Anal. Calcd. for $C_6H_5CH_2NH_2{\cdot}HF{\cdot}H_2O$: F, 13.1; N, 9.7. Found: F, 12.7; N, 10.4.

The fact that the fluorine content was found to be too low, the nitrogen too high, can be explained by a certain tendency of the salt to lose HF, benzylamine remaining in the residue. This was shown in the following way. (a) The salt dissolves in water with neutral reaction; but after standing for a while, the solution becomes alkaline, probably by loss of HF. (b) When the dry salt is heated in suspension with benzene in a test-tube, the glass becomes etched and the benzene contains an alkaline substance, probably benzylamine.

Guanidine Salt of Diisopropylphosphoric Acid (a).—Three hundred mg. of the barium salt of diisopropylphosphoric acid was dissolved in a small amount of water and passed through a column of Dowex 50 ion-exchange resin. The column was washed twice with water; the solution and washings were caught in an evaporating dish and concentrated by evaporation. Guanidine carbonate was added and carbon dioxide was liberated. The solution was filtered and the guanidine salt of diisopropylphosphoric acid crystallized from the mixture after adding acetone; m.p. 152–154°.

(b).—2.5 g. of the barium salt of diisopropylphosphoric acid was dissolved in a small amount of water and 2.1 ml. of 5 *N* H_2SO_4 added, the precipitated barium sulfate centrifuged off, and 900 mg. of guanidine carbonate added to the clear solution. After concentration on a boiling water-bath, acetone was added to the solution. The precipitate so obtained, which melted at 155–156°, was redissolved in distilled water and reprecipitated with acetone; beautiful long needles, m.p. 155–157°, were obtained. The material was insoluble in ether or petroleum ether.

(c).—One ml. of DFP, 450 mg. of guanidine carbonate and 2 ml. of distilled water were heated on a boiling water-bath until no more carbon dioxide was evolved. After cooling and addition of acetone, silky needles, m.p. 267–270°, were obtained. The material contained nitrogen and fluorine and was presumably guanidine hydrofluoride. To the filtrate more acetone was added and the crystals obtained were reprecipitated twice from water–acetone; m.p. 153–158°; yield 100 mg. For analysis the material was dried over phosphorus pentoxide in a vacuum.

Anal. Calcd. for $C_7H_{20}N_3O_4P$: C, 34.9; H, 8.35; N, 17.42; P, 12.88. Found: C, 34.9; H,8.3; N, 17.59; P, 13.3.

ARMY CHEMICAL CENTER, MARYLAND

RECEIVED MARCH 3, 1951

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

A Study of *n*-Octadecenoic Acids. III. X-Ray Diffraction Behavior of 6,7- through 12,13-Dihydroxystearic Acids

BY E. S. LUTTON, W. F. HUBER, A. J. MABIS AND C. B. STEWART

Both the low-melting and the high-melting series of 6,7- through 12,13-dihydroxystearic acids (obtainable, respectively, from the *cis* and *trans* series of octadecenoic acids by performic acid oxidation) show alternation of properties. By m.p.'s and interplanar spacings, it is possible to classify these acids into four sub-groups, namely, the even (6,7-, 8,9-, etc.) and the odd (7,8-, 9,10-, etc.) low-melting and the even and odd high-melting isomers. Within each sub-group the individual members cannot be satisfactorily distinguished by means of m.p. and interplanar spacings. They can be distinguished, however, by the relative intensities of the different orders of their long spacings. These relative intensities fall in line with calculated values. An incomplete correspondence of the 6,7-acids with other even acids was partially accounted for by their polymorphism. (The 9,10-compounds were also found to be polymorphic.)

The characterization of individual *cis* and *trans* 6- through 12-octadecenoic acids is a difficult matter. The first two papers of this series,[1,2] which describe the synthesis of both *cis* and *trans* acids and diffraction patterns of the latter, reveal an alternation in both m.p. and interplanar spacings, such that classification of either a *cis* or a *trans* acid as a member of an "even" (6-, 8-, etc.) or "odd" (7-, 9-, etc.) sub-group is readily made, but positive identification of any individual odd (or even) acid is not easy. It is true that odd (or even) *trans* acids show diffraction differences, but only in fine details revealed by high resolution technique. Mixed m.p. methods can, of course, be used; and Bumpus, *et al.*,[3] have shown that it is possible to characterize the octadecenoic acids according to double bond position by chromatographic examination of their monocarboxylic degradation products.

A simple and reasonably direct means of characterizing individual octadecenoic acids was therefore still to be sought. It seemed that the relative intensities of the long spacings ((001) reflections) of their dihydroxy derivatives should give clear-cut distinction between individual octadecenoic acids because of the differences in relative position along the diffracting unit of the added strongly diffracting hydroxyl groups. In other words, it was to be expected that the relative intensities of a pair of successive long spacing orders, for example, should change with change in hydroxyl positions. On testing this idea, it proved successful, for the most part, as shown by the results reported in this paper.

An excellent method for preparing dihydroxy acids has been described by Swern, *et al.*,[4] and diffraction data for products thus prepared from *cis*- and *trans*-9-octadecenoic acids have been reported by Witnauer, *et al.*[5]

In the first paper of the present series[1] the preparation and m.p.'s of the low-melting and high-melting dihydroxy derivatives (hereafter referred to as LMDH and HMDH, respectively) of the 7- through 12-octadecenoic acids were reported. These samples were used in the present diffraction study. Data are also reported which were obtained by studying the LMDH and HMDH derivatives of 6-octadecenoic acid.

It has been shown by various workers[6,7] that the

---

[1] W. F. Huber, THIS JOURNAL, **73**, 2730 (1951).

[2] E. S. Lutton and D. G. Kolp, *ibid.*, **73**, 2733 (1951).

[3] F. M. Bumpus, W. R. Taylor and F. M. Strong, *ibid.*, **72**, 2116 (1950).

[4] D. Swern, G. H. Billen, T. W. Findlay and J. T. Scanlan, *ibid.*, **67**, 1786 (1945).

[5] L. P. Witnauer and D. Swern, *ibid.*, **72**, 3364 (1950).

[6] A. W. Ralston, "Fatty Acids and Their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 422–426.

[7] K. S. Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N. Y., 1947, pp. 437-440.

oxidation of oleic acid by peracids yields a dihydroxystearic acid, m.p. 95°, which is isomeric with that obtained from elaidic acid, m.p. 132°, but identical with that obtained by alkaline permanganate oxidation of elaidic acid. This same relation has been reported for the dihydroxy derivatives of *cis*- and *trans*-6-[6] and 11-octadecenoic acids.[3] It was found to be valid in the present work for the dihydroxy derivatives of 8- and 12-octadecenoic acid. Presumably it holds for all the dihydroxy acids investigated in the present study.

Just as the octadecenoic acids were classifiable according to geometric configuration and physical behavior into four groups—*cis* odd and *cis* even and *trans* odd and *trans* even—so did the derived dihydroxy acids fall into four groups—LMDH even (6,7-, 8,9-, etc.) and odd (7,8-, 9,10-, etc.) and HMDH even and odd.

Experimental

The preparation of 7,8- through 12,13-LMDH and -HMDH acids has been described.[1] The corresponding 6,7-acids were prepared by both performic acid[4] and alkaline permanganate oxidation of natural petroselinic acid and its *trans* isomer, petroselaidic acid.[8] When made by either method of oxidation, the 6,7-LMDH acid melted at 119° and the HMDH acid at 124°[9] after crystallization from ethanol or ethanol–petroleum ether. For m.p. and diffraction studies, preparations made with either oxidizing agent were used interchangeably.

M.p.'s on solvent-crystallized samples were carried out in typical fashion by raising capillary tube samples at the rate of approximately 1° per minute. Both m.p. and diffraction results on the 6,7-compounds were at such variance with data for other compounds that a brief investigation of possible polymorphism was carried out. For both 6,7- and 9,10-LMDH and HMDH compounds, m.p. and diffraction study of samples chilled from their melts was made. M.p.'s, actually softening points, were determined by a "thrust in" technique[10] with the intention of avoiding possible transformations by the slow heating process of the normal m.p. procedure. Polymorphism was definitely established for all four individuals tested. Thermal data are recorded in Fig. 1 and Table II[11] (which also includes previous data[1] on solvent-crystallized 7,8- through 12,13-dihydroxy acids).

X-Ray diffraction data were obtained by both film and spectrometer techniques. A G.E. XRD-1 unit, using nickel-filtered CuKα (λ 1.5418 Å.), 0.025" pinhole collimators, and a flat film with 10-cm. sample-to-film distance, was employed for the film studies. Solvent-crystallized samples were prepared as rod pellets; melt-crystallized samples were prepared in thin-walled Pyrex glass capillaries. During exposure the samples were oscillated through 180° around the X-ray beam as an axis. Short and long spacing magnitudes, Table I and Fig. 2, were determined by film measurements. Relative intensities for both short (Table I) and long spacings (Table II[11]) were obtained by visual estimation.

Relative long spacing intensities were also determined quantitatively with a Norelco horizontal type spectrometer using vanadium oxide-filtered CrKα radiation (λ 2.2909 Å.) for better resolution of the long spacings. Sample holders were rectangular $^1/_{16}$" aluminum plates with a $^1/_2$" × $^7/_8$" hole cut through them. Samples were packed in these holes from the back side against a ground glass plate. The probable preferred orientation of the plate-like crystals was ignored, since only relative intensities of the various orders of the long spacings were to be measured. Patterns were obtained by automatic scanning at 1° per minute. Intensities were measured as counts per second (c.p.s.), by approximate conversion of chart units to c.p.s., corrected for non-linear response of the Geiger tube at high intensities. The intensities were then expressed on a relative scale, with the strongest order (other than the 1st) arbitrarily given a

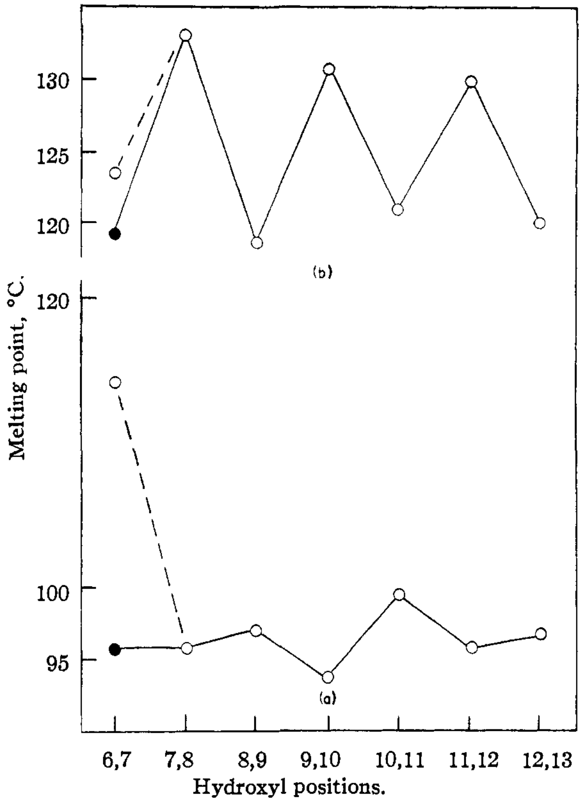


Fig. 1.—Melting points of dihydroxy acids (a) LMDH, (b) HMDH: ●, crystallized from melt; ○, crystallized from solvent.

TABLE I

CHARACTERISTIC DIFFRACTION DATA FOR DIHYDROXY STEARIC ACIDS

Hydroxyl positions	LMDH L. S.,[a] Å.	LMDH S. S.,[b] Å.	HMDH L. S., Å.	HMDH S. S., Å.
		From solvent		
6,7	22.2 (44.4)	4.69S[c] 4.84S+ 3.91S+ 3.57S (8.37S)	22.5 (45.0)	4.72M 4.47S 4.37M− 3.87VS 3.56M− (8.37S)
Odd-7,8; 9,10; 11,12	38.8	4.51VS 4.10VS− 3.62S	42.2	4.35M 4.16S 3.99W+ 3.56M−
Even-8,9; 10, 11; 12,13	45.5	4.71S 4.55M 4.02S 3.66M+	43.9	4.73M− 4.31M+ 4 13S
		From melt		
6,7	45.5	4.71S 4.55M 4.02S 3.66M+	45.4	4.51S 4.11S 3.95S
9,10	48.9	4.70S 4.19S 3.72W	48.7	4.28S

[a] L. S. is long spacing. [b] S. S. is short spacing. [c] VS very strong, S strong, M medium, W weak.

---

(8) Prepared by Mr. R. G. Folzenlogen of this Laboratory.

(9) K. S. Markley, ref. 8, p. 437, reports m.p.'s of 115° and 122° for the LMDH and HMDH compounds, respectively.

(10) E. S. Lutton, F. L. Jackson and O. T. Quimby, THIS JOURNAL, **70**, 2441 (1948).

(11) For detailed tables of data order Document 3303 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

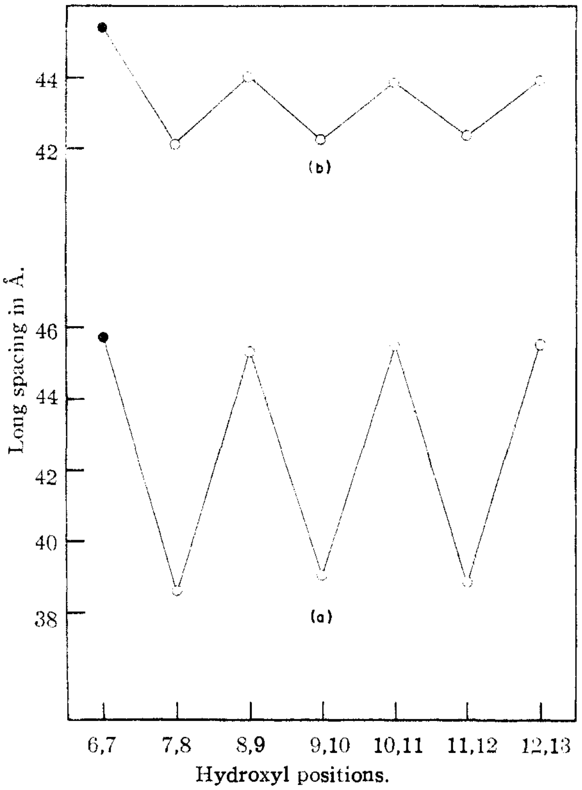


Fig. 2.—Long spacings of dihydroxy acids (a) LMDH, (b) HMDH: ●, crystallized from melt; ○, crystallized from solvent.

value of 1000. Accuracy of the intensity measurements is estimated at no better than ±10%.

The normal double-chain-length forms were studied by spectrometer technique, *i.e.* the solvent-crystallized 7,8- through 12,13-LMDH and HMDH compounds and the melt-crystallized 6,7-HMDH compound, but not 6,7-LMDH since a large enough sample of double structure could not be made. Data for the two series appear in Fig. 4, where comparison is made with calculated intensities. (Actual numerical data for the 9,10-compounds, both experimental and calculated, appear in Table IV.[11])

Discussion

There is an alternation in both melting and diffraction behavior for solvent-crystallized acids of the LMDH and HMDH series when the hydroxyls are in the 7,8- through 12,13-positions. For a given series, e.g. LMDH, m.p.'s and long spacings of the "odd" acids appear at a different level from those of the "even" acids. This is shown in Tables I (and II[11]) and in Figs. 1 and 2. The solvent-crystallized 6,7-acids show single-chain-length instead of the normal double-chain-length structures and melt abnormally high. (They also show apparent short spacings at 8.37 Å., in the normal long spacing region.) However, their solidified melts have double structures and melt in the expected range. The 6,7-LMDH isomer (from melt) agrees closely in diffraction behavior with other even members (from solvent). The HMDH isomer shows less satisfactory agreement; thus its long spacing is abnormally large. (In most trials the 6,7-LMDH isomer showed both single and double structures in solidified melts, but a pure double structure was observed with a sample prepared by the action of alkaline permanganate on *trans*-6-octadecenoic acid.)

As in the case of the *trans*-octadecenoic acids, there are detailed differences between similar diffraction patterns (as for the odd LMDH isomers), but these differences were not explored because of clearer distinctions possible on the basis of long-spacing intensities.

Diffraction data on the solvent-crystallized 9,10-compounds are in satisfactory agreement with those of Witnauer, *et al.*,[5] except that their 3.92 M line reported for their low melting isomer was found to be no stronger than W.

Solidified melts of 9,10-acids like those of 6,7-acids show behavior contrasting with that of corresponding solvent-crystallized compounds. Although both melt- and solvent-crystallized 9,10-acids appear to have double-chain-length structures, the former show perpendicular and the latter tilted chains and the relative intensities of various long spacing orders show major differences. As will be indicated later, certain main features of long-chain arrangement in solvent-crystallized samples must be analogous to those of stearic acid. It is surprising that any double-chain-length structure for these 9,10-acids should differ from this in a way to affect long-spacing intensities. Another unexpected feature was the single strong short-spacing of the melt-crystallized 9,10-HMDH isomer, which suggests possible rotational freedom about the long chain axis as in the "alpha" forms of many other long-chain compounds. Despite diffraction pattern differences no melting point differences were observed between a given melt- and solvent-crystallized 9,10-compound.

In the present state of knowledge it is not possible to say whether the alternation of properties between odd and even compounds of a series, *e.g.* HMDH, involves anything more basic than the inevitable difference in spatial arrangement that would occur with tilted chains.

In the present study, perhaps the greatest interest lay in the relative intensities of the various long spacing orders. An attempt was made to determine from fundamental principles what effect the shift of hydroxyls along the carbon chain would have on the long-spacing intensities in the dihydroxy stearic series; in other words, to estimate how sensitive X-ray diffraction tests should be to double-bond shift in the original octadecenoic series. Accordingly a calculation was made after the manner of Velick[12] for methyl substituted stearic acids as adapted from the procedure of Wilson and Ott[13] for long-chain alcohols. The intensities for stearic acid follow the relationship

$$I_{001} = K\,\frac{1+\cos^2 2\theta}{\sin 2\theta}\left[9(\cos 2\pi l\delta_1) + 8\sum_{2}^{17}(\cos 2\pi l\delta_n) + 14\,(\cos 2\pi l\delta_{18}) + 9(\cos 2\pi l\delta_{OH})\right]^2$$

where

l = long spacing order
K = constant
θ = Bragg angle

---

[12] S. F. Velick, *J. Biol. Chem.*, **154**, 497 (1944).

[13] D. Wilson and R. Ott, *J. Chem. Phys.*, **2**, 239 (1935).

$\delta_n = (n - 1)\delta + \delta_1$ = fractional long spacing distance from the (001) reference plane to the nth carbon atom counted from the methyl end of the chain. Here δ is the projection of the carbon–carbon distance on the normal to the (001) plane and δ_1 = fractional long spacing distance from (001) reference plane to center of CH_3 group. This relation, which is strictly correct for chains perpendicular to the (001) planes, was found by Velick (although he did not give it explicit expression) to be a good approximation in the stearic acid case where the angle of tilt is large. Velick's value for δ was 0.0261 and empirically he found the same value to be acceptable for δ_1. Hence the relation conveniently reduces to $\delta_n = n\delta_1$.

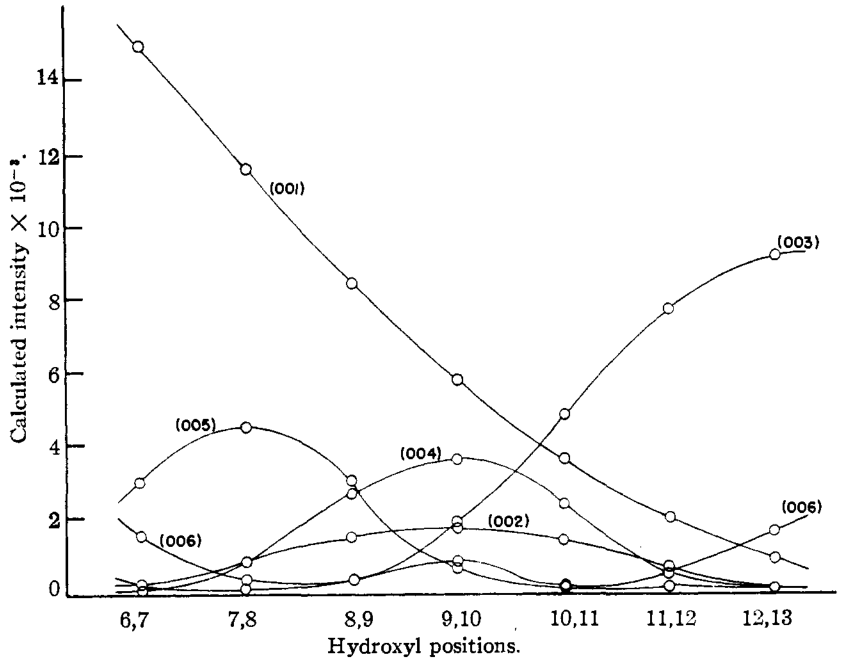


Fig. 3.—Variation of calculated long spacing intensities with hydroxyl positions.

δ_{OH} = fractional long spacing distance from (001) reference plane to OH in the carboxyl group. With δ_1 set at the aforementioned value, δ_{OH} had a value of 0.4911.

9, 8, 14 and 9 = scattering factors for CH_3, CH_2, CO and OH groups, respectively.

To modify this expression for dihydroxy acids it is necessary to assume a comparable COOH to COOH structure with similar angle of tilt. Then it is necessary only to add appropriate terms within the brackets corresponding to substitution of hydroxyls for hydrogens at the assumed positions. Thus for 6,7-dihydroxystearic acid the added terms are

$$8 \cos 2\pi l\delta_{(18-6+1)} + 8 \cos 2\pi l\delta_{(18-7+1)}$$

In applying the θ term correction (outside the brackets) it was assumed that for given order,

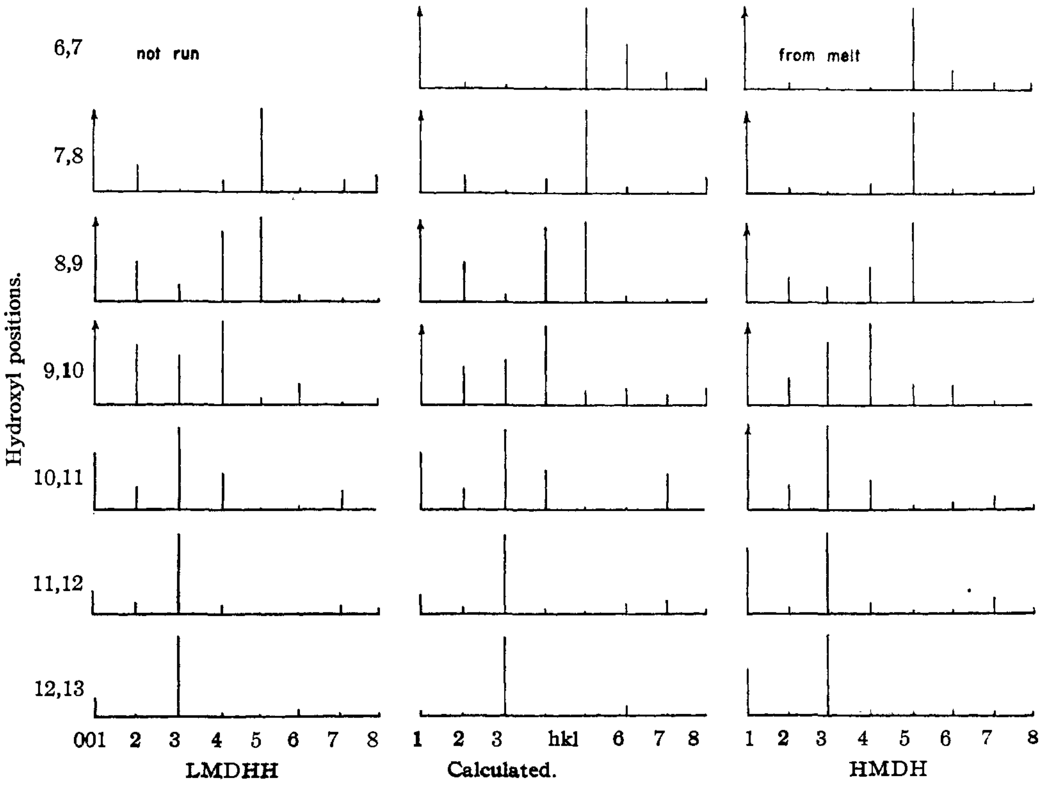


Fig. 4.—Long spacing intensities of dihydroxy acids (strongest except 1st set at 1000).

1, θ was determined on the basis of an assumed long spacing of 43 Å. which is an approximately average value for the acids involved. The values of θ were obtained for Cr radiation, λ 2.2909 Å. It is seen in Fig. 3 how calculated intensity (for the first six orders) varies with hydroxyl shift along the chains. The first order variation is large but not likely to be easy to observe. The relative values for 3rd and 4th order suggest an index very sensitive to hydroxyl shift. For simple identification purposes the relative intensities are particularly sensitive since odd and even acids are distinguished by short spacing; hence the problem is only to distinguish among individual even acids or among individual odd acids, as the case may be.

It was desired to compare experimental intensities with each other and with calculated intensities. It was found impossible, however, to obtain experimental intensities with sufficient reproducibility on an absolute basis to use for convenient comparison, due mainly it seemed to variations in crystallization.

To permit intercomparison of intensities it was decided to equate arbitrarily the strongest intensity, except that of the 1st order, to 1000 for any given case. (The first order was given less consideration because of uncertainties in the experimental evaluation.) The other intensities were adjusted in proportion. In Fig. 4 it is shown how the values followed an orderly sequence and showed remarkably good agreement between calculation and experiment. It is plain to see that the intensity sequence serves as a clear-cut characterization of an individual dihydroxy (or original octadecenoic) acid. This is especially evident when the alternation in m.p. and short spacings between odd and even acids is remembered. Thus a distinction to be looked for among 7,8- and 9,10- and 11,12-dihydroxystearic acids, for instance, is readily made. Accordingly it is plain that synthetic vaccenic (11-octadecenoic) acid is clearly distinguishable from synthetic or "natural" elaidic (9-octadecenoic) acid.

The agreement of calculated with experimental intensities constitutes a further confirmation of the already well-established structures of the octadecenoic acids.

Acknowledgment.—The authors are indebted to a number of members of this Laboratory for experimental assistance and advice in the preparation of this paper.

CINCINNATI 17, OHIO RECEIVED APRIL 30, 1951

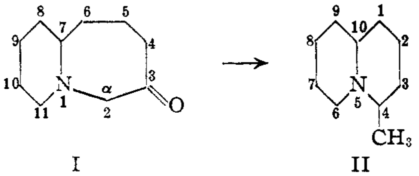
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Rearrangement of α-Aminoketones during Clemmensen Reduction. VII. The Rearrangement of 3-Keto-1-azabicyclo[5.4.0]hendecane[1]

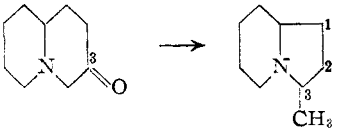
BY NELSON J. LEONARD AND ERNEST D. NICOLAIDES

It has been shown that a bicyclic α-aminoketone having fused six- and seven-membered rings undergoes rearrangement during Clemmensen reduction. Specifically, 3-keto-1-azabicyclo[5.4.0]hendecane is converted to a mixture of the two racemates of 4-methylquinolizidine upon reduction with zinc amalgam and hydrochloric acid.

The contraction of a seven-membered monocyclic α-aminoketone during Clemmensen reduction has been established,[2] as has the similar contraction of a bicyclic α-aminoketone (6-keto-1-azabicyclo[5.3.0]decane) possessing fused five- and seven-membered rings.[3] Because of certain previously observed differences in behavior due to ring size,[4] the result of the Clemmensen reduction of a bicyclic α-aminoketone possessing fused six- and seven-membered rings was also sought. The compound 6-keto-1-azabicyclo[5.4.0]hendecane (see I for numbering system) could not serve as a model since reduction either with or without rearrangement would produce the same compound, 1-azabicyclo[5.4.0]hendecane. 3-Keto-1-azabicyclo[5.4.0]hendecane (I) was therefore selected for study, since Clemmensen reduction with rearrangement should yield 4-methylquinolizidine (II), rather than 1-azabicyclo[5.4.0]hendecane. Moreover, it has been shown recently in this Laboratory[5] that the Clemmensen reduction of the analogical 3-ketoquinolizidine (III) gives 3-methyloctahydropyrrocoline (IV) (both racemates) predominantly, rather than quinolizidine.



I II



III IV

The two racemates represented by II have been obtained previously as their picrate derivatives, m.p. 195° and 187°,[6] but separation of the free bases was not achieved. We have now been able to separate the isomers of 4-methylquinolizidine by careful fractional distillation and to characterize both racemates by infrared absorption spectra.

---

[1] This work was supported by a grant from E. I. du Pont de Nemours and Company, Inc.

[2] N. J. Leonard and E. Barthel, Jr., THIS JOURNAL, **71**, 3098 (1949).

[3] N. J. Leonard and W. C. Wildman, *ibid.*, **71**, 3100 (1949).

[4] G. R. Clemo, R. Raper and H. J. Vipond, *J. Chem. Soc.*, 2095 (1949).

[5] N. J. Leonard and S. H. Pines, THIS JOURNAL, **72**, 4931 (1950).

[6] R. Lukeš and F. Šorm, *Collection Czechoslov. Chem. Communs.*, **12**, 356 (1947).