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.

Acknowledgment.—The author wishes to express his appreciation to Mr. Gerald E. Burnett for assistance in the experimental work.

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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.

CINCINNATI 17, OHIO RECEIVED DECEMBER 13, 1950

[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 $CuK\alpha$ 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).

($K\beta$ eliminated with nickel filter), flat film technique and 10 cm. sample-to-film distance. Routinely, a 0.025″ collimating pinhole was used and samples were oscillated. For high resolution, particularly well ground stationary samples were used in conjunction with a 0.010″ collimating slit. In Table I characteristic data for odd acids (having the double bond begin at an odd numbered carbon as in 9-octadecenoic) and even acids (*e.g.* 6-octadecenoic) are given, and in Fig. 1a and b differences between individual odd and between individual even acids are clearly indicated. In Fig. 1 the intensities are plotted after assigning arbitrary numerical values to qualitative visual ratings (VS = 5, S = 4, M = 3, W = 2, VW = 1, + = +0.33, − = −0.33; *e.g.*, M + = 3.33).

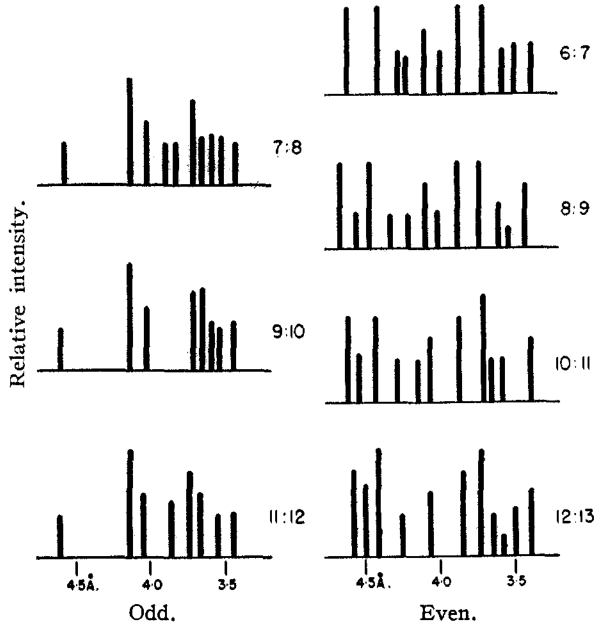


Fig. 1.—Comparison of detailed short spacings for *trans*-octadecenoic acids.

Discussion

No polymorphism was observed for the *trans*-octadecenoic acids. This is in contrast with the three forms observed for stearic[4] and two forms for oleic acid.[5] The main feature of the series as a whole is the alternation between odd and even acids in pattern type as indicated in Table I. This is in accord with the m.p. alternation reported by Huber.[2] From the magnitude of the long spacings it is probable that in the odd acid structure the hydrocarbon chains are perpendicular (or very nearly so) and that in the even structure chains are tilted with respect to the carboxyl planes.

Table I

Characteristic Diffraction Spacing (Å.) for Odd and Even *trans*-Octadecenoic Acids

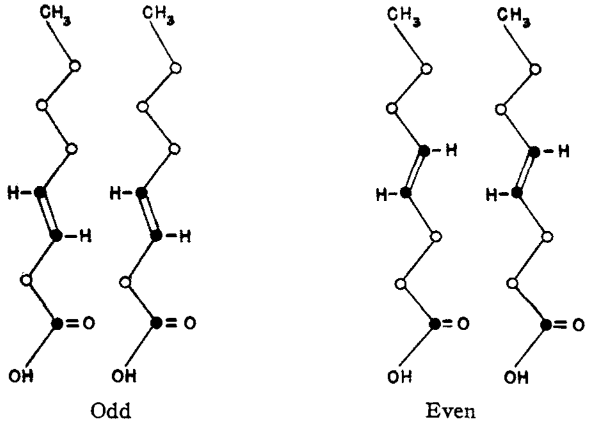
Classification	Long spacing	Short spacing
Odd (7-, 9-, 11-)	49.5	4.15 VS, 3.74 S
Even (6-, 8-, 10-, 12-)	45.5	4.61 S, 4.43 S, 3.87 S, 3.72 S +

It is shown in Fig. 1a that the spacings of odd acids, although very similar, are definitely different in detail. A similar small but definite difference between even acids is shown in Fig. 1b. Specifically there is a difference between elaidic (9-) and vaccenic (11-) acids, although Benedict and Daubert reported identical patterns differing from that of natural vaccenic. For instance, at 3.9 Å. vaccenic acid has a definite spacing which is missing or extremely weak for elaidic. It is of interest that synthetic and "natural" elaidic gave identical patterns.

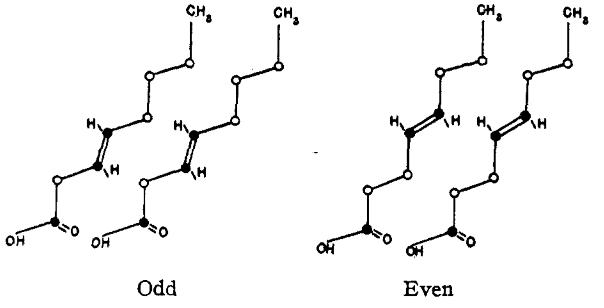
The fundamental difference between the elaidic and vaccenic preparations of this study was shown also by mixed m.p., 37.2° for the mixture as compared with 45.5 and 44.5° for elaidic and vaccenic, respectively. Moreover, diffraction data on the 2,4-dinitrophenylhydrazones of aldehydic scission products show a difference and agree with data on compounds prepared from the supposed corresponding "known" aldehydes.[2,6]

Bumpus, *et al.*,[7] have shown by chromatographic study of degradation products that their synthetic vaccenic is truly an 11-octadecenoic acid. By mixed m.p. of dihydroxy derivatives they have distinguished between vaccenic and elaidic acids. Diffraction studies in this Laboratory on a series of dihydroxy acids[8] have further established the individuality and authenticity of synthetic vaccenic and elaidic acids.

Alternation in a series of constant chain length such as the *trans*-octadecenoic acid series has not



(a) Vertical



(b) Tilted

Fig. 2.—Effect of tilting on configuration at the double bond in hypothetical alkenoic acid structures.

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[4] F. Francis, F. J. E. Collins and S. H. Piper, *Proc. Roy. Soc.* (*London*), **158A**, 691 (1937).

[5] E. S. Lutton, *J. Am. Oil Chem. Soc.*, **23**, 265 (1946).

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

[7] F. M. Bumpus, W. G. Taylor and F. M. Strong, This Journal, **72**, 2116 (1950).

[8] E. S. Lutton, W. F. Huber and A. J. Mabis, *ibid.*, **73**, in press (1951).

been emphasized in the literature. It is simple to associate m.p. alternation in the present compounds with the diffraction pattern alternation, specifically with long spacing alternation, *i.e.*, the vertical chains of odd acids and the tilted chains of even acids. But there remains the somewhat deeper question of what, in the geometry of the crystallized molecule, lies behind the differences in tilt (it being assumed that alternation is a phenomenon of the solid state in this case as in the case of homologous series).

In considering separately the cases for vertical and tilted chains, it appears to the authors that alternation is not predictable for vertical structures from what we now know, but that it is predictable for tilted structures. That is, a tilted structure for an individual even octadecenoic acid, presumably one of a series of similarly tilted structures, would be expected to show alternation with odd acid structures whether the latter were vertical (as in the present case), differently tilted or even very similarly tilted.

In Fig. 2a there is illustrated a possible alinement of vertical odd and even chains for a pair of alkenoic (*i.e.*, *trans*-octenoic) acids comparable to the *trans*-octadecenoic acids of this paper. There is a certain amount of lateral shifting of elements of the chains which is different in the two cases. This might give rise to measurable alternation, but it is conceivable that it would not, and it appears probable that any alternation would be small. In the different but nevertheless related case of homologous series, Malkin[9] has shown that the lateral shifting involving methyl groups is not associated with measurable alternation in properties associated with vertical structures.

In the absence of relevant experimental data, the case for alternation in vertical *trans*-octadecenoic structures cannot be settled. However, it appears possible to demonstrate a definite basis for alternation with tilted chains. In Fig. 2b it can be seen that the inter-relationship of double bonds, hence of CH groups, in the odd tilted structure is different from that in the even structure. Just this sort of geometric difference should give rise to stability differences, hence alternation of properties for odd and even compounds. It must be that the spacial configuration of tilted odd chains is somehow so unfavorable as to give way to a vertical structure.

The *trans*-octadecenoic forms show no great similarity to stearic acid forms. The perpendicular odd form has no counterpart among stearic forms[4] although in short spacing type it resembles the B and C forms of stearic in the prominence of 4.2 and 3.8 Å. spacings. The tilted even form shows some similarity to the A form of stearic in both short[10] and long spacings.

Acknowledgment.—The authors express their appreciation to those of this Laboratory who have contributed to the experimental work.

[9] T. Malkin, *Nature*, **127**, 126 (1931).

[10] E. S. Lutton, to be reported.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TASMANIA]

Urea–Formaldehyde Kinetic Studies. I. Variation in Urea Solutions

BY LLOYD E. SMYTHE

Previous work on urea–formaldehyde kinetic studies[1,3] indicated variations in the reaction rate and in *p*H upon blending solutions of urea and formaldehyde. This appeared to be connected with variations in the urea solutions and suggested a study of the stability of aqueous urea solutions with keeping and the effect of various urea solutions on the initial urea-formaldehyde reaction. It was found that solutions of urea at room temperature attain equilibrium with small amounts of ammonium carbonate and ammonium cyanate. While traces of such compounds do not affect the general nature of the reaction they have a retarding effect on reaction rate. Reaction rates are given for various urea solutions and the initial reaction is further examined in the light of experiments carried out in relation to the nature of urea and formaldehyde in aqueous solution. It is suggested that the initial bimolecular reaction is between that portion of the 8 *M* urea solution (40–50%) which exists in an activated form as an anion and that this reacts with the formaldehyde in the dehydrated form. The subsequent and slower bimolecular reaction then takes place as indicated previously[1] with the additional concept of dehydration of the remaining ethylene glycol.[2] Work carried out so far indicates that some 40–50% of urea in aqueous 8 *M* solutions exists as an anion available for rapid reaction.

A previous paper[1] gave kinetic data for the reaction between urea and formaldehyde in aqueous solution. While the observations presented in this paper have been subsequently confirmed and extended by Crowe and Lynch[2] and Bettelheim and Cedwall,[3] the latter authors pointed out that under their conditions changes of *p*H during the reaction are either constant or show little decrease for 1:1 mole ratios using 4.36 *M* solutions of urea and formaldehyde. This contrasted with the sudden drop in *p*H to 4.95 followed by a gradual rise to *p*H 6.5, upon mixing equal volumes of an 8 *M* urea solution (*p*H 8.66) with 8 *M* formaldehyde solution (*p*H 7.0).[1]

Bettelheim and Cedwall in their investigation of *p*H values immediately after blending, adjusted the solutions to the experimentally required conditions with 1 *N* sodium hydroxide or sulfuric acid and also by adding to the urea, small amounts of ammonia or ammonium salt. By the latter procedure, a lowering of *p*H after blending, to about 5 was obtained but as the reaction progressed the *p*H dropped further.

It seemed desirable, while carrying out a program of investigation of the kinetics of the formation of substituted diamides of carbonic acid, to study the

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[1] Smythe, *J. Phys. Colloid Chem.*, **51**, 369 (1947).

[2] Crowe and Lynch, THIS JOURNAL, **70**, 3795 (1948); **71**, 3731 (1949); **72**, 3622 (1950).

[3] Bettelheim and Cedwall, *Svensk Kem. Tid.*, **60**, 208 (1948).