cyanide and all of the chloride were in solution before heating. After the refluxing was completed, the solution was decanted, and the insoluble salts washed thoroughly with ethanol.

The combined ethanolic solutions were returned to the flask with 9.5 g. (0.237 mole) of sodium hydroxide dissolved in 50 ml. of water, and the resulting solution was refluxed for ninety-six hours. The product was evaporated to dryness, redissolved in 20% ethanol, and twice extracted with ether. After acidification of the aqueous layer with dilute hydrochloric acid the precipitated organic acid was removed with ether. Evaporation of the ether left 33.5 g. (98.9%) of a yellow-white, crystalline solid. Low temperature recrystallization of this solid from acetone gave 29 g. (85.5%) of white platelets, m. p. 45.5–46.5°.

*Anal.* Calcd. for $C_{18}H_{32}O_2$: C, 77.13; H, 11.51; neut. equiv., 280.4; hydrogen uptake, 2 moles. Found: C, 76.9; H, 11.27; neut. equiv., 280.5; hydrogen uptake, 2.01 moles.

*cis*-**11-Octadecenoic Acid.**—A solution of 14.1 g. (0.05 mole) of 11-octadecynoic acid in 150 ml. of absolute

(11) Piros-Glover micro still, manufactured by the H. S. Martin Company. The assistance of Mr. J. M. Woods and the Department of Chemical Engineering, University of Wisconsin, in the use of this equipment is gratefully acknowledged. The efficiency of the column under the operating conditions used was approximately 50–75 plates.

(12) Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **2**, 1–22 (1937).

alcohol was shaken with 1 g. (wet weight) of Raney nickel catalyst[13] at room temperature under an initial hydrogen pressure of 50 p. s. i. until 0.05 mole of hydrogen had been absorbed.[10] This required ten to sixty minutes in various runs. The catalyst and solvent were removed, and the colorless oily product crystallized from acetone at successively lower temperatures ranging from 0 to −30°. The material crystallizing at the higher temperatures was solid at room temperature and on further recrystallization from acetone proved to be stearic acid. The yield was 1.7 g., m. p. 69°.

The bulk of the material was recovered by crystallization at −30°, and formed glistening white platelets, m. p. 10.5–12°. (Thermometer bulb inserted in the melting mass.) The yield was 12.2 g., 86.5%.

*Anal.* Calcd. for $C_{18}H_{34}O_2$: C, 76.53; H, 12.13; neut. equiv., 282.5; iodine number, 89.9; hydrogen uptake, 1.0 mole. Found: C, 76.59; H, 12.02; neut. equiv., 282.4; iodine number, 88.1; hydrogen uptake, 1.03 mole.

**Vaccenic Acid.**—A mixture of 14.5 g. of *cis*-11-octadecenoic acid and 0.15 g. of powdered selenium was heated at 180–200° for seven minutes. After cooling, the dark semi-solid was dissolved in 70 ml. of acetone, decolorized with Norite, and crystallized at −7°. The crystalline product melted at 36–37°, and weighed 6.7 g. Repeated crystallizations from acetone gave pure white platelets, m. p. 43–44°.

*Anal.* Calcd. for $C_{18}H_{34}O_2$: C, 76.53; H, 12.13; neut. equiv., 282.5; iodine number, 89.9; hydrogen uptake, 1.0 mole. Found: C, 76.48; H, 12.2; neut. equiv., 283.7; iodine number, 87.3; hydrogen uptake, 1.03 mole.

**11,12-Dihydroxystearic Acids.**—Oxidation of 0.99 g. of *cis*-11-octadecenoic acid with permanganate in dilute aqueous alkaline solution according to the method of Robinson and Robinson[14] gave 1.12 g. of crude 11,12-dihydroxystearic acid, m. p. 119–124°, which on recrystallization from ethanol yielded 0.92 g. (82%), m. p. 127–128°.

*Anal.* Calcd. for $C_{18}H_{36}O_4$: C, 68.31; H, 11.46. Found: C, 67.98; H, 11.04.

Oxidation of vaccenic acid in the same manner gave a 77.4% yield of a 11,12-dihydroxystearic acid, m. p. 93–94°.

*Anal.* Calcd. for $C_{18}H_{36}O_4$: C, 68.31; H, 11.46. Found: C, 68.6; H, 11.3.

**Oxidative Degradation of 11,12-Dihydroxystearic Acids.**—To a solution of 0.4 g. of 11,12-dihydroxystearic acid, m. p. 127–128°, prepared from *cis*-11-octadecenoic acid, in 5 ml. of anhydrous acetic acid was added 0.50 g. of lead tetraacetate. After shaking for twenty minutes at room temperature and five minutes at 45°, the mixture was cooled, diluted with 5 ml. of water, sufficient dilute hydrochloric acid added to dissolve the precipitated lead oxide, and the solution thoroughly shaken out with ether. The ether extract was then repeatedly shaken out with 5% sodium carbonate solution.

The ether solution was dried over anhydrous sodium carbonate, and the solvent removed. The semicarbazone prepared from the residue melted at 107–108°. *n*-Heptaldehyde semicarbazone melts at 109°, and a mixed melting point with an authentic specimen showed no depression.

The alkaline extract was acidified, extracted with ether, and the aldehydoacid fragment separated from the ether as the sodium bisulfite addition product. The free acid obtained upon acidification was oxidized to the dibasic acid by dilute alkaline permanganate at room temperature.[15] The dicarboxylic acid isolated melted at 111°. An authentic sample of undecanedioic acid prepared from

(13) Adkins and Billica, THIS JOURNAL, **70**, 695 (1948).

(14) Robinson and Robinson, *J. Chem. Soc.*, **127**, 175 (1925).

(15) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 141–142.

1,9-dichlorononane via the dinitrile melted at 110°, and a mixed melting point showed no depression.

To a solution of 222 mg. of 11,12-dihydroxystearic acid, m. p. 93–94°, prepared from vaccenic acid, in 15 ml. of alcohol was added a solution of 182 mg. of periodic acid in 15 ml. of water. The solution was stirred up at room temperature for twenty minutes, then diluted with 150 ml. of water, and thoroughly extracted with ether. The ether solution was worked up as described above, and *n*-heptaldehyde semicarbazone was obtained. The yield of heptaldehyde was 58%. The sodium bisulfite addition product of the aldehydo acid fragment was precipitated as before, and was obtained in 52% yield. This product was unfortunately lost before it could be further examined.

## Summary

*cis*-11-Octadecenoic and *trans*-11-octadecenoic (vaccenic) acids have been synthesized in good yield by condensation of 1-octyne with 1-chloro-9-iodonane, conversion of the resulting 1-chloro-10-heptadecyne, via the nitrile, to the acid, and partial hydrogenation of the acetylenic bond. The above synthesis yielded only the *cis* form which was isomerized to the *trans* form with selenium.

MADISON, WISCONSIN RECEIVED APRIL 2, 1948

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

# 1,3,5-Hexatriene

BY G. FORREST WOODS AND LOUIS H. SCHWARTZMAN[1]

As Farmer and co-workers indicate,[2] 1,3,5-hexatriene is still of interest, inasmuch as (1) it is the simplest conjugated triene, and (2) its structure predicts two geometrical isomers, the *cis* form being the open chain analog of benzene.

1,3,5-Hexatriene has been prepared by (1) pyrolysis of *s*-divinylglycol diformate,[3] (2) condensation of allyl chloride with sodamide,[4] (3) phthalic anhydride dehydration of 1,5-hexadiene-3-ol[5] and (4) debromination of 3,4-dibromohexadiene-1,5 with zinc.[2] The product in method (3) contained cyclohexadiene, and the purification of the substance seems to have been incomplete in all cases.[3,5,6]

2,4-Pentadienal[7] is an excellent starting material for the preparation of 1,3,5-hexatriene, as shown by the following reactions

$$CH_2=CHCH=CHCHO + CH_3MgBr \longrightarrow$$
I

$$CH_2=CHCH=CHCHCH_3 \xrightarrow[Al_2O_3]{325°}$$
$$\underset{OH}{\overset{|}{\phantom{x}}}$$
II

$$CH_2=CHCH=CHCH=CH_2$$
III

Heilbron, et al.,[8] prepared (II) by rearrangement of propenylvinylcarbinol (V), a partial reduction product of propenylethynylcarbinol (IV)

$$CH_2=CHCH_2CHC\equiv CH \longrightarrow$$
$$\underset{OH}{\overset{|}{\phantom{x}}}$$
IV

$$CH_2=CHCH_2CHCH=CH_2 \longrightarrow$$
$$\underset{OH}{\overset{|}{\phantom{x}}}$$
V

$$CH_2=CHCH=CHCHCH_3$$
$$\underset{OH}{}$$
II

We made 1,3-hexadien-5-ol (II) as shown and its properties agree excellently with those reported by Heilbron, et al.,[8] who identified it by reduction to the saturated alcohol, oxidation of the saturated alcohol to hexanone-2 and comparison with known samples.

Catalytic dehydration at reduced pressures of the 1,3-hexadien-5-ol over alumina in a nitrogen atmosphere gave a 60% yield of the hydrocarbon boiling at 79–80° and crystallizing on cooling below −12°; it absorbed three moles of hydrogen with Adams catalyst at room temperature and pressure. Crystallization of the unsaturated hydrocarbon at low temperature is an important step, since it assures good purification and gives a single sharp melting substance, apparently one of the geometric isomers. Van Romburgh and Mueller[3] also obtained 1,3,5-hexatriene in solid state (m. p. −11°) by converting the impure hexatriene to pure dibromide, and debrominating it with zinc in boiling alcohol (*cf.* Farmer, et al.[2]). Table I contains collected data of various investigators for ready comparison. The refractive indices show wide variations; only Farmer, et al., have reported analyses previously and their values fit more closely the formula $C_6H_{10}$ than $C_6H_8$.

The dipole moment[9] of 1,3,5-hexatriene in benzene is $0.2D$. If an atomic polarization value larger than 5% of the electronic polarization is assumed, then this small value might indicate a zero dipole moment, but an examination of models of both *cis* and *trans* forms shows that neither should have a zero moment. Thus this measurement gives no convincing evidence on geometrical structure.

(1) National Institute of Health Predoctorate Research Fellow.

(2) Farmer, Laroia, Switz and Thorp, *J. Chem. Soc.*, 2937 (1927).

(3) Van Romburgh, *ibid.*, **90**, 130 (1906); *Verslag. K. Akad. Wetenschappen*, **8**, 568 (1905); **22**, 1044 (1914).

(4) Kharasch and Sternfeld, THIS JOURNAL, **61**, 2320 (1939).

(5) Butz, *et al.*, *J. Org. Chem.*, **5**, 178 (1940); Butz and Butz, *ibid.*, **7**, 199 (1942).

(6) Butz, THIS JOURNAL, **64**, 1978 (1942).

(7) Woods and Sanders, *ibid.*, **69**, 2927 (1947).

(8) Heilbron, Jones, McCombie and Weedon, *J. Chem. Soc.*, 84 (1945).

(9) The authors are indebted to Prof. W. J. Svirbely for aid both in the determination of the dielectric constant and in the interpretation of this measurement.