[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE CO.]

A Study of *n*-Octadecenoic Acids. I. Synthesis of *cis*- and *trans*-7- through 12- and of 17-Octadecenoic Acids[1]

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As the first step in a systematic study of the more important *n*-octadecenoic acids. the *cis* isomers of 7- through 12-octadecenoic acids were prepared by partial hydrogenation of the corresponding synthetic octadecynoic acids. Isomerization of the *cis* acids in the presence of selenium yielded the *trans* forms. 17-Octadecenoic acid was obtained by condensing the Grignard reagent of 10-undecenyl bromide with 6-carbethoxycaproyl chloride to form ethyl 7-keto-17-octadecenoate which. after saponification to 7-keto-17-octadecenoic acid. was reduced with hydrazine hydrate to 17-octadecenoic acid. The double bond positions of the octadecenoic acids were confirmed by periodic acid oxidation of the corresponding dihydroxystearic acids. to obtain the expected degradation products.

On the basis of m.p.'s both the *cis*- and the *trans*-octadecenoic acids fall into two sub-groups. one containing the higher melting 8-. 10- and 12-isomers and the other the lower melting 7-. 9- and 11-isomers. A plot of the m.p.'s of either the *cis* or the *trans* acids against double bond position forms a zigzag line resulting from the alternation of the melting points.

The fatty acids from unsaturated fats which have undergone partial catalytic hydrogenation contain position and configuration isomers of oleic (*cis*-9-octadecenoic) acid. Identity and properties of most of these so-called "isoöleic" acids, although frequently referred to in the literature, have not been determined reliably.

The preparation of a series of *n*-octadecenoic acids is herein reported. The reaction sequence reported by Strong and co-workers for the preparation of 6-hendecenoic acid[2a] and 11-octadecenoic acid[2b] was adopted for the synthesis of 7- through 12-octadecenoic acids. Since the completion of this work, Strong has also reported the preparation by this method of a number of 6- and 7-alkenoic acids.[3]

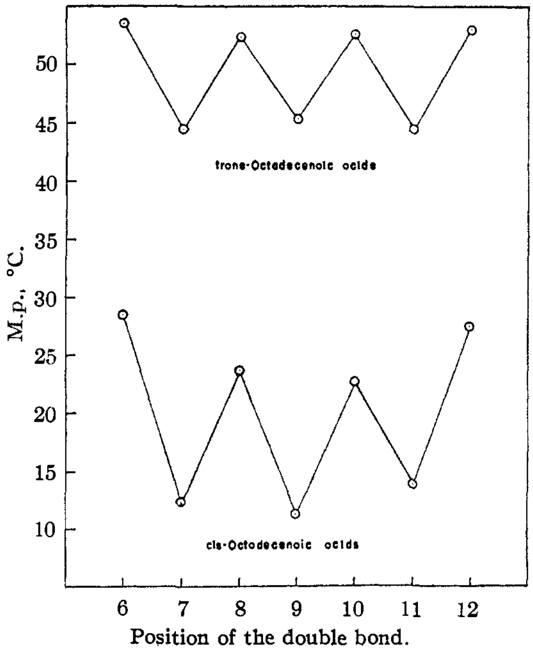

Fig. 1.—Melting points of the octadecenoic acids. The m.p.'s of *cis*-6-octadecenoic acid. 28.6°. and *trans*-6-octadecenoic acid, 53.6°, were determined on natural petroselinic and petroselaidic acid. prepared by Mr. R. G. Folzenlogen of this Laboratory.

In the present work an alkylacetylene was condensed with a chloroiodoalkane to a 1-chloroheptadecyne which was converted through the nitrile into the octadecynoic acid. Partial hydrogenation of the latter gave the *cis* form of the octadecenoic acid which by selenium-catalyzed isomerization was partially converted to the *trans* form. In order to have a continuous series of reference compounds, the synthesis of *cis*- and *trans*-11-octadecenoic acid as reported by Strong, *et al.*,[2b] was repeated and gave products with properties in agreement with their data. Although the melting point of *cis*-9-octadecenoic acid was slightly lower than that of natural oleic acid, it did not depress the melting point of the latter. Likewise, a similar comparison of the synthetic *trans*-9-octadecenoic acid and elaidic acid of natural origin showed the two acids to be identical.

17-Octadecenoic acid was prepared by a different reaction sequence. Ethyl 10-undecenoate was reduced with lithium aluminum hydride to 10-undecen-1-ol which in turn was converted to the bromide by reaction with phosphorus tribromide. The Grignard reagent of 10-undecenyl bromide was treated with cadmium chloride to form di-10-undecenylcadmium which reacted with 6-carbethoxycaproyl chloride to yield ethyl 7-keto-17-octadecenoate. This was hydrolyzed to 7-keto-17-octadecenoic acid and reduced with hydrazine hydrate to 17-octadecenoic acid. The physical properties of the product, which cannot exist in geometric isomers, agreed with those reported by Kapp and Knoll[4] who previously synthesized 17-octadecenoic acid by an alternate method.

The octadecenoic acids were oxidized to the corresponding dihydroxystearic acids with performic acid.[5] Oxidative scission of the dihydroxy compounds gave the expected aldehyde and dibasic acid in each case, thus furnishing a proof of structure for the octadecenoic acids.

Both the *cis*- and *trans*-octadecenoic acids fall into two sub groups, one containing the higher melting 8-, 10- and 12-isomers and the other the lower melting 7-, 9- and 11-isomers. When the melting points of the octadecenoic acids are plotted on the ordinate against double-bond position on the abscissa (Fig. 1), the melting points of the *cis*- and *trans*-octadecenoic acids fall on two distinct

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(1) The *cis*- and *trans*-*n*-octadecenoic acids other than *cis*-9-octadecenoic (oleic) acid are commonly referred to as "isoöleic" acids.

(2) (a) K. Ahmad and F. M. Strong. THIS JOURNAL, **70**, 1699 (1948); (b) K. Ahmad, F. M. Bumpus and F. M. Strong, *ibid.*, **70**, 3391 (1948).

(3) W. R. Taylor and F. M. Strong, *ibid.*, **72**, 4263 (1950).

(4) R. Kapp and A. Knoll, *ibid.*, **65**, 2062 (1943).

(5) D. Swern, G. H. Billen, T. W. Findley and J. T. Scanlan, *ibid.*, **67**, 1786 (1945).

curves, each curve appearing in a saw-tooth pattern in accordance with the alternation of melting points. This behavior is reminiscent of that of the homologous series of saturated normal fatty acids which exhibit a melting point alternation between compounds of odd and even numbers of total carbon atoms.

Experimental[6]

7-. 8-. 9-, 10-, 11-, and 12-Octadecenoic Acid

Alkylacetylenes.—1-Heptyne and 1-dodecyne were obtained commercially[7]; 1-Octyne, 1-nonyne, 1-decyne and 1-undecyne were synthesized.[8]

Alkanediols.—Hexamethylene glycol was obtained commercially.[9] The other glycols were prepared by reduction of the methyl or ethyl esters of the corresponding dibasic acids with lithium aluminum hydride.[10]

TABLE I

Dichloroalkane	B.p.. °C.	Mm.	n^{25}D	d^{25}_4	Yield. %
1,6-Dichlorohexane[a]	116	48	1.4561	1.0724	93.3
1,7-Dichloroheptane[b]	124-125	35	1.4565	1.0408	82.2
1,8-Dichlorooctane[c]	118-119	14	1.4572	1.0248	94.5
1,9-Dichlorononane[d]	86-89	2	1.4586	1.0173	93.0
1,10-Dichlorodecane[e]	115-120	4	1.4586	0.9945	94.2

Properties previously reported are: [a] B.p. 94° (22 mm.), J. v. Braun and C. Müller. *Ber.*, **38**, 2344 (1905). [b] B.p. 120° (28 mm.), *ibid.* [c] B.p. 240–242°. W. Solonina, *Chem. Zentr.*, **70**, I, 26 (1899). [d] B.p. 90–92° (0.1 mm.) n^{20}D 1.4591, K. Ahmad, *et al.*[2b] [e] B.p. 147–148° (11 mm.), d^{22}_4 0.9941, S. Kawai, *et al.*, *Chem. Zentr.*, **102**, II, 1694 (1931).

TABLE II

1-Chloro-iodoalkane	B.p.. °C.	Mm.	n^{25}D	d^{25}_4	Yield.[a] %	Iodine. % Calcd.	Found
5-Iodopentane[b]	125–127	36[c]	1.5297	1.6789	70.7	54.59	53.95
6-Iodohexane	96–98	6	1.5214	1.5799	46.4	51.48	51.17
7-Iodoheptane	110	6.5[d]	1.5158	1.5089	41.5	48.71	48.76
8-Iodoöctane	101–105	2.5	1.5113	1.4516	35.8	46.22	45.62
9-Iodononane	123–126	4[e,f]	1.5074	1.4028	35.5	43.98	44.22
10-Iododecane	140	3	1.5036	1.3589	34.0	41.94	41.79

[a] Yield based on sodium iodide. [b] Prepared by refluxing a solution of 1006 g. (7.14 moles) of 1.5-dichloropentane with 357 g. (2.38 moles) of sodium iodide in 2000 ml. of acetone for ten hours. British Patent 581.899. *C. A.*, 41, 3477 (1947), reports: [c] B.p. 95° (10 mm.). n^{20}D 1.5284. [d] B.p. 95° (2 mm.), n^{20}D 1.5153. [e] B.p. 122° (2 mm.). n^{20}D 1.5088. [f] K. Ahmad, *et al.*,[2b] found b.p. 123–124° (2.8–2.9 mm.). n^{25}D 1.5060.

The ester (1.75 moles) of the dibasic acid was added to a stirred suspension of 76 g. (2.0 moles) of lithium aluminum hydride in 1300 ml. of anhydrous ether at a rate sufficient to maintain gentle reflux. After addition was complete, the mixture was hydrolyzed by the gradual addition of 225 ml. of concd. sulfuric acid in 1300 ml. of water. The ether layer was separated, washed and evaporated to yield the glycol which was purified by distillation with the exception of 1,10-decanediol. which was purified by crystallization.

By this procedure ethyl pimelate gave a 60.1% yield of 1,7-heptanediol. b.p. 112–115° (3 mm.), n^{25}D 1.4520, d^{25}_4 0.9569, m.p. 20–22°: methyl suberate gave a 58.8% yield of 1,8-octanediol, b.p. 138–142° (3.5 mm.), m.p. 55–58°; ethyl azelate gave a 75.0% yield of 1,9-nonanediol, b.p. 121–125° (3 mm.), m.p. 42.5–45.5° and ethyl sebacate gave a 93.0% yield of 1.10-decanediol, m.p. 73–76° after one recrystallization from benzene.

Dichloroalkanes.—1,5-Dichloropentane was obtained commercially.[9] The other dichloroalkanes were prepared by treating the alkanediols with thionyl chloride in the presence of pyridine as described for the preparation of 1.9-dichlorononane.[2b] The products are presented in Table I.

Chloroiodoalkanes.—The dichloroalkanes were converted to the chloroiodoalkanes by reaction with sodium iodide in acetone solution in accordance with the procedure described for 1-chloro-9-iodononane.[2b] Properties of the chloroiodoalkanes are summarized in Table II.

Chloroheptadecynes.—Condensation of the appropriate alkylacetylene and chloroiodoalkane with sodium amide as the condensing agent in liquid ammonia solution according to described procedure[2a] gave the chloroheptadecynes given in Table III.

Octadecynoic Acids.—The octadecynoic acids described in Table IV were prepared in conventional manner by converting the chloroheptadecynes *via* the nitriles to the desired acids.[2a] Purification was obtained in each case by crystallization from 10 volumes of acetone at −20°.

***cis*-Octadecenoic Acids.**—Partial hydrogenation of the octadecynoic acids yielded the corresponding *cis*-octadecenoic acids.[2a] The crude acid was dissolved in ten volumes of acetone, by-product stearic acid was removed at −15° and the octadecenoic acid was isolated at −30°. A second fractional crystallization from acetone followed by distillation under diminished pressure yielded the pure *cis*-octadecenoic acids described in Table V.

***trans*-Octadecenoic Acids.**—The *cis*-octadecenoic acids were isomerized with selenium[2b] and the resultant *trans*-octadecenoic acids, described in Table VI, were isolated by two fractional crystallizations from ten volumes of acetone at −15°.

17-Octadecenoic Acid

10-Undecen-1-ol.—Five hundred two grams (2.73 moles) of 10-undecylenic acid[11] was esterified with ethanol in the conventional manner to yield 468 g. (81%) of ethyl 10-undecenoate, b.p. 140–141° (20 mm.), $n^{30.5}$D 1.4341.

Analogous to the procedure described above for the preparation of the alkanediols, 424.6 g. (2 moles) of ethyl 10-undecenoate was reduced with 47.4 g. of lithium alumi-

TABLE III

1-Chloro-heptadecyne	B.p.. °C.	Mm.	n^{25}D	d^{25}_4	Cl.[a] %	Yield. %
6-Heptadecyne[b]	136–140	2	1.4647	0.9023	13.04	15.1
7-Heptadecyne[b]	118–120	0.5	1.4640	.8990	13.47	26.5
8-Heptadecyne	156–158	4	1.4632	.8882	12.84	71.2
9-Heptadecyne	149–151	2	1.4631	.8951	13.49	53.5
10-Heptadecyne[c]	128–130	1	1.4629	.8865		87.6
11-Heptadecyne	159–162	3.5	1.4635	.8935	12.95	69.0

[a] Calcd. for $C_{17}H_{31}Cl$: Cl, 13.09. [b] Lithium amide was used as the condensing agent; M. S. Newman, M. W. Renoll and I. Auerbach, THIS JOURNAL, **70**, 1023 (1948). [c] K. Ahmad, et al.,[2b] report b.p. 121–122° (2.8 mm.), n^{20}D 1.4644.

TABLE IV

Octa-decynoic acid	Yield. %	M.p.. °C.	Neut. equiv.	I.V.	H_2 uptake moles	C. %	%
Theory			280.4	90.5	2.00	77.09	11.50
7-	77.5	48.5–49.5	284.2	87.8	1.99	77.27	11.35
8-	81.6	46.5–47.5	279.3	88.2	2.00	77.23	11.32
9-	24.2	46.4–47.6[a]	282.4	87.7	2.00		
10-	72.8	45.5–46.5	278.8	88.6	2.00	77.20	11.29
11-	77.2	46.0–47.3[b]	280.5	87.7	2.00		
12-	76.2	46.2–47.2	280.4	87.4	2.00	77.26	11.40

[a] 9-Octadecynoic acid (stearolic acid) melts at 48°; K. S. Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N.Y., 1947. p. 37. [b] K. Ahmad, *et al.*,[2b] report m.p. 45.5–46.5°.

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[6] All boiling points and melting points are uncorrected.

[7] Farchan Research Laboratories. Cleveland. Ohio.

[8] (a) T. H. Vaughn. G. F. Hennion. R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.*, **2**, 1 (1937); (b) T. L. Jacobs. "Organic Reactions." Vol. V, John Wiley and Sons. Inc., New York. N. Y., 1949, p. 1.

[9] Halogen Chemicals, Inc., Columbia, S. C.

[10] R. F. Nystrom and W. G. Brown. THIS JOURNAL. **69**. 1197 (1947).

[11] Eastman Kodak Company. Rochester. N. Y.

TABLE V

cis-Octadecenoic acid	Yield, %	M.p., °C.	Setting point, °C.	Neut. equiv.	I.V.	H_2 uptake, moles	C, %	H, %
Theory				282.5	89.9	1.00	76.54	12.13
7-Octadecenoic	49.8	11.8–12.5	11.3	282.1	87.7	0.986	77.02	11.76
8-Octadecenoic	64.1	22.7–23.8	23.1	280.2	88.8	.989	77.02	11.88
9-Octadecenoic	63.7	10.9–11.5[a]	10.9	282.9	88.4	.972	76.39	11.75
10-Octadecenoic	70.4	22.2–22.8	21.5	284.8	87.2	.975	76.86	11.80
11-Octadecenoic	61.3	13.0–14.0[b]	12.9	284.3	89.1	.998	76.15	11.87
12-Octadecenoic	64.5	26.8–27.6	27.2	282.5	87.3	.958	77.08	12.26

[a] Pure natural oleic acid has m.p. 13°. A. W. Ralston. "Fatty Acids and Their Derivatives." John Wiley and Sons. Inc., New York, N. Y., 1948. p. 109; [b] Ahmad, *et al.*,[2b] report m.p. 10.5–12.0°.

TABLE VI

trans-Octadecenoic acid	Yield, %	M.p., °C.	Setting point, °C.	Neut. equiv.	I.V.	H_2 uptake, moles	C, %	H, %
Theory				282.5	89.9	1.00	76.54	12.13
7-Octadecenoic	53.4	43.5–44.5	43.6	282.8	87.9	0.983	76.50	12.07
8-Octadecenoic	50.0	51.5–52.3[a]	51.3	282.3	88.3	.990	76.90	11.66
9-Octadecenoic	54.5	44.5–45.5[b]	43.4	279.2	88.6	.993	76.13	11.99
10-Octadecenoic	56.0	52.0–52.6	51.2	279.7	86.2	.994	76.58	11.69
11-Octadecenoic	55.0	43.5–44.5[c]	43.3	284.0	88.7	.990	76.67	11.90
12-Octadecenoic	55.8	52.0–53.0	51.5	279.2	86.9	.998	76.54	11.75

[a] J. H. Benedict and B. F. Daubert. THIS JOURNAL. **72**, 4357 (1950). isolated *trans*-8-octadecenoic acid. m.p. 52.4–53.4° from the isoöleic acid fraction of partially hydrogenated triolein. [b] Pure natural elaidic acid has m.p. 44.5°. A. W. Ralston. Table V, ref. *a*. p. 111. [c] K. Ahmad. *et al.*,[2b] report m.p. 43–44°.

num hydride in 1200 ml. of ether to yield 330 g. (97%) of 10-undecen-1-ol, b.p. 134–135° (18 mm.), n^{30}_{D} 1.4468.[12]

6-Carbethoxycaproyl Chloride.—A mixture of 120 g. (0.64 mole) of ethyl hydrogen pimelate[13] and 95 g. (58 ml., 0.8 mole) of thionyl chloride was allowed to stand overnight, warmed at 40° for one hour and then distilled to yield 123.5 g. (93.7%) of 6-carbethoxycaproyl chloride, b.p. 126–129° (8.5 mm.).[14] n^{25}_{D} 1.4440, d^{25}_{4} 1.0790. *MR* calcd.. 50.18. *MR* found. 50.88.

Anal. Calcd. for $C_9H_{15}O_3Cl$: Cl, 17.16. Found: Cl. 17.07. 17.16.

Ethyl 7-Keto-17-octadecenoate.—Di-10-undecenylcadmium was prepared from 93.3 g. (0.4 mole) of 10-undecenyl bromide[15] and treated at reflux in benzene solution[16] with 62 g. (0.3 mole) of 6-carbethoxycaproyl chloride to yield. after distillation through a 4-inch Vigreux column, 65.5 g. (67.3%) of ethyl 7-keto-17-octadecenoate, b.p. 192–198° (2 mm.), n^{25}_{D} 1.4532. d^{25}_{4} 0.9086. *MR* calcd.. 95.70, *MR* found, 96.57.

On standing the ester solidified to give white crystals melting at 32.5–34° after a recrystallization from petroleum ether.

Anal. Calcd. for $C_{20}H_{36}O_3$: C, 74.02; H, 11.18; sapn. equiv., 324.5. Found: C, 74.16; H, 10.98, sapn. equiv., 319.4.

7-Keto-17-octadecenoic Acid.—A mixture of 55.5 g. (0.17 mole) of ethyl 7-keto-17-octadecenoate and 27 g. (0.68 mole) of sodium hydroxide dissolved in 500 ml. of water was refluxed five hours. After cooling, the clear solution was acidified with dilute sulfuric acid to yield 47.2 g. (93.1%) of 7-keto-17-octadecenoic acid, m.p. 65–69.5°. Two recrystallizations from 95% ethanol at 0° yielded 35.4 g. of product, m.p. 70.5–73.5°. A 5-g. sample was further purified, for analysis, by two recrystallizations from an alcohol–petroleum ether mixture at ice–salt temperatures, m.p. 74–75.5°.

Anal. Calcd. for $C_{18}H_{32}O_3$: C, 72.93; H, 10.88; neut. equiv., 296.4; hydrogen uptake, 1.00 mole. Found: C, 73.24; H. 11.02; neut. equiv., 295.8; hydrogen uptake, 0.983 mole.

17-Octadecenoic Acid.—The reduction of 29.6 g. (0.1 mole) of 7-keto-17-octadecenoic acid with hydrazine in diethylene glycol[17] yielded 27.9 g. (99%) of crude 17-octa-

TABLE VII

DIHYDROXYSTEARIC ACIDS FROM THE *cis*-OCTADECENOIC ACIDS

Stearic acid	Yield of crude acid, %	Yield of recrystd. acid, %	M.p., °C.	O,[a] %	H,[b] %
7,8-Dihydroxy-	96.6	81.9	95–96	68.02	11.68
8,9-Dihydroxy-	92.1	60.9	96–97	68.24	11.37
9,10-Dihydroxy-	95.5	63.0	93–94[c]	68.11	11.42
10,11-Dihydroxy-	98.2	68.8	98–99.5	68.40	11.30
11,12-Dihydroxy-	97.0	72.7	94.5–96[d]		
12,13-Dihydroxy-	97.3	68.1	98.5–97	68.56	11.23

[a] Calcd. for $C_{18}H_{36}O_4$: C, 68.31. [b] H, 11.47. [c] D. Swern, *et al.*, ref. 5, report m.p. 94°. [d] K. Ahmad, *et al.*. ref. 2b, report m.p. 93–94° for the acid obtained by permanganate oxidation of *trans*-11-octadecenoic acid.

TABLE VIII

DIHYDROXYSTEARIC ACIDS FROM THE *trans*-OCTADECENOIC ACIDS

Stearic acid	Yield of crude acid, %	Yield of recrystd. acid, %	M.p., °C.	C,[a] %	H,[b] %
7,8-Dihydroxy-	83.9	73.2	132–133	68.35	11.51
8,9-Dihydroxy-	84.5	80.4	118–119[c]	68.19	11.29
9,10-Dihydroxy-	94.6	86.7	129–131[d]	68.51	11.58
10,11-Dihydroxy-	94.6	87.6	120–121	68.24	11.37
11,12-Dihydroxy-	98.2	79.7	129–130[e]	67.99	11.34
12,13-Dihydroxy-	89.3	59.5	119–120	68.28	11.32

[ab] See footnotes *a* and *b* under Table VII. [c] J. H. Benedict and B. F. Daubert. THIS JOURNAL. 72. 4357 (1950), report m.p. 127–128°. [d] D. Swern, *et al.*. ref. 5. report m.p. 130–130.5°. [e] Ahmad, *et al.*, ref. 2b, report m.p. 127–128° for the acid obtained by permanganate oxidation of *cis*-11-octadecenoic acid.

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(12) I. M. Heilbron. "Dictionary of Organic Compounds." Vol. III. Oxford University Press. New York. N. Y., 1938. p. 903. reports b.p. 132–133° (15 mm.). n^{19}_{D} 1.4506.

(13) Ethyl hydrogen pimelate. b.p. 127–130° (1.5 mm.). n^{25}_{D} 1.4392. was prepared in 65.8% yield in a manner analogous to that given for ethyl hydrogen sebacate in "Organic Syntheses." Coll. Vol. II. p. 276; I. M. Heilbron. *ibid.*. p. 492. reports b.p. 162° (6 mm.). n^{20}_{D} 1.4415.

(14) I. M. Heilbron. ref. 12. gives b.p. 138° (17 mm.).

(15) 10-Undecenyl bromide, b.p. 125–127° (12 mm.), n^{30}_{D} 1.4640. was prepared in 43.3% yield from 10-undecen-1-ol according to the directions of C. G. Tomecko and R. Adams. THIS JOURNAL. **49**. 527 (1927).

(16) J. Cason and F. S. Prout, *Org. Syn.*, Vol. 28, p. 75.

(17) Huang-Minlon. THIS JOURNAL, **68**, 2487 (1946).

TABLE IX

DEGRADATION PRODUCTS OF THE DIHYDROXYSTEARIC ACIDS

Dihydroxystearic acid from octadecenoic acid	Aldehyde 2,4-dinitrophenylhydrazone			Dibasic acid		
	Yield, %	M.p., °C.	Mixed m.p., °C.	Yield, %	M.p., °C.	Mixed m.p., °C.
cis-7-	88.8	105–106	105–106	26.9	99–100.5	100–103
trans-7-	80.8	105–106	105–107	10.4	100–101	101–101.5
cis-8-	47.8	103.5–104	105–106	60.3	139–141	141–142.5
trans-8-	67.6	104.5–105.5	107–108	56.4	140–141	140.5–142.5
cis-9-	66.0	102–104	103–104.5	50.5	105–106	105–106.5
trans-9-	81.4	103.5–105	104–105	50.4	105–106	105–106
cis-10-	58.7	105–106	105.5–107	68.2	130–132	130–132
trans-10-	47.2	105–106	104–105.5	76.6	130–132	130–132
cis-12-	55.3	100–101.5	104–106	71.0	124.5–126	[b]
trans-12-[a]	..	....	....	76.9	125.5–127	[b]

[a] The 2,4-dinitrophenylhydrazone of *n*-hexaldehyde from this acid was accidentally lost. [b] J. Walker and J. S. Lumsden, *J. Chem. Soc.*, 1201 (1901), report 1,10-decanedicarboxylic acid melts at 126.5°.

decenoic acid, m.p. 49.5–54°. The product was dissolved in a solution of 11 g. of potassium hydroxide in 800 ml. of 15% ethanol and extracted with ether. The aqueous layer was acidified with dilute sulfuric acid, the separated 17-octadecenoic acid taken up in ether and treated with Nuchar to remove colored impurities. Evaporation of the ether and recrystallization of the residue from 200 ml. of 70% ethanol yielded 19.5 g. (69%) of pure 17-octadecenoic acid, m.p. 55.5–56.1°.[18]

Anal. Calcd. for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13; neut. equiv., 282.5; iodine no., 89.9; hydrogen uptake, 1.00 mole. Found: C, 76.77; H, 11.86; neut. equiv., 282.6; iodine no. 88.7; hydrogen uptake, 0.994 mole.

Dihydroxystearic Acids.—Each of the octadecenoic acids was oxidized according to the method of Swern[5] to form the corresponding dihydroxystearic acid which was purified by recrystallization from ethanol. The yields and properties of the dihydroxystearic acids resulting from the oxidation of 1 gram of the *cis*-octadecenoic acids are recorded in Table VII and those from the oxidation of 1 gram of the *trans*-octadecenoic acids in Table VIII.

Oxidation Degradation of the Dihydroxystearic Acids.—The general method used was a modification of that of King.[19]

A solution of 200 mg. of periodic acid in 10 ml. of water was added to a solution of 200 mg. of the dihydroxystearic acid in 15 ml. of 95% ethanol at 40°. The mixture was allowed to stand at room temperature for 3 hours with occasional shaking and then poured into 100 ml. of water. The aqueous mixture was extracted with 150 ml. of ether in 5 portions, the ether solution evaporated and the residual oil steam distilled until 75 ml. of distillate was collected. The distillate was extracted with 100 ml. of ether in 5 portions and the ether evaporated to yield a residue of aliphatic aldehyde which was isolated as the 2,4-dinitrophenylhydrazone. The latter was purified by recrystallization from alcohol and identified by mixed melting point with an authentic sample. X-Ray diffraction patterns of the 2,4-dinitrophenylhydrazones[20] also agreed with those of authentic samples.

The aqueous solution (*ca.* 25 ml.) remaining from the steam distillation contained the aldehydrocarboxylic acid. The solution was acidified with 1 ml. of concd. sulfuric acid, warmed to 50° and treated with powdered potassium permanganate to excess. The mixture was then decolorized by the addition of solid sodium bisulfite, cooled and filtered to yield the dibasic acid which was recrystallized and identified by mixed melting point with an authentic sample.

Table IX lists the dihydroxystearic acids which were degraded and the resultant degradation products.

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[18] R. Kapp and A. Knoll, ref. 4, report, m.p. 55–55.5°.

[19] G. King, *J. Chem. Soc.*, 1826 (1938).

[20] C. B. Stewart, W. F. Huber and E. S. Lutton, to be reported.

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE CO.]

A Study of *n*-Octadecenoic Acids. II. Diffraction Patterns of *trans*-6- through 12-Octadecenoic Acids

BY E. S. LUTTON AND DON G. KOLP

An X-ray diffraction study of the *trans*-6- through 12-octadecenoic acids reveals an alternation of pattern corresponding to the previously reported m.p. alternation. The odd compounds, *i.e.*, those whose double bond begins at an odd-numbered carbon, *e.g.*, 9-octadecenoic acid, have greater long spacings and lower melting points. Short spacing data of the several acids within each series, odd or even, are quite similar, but detailed observation reveals definite differences which are sufficient to help in identifying an individual pure acid, and which distinguish between elaidic (9-) and vaccenic (11-octadecenoic) acids, for example.

Diffraction data have been reported by Benedict and Daubert[1] on elaidic (*trans*-9-) and vaccenic (*trans*-11-octadecenoic) acids. The patterns were reported to be essentially identical but different from that of natural vaccenic. The synthesis by Huber[2] of a series of *trans*- (and *cis*) octadecenoics, 7- through 12-, permitted close inter-comparison of the diffraction behavior of this whole family of compounds. Petroselaidic acid (*trans*-6-octadecenoic) was available from natural sources to extend the series.

Experimental

Samples of each compound were prepared for diffraction study by crystallization both (1) from solvent (acetone) and (2) from melt. Solvent-crystallized materials were ground in mortar and pestle, and rod-shaped specimens for X-ray exposure were made by a method previously described.[3] Specimens from melt were solidified in 1-mm. thin-walled Pyrex capillaries. Diffraction patterns were obtained with a G.E. XRD unit employing CuKα radiation

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[1] J. H. Benedict and B. F. Daubert, THIS JOURNAL, 71, 4113 (1949).

[2] W. F. Huber, *ibid.*, 73, 2730 (1951).

[3] E. S. Lutton and F. L. Jackson, *ibid.*, 70, 2445 (1948).