diffusion of which is slow compared with the rate of polymer chain growth.

4. Employing a model based on this concept, it is calculated that gelation can only occur after these swollen molecules have filled 13–23% of the reaction mixture. Experimental results indicate 25–46% in fair agreement with calculation.

PASSAIC, NEW JERSEY RECEIVED OCTOBER 27, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE STANDARD OIL COMPANY (INDIANA)]

The Acidic Constituents of Degras. A New Method of Structure Elucidation[1]

BY A. W. WEITKAMP

Introduction

Because of the unique complexity of degras (wool fat, wool wax) the identities of the individual acidic constituents have remained obscure. Early investigators[2,3,4] recognized the presence of two types of acids: (a) hydroxy acids ($C_nH_{2n}O_3$) and (b) acids of normal oxygen content ($C_nH_{2n}O_2$). Attempts to resolve the mixture by ester distillation were unsuccessful. Kuwata[5] obtained about 7% of impure $C_{16}H_{32}O_3$ by selective extraction with 90% methanol, followed by fractional distillation of the methyl esters of the extract. This acid was shown to be a "stereoisomer of synthetic α-hydroxyhexadecanoic acid." The structures of the acids of normal oxygen content have been variously postulated as normal,[6,7,8,9] branched[3,4,10,11] or even cyclic,[10] but there is no evidence that any such acids were isolated or identified.

The ester distillation method seemed to us to offer greater possibilities than solvent extraction as a means of separating the individual constituents, particularly since recent advances in column packings[12,13] have made possible the construction of highly efficient laboratory stills. The greatest deficiency of the ester distillation method as applied to this problem is that the methyl esters of the hydroxy acids are thermally unstable. Members of the 2-hydroxy series above $C_{16}H_{32}O_3$ have not been recovered.

The laboratory vacuum still used in this investigation was identical with one described in an earlier paper[14] except for the substitution of a more efficient, spiral-conical-pattern, wire gauze packing.[15] The packed section was 44 inches in length by one inch inside diameter. The over-all efficiency was approximately 100 theoretical plates.

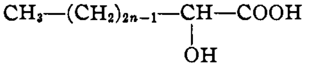
The specimen of degras used in this study was taken from a commercial lot purchased in 1941 from Arlington Mills, 80 Chauncy St., Boston, Mass., under the brand name, "Centrifuged Degras." Its composition was as follows:

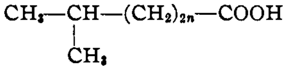
COMPOSITION OF DEGRAS, WT. %

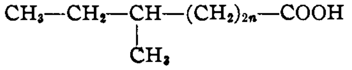
Moisture	1.2
Free acids	11.0
Combined acids	44.0
Unsaponifiable (sterols, etc.)	46.1

The work reported in this paper was restricted to those acids originally present as sterol esters because of the possibility that the free acids might include extraneous acidic material, originating from the detergents used for scouring the wool. Altogether 32 acidic constituents have been isolated. These are distributed among four homologous series: (I) normal fatty acids, (II) optically active 2-hydroxy acids, (III) iso acids (methyl side chain in the penultimate position) and (IV) dextrorotatory *anteiso*[16] acids (methyl side chain in the antepenultimate position).

I $CH_3{-}(CH_2)_{2n}{-}COOH$ $n = 4$ to 12 incl.

II 
$CH_3{-}(CH_2)_{2n-1}{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}COOH$ $n = 6, 7$

III 
$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}(CH_2)_{2n}{-}COOH$ $n = 3$ to 11 incl.

IV 
$CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}(CH_2)_{2n}{-}COOH$ $n = 2$ to 13 incl.

Isolation of Constituents

The free acids (110 g.) were extracted with alkaline 60% ethanol from a petroleum ether solution of degras (1000 g.). The sterol esters (878 g.) were saponified with potassium hydroxide and separated with petroleum ether and 60% ethanol into sterols (461 g.) and acids (440 g.). These acids were esterified with methanol and dry hydrogen chloride and finally filtered in petroleum ether solution through Attapulgus clay. The yield of neutral, straw-colored esters was 405 g. or 88% of the theoretical based on an average

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[1] Presented before the Division of Organic Chemistry, New York meeting of the American Chemical Society, September 14, 1944.

[2] Chevreul, *Compt. rend.*, **42**, 130 (1856).

[3] Lewkowitsch, *J. Soc. Chem. Ind.*, 11, 136 (1892); **15**, 14 (1896).

[4] Darmstaeder and Lifschutz, *Ber.*, **28**, 3133 (1895); **29**, 618, 1474, 2890 (1896); **31**, 97, 1122 (1898).

[5] Kuwata, THIS JOURNAL, **60**, 559 (1938).

[6] Busine, *Wagners Jahresber.*, **30**, 1189 (1884).

[7] Herbig, *J. Soc. Chem. Ind.*, **15**, 138 (1896).

[8] Rohmann, *Biochem. Z.*, **77**, 298 (1916).

[9] Drummond and Baker, *J. Soc. Chem. Ind.*, **48**, 232T (1929).

[10] Abraham and Hilditch, *ibid.*, **54**, 398T (1935).

[11] Kuwata and Ishii, *J. Soc. Chem. Ind.*, Japan, **39**, 317B, 318B, 358B (1936).

[12] Bragg, *Ind. Eng. Chem., Anal. Ed.*, 11, 283 (1939).

[13] Lecky and Ewell, *ibid.*, **12**, 544 (1940).

[14] Weitkamp and Brunstrum, *Oil & Soap*, **18**, 47 (1941).

[15] Weitkamp and Oblad (to Standard Oil Co. (Ind.)), U. S. Patent 2,325,818.

[16] Apparently there has been no name comparable to *iso* applied to the series of compounds having a methyl group at the third carbon atom. To fill this need the term, *anteiso*, was coined.

TABLE I

ACIDIC CONSITUTENTS OF DEGRAS

Name of acid	Melting point of acid, °C., cor.[a]		Melting point of amide, °C., cor.[a]		Neutralization equivalent		Methyl esters	
	From literature	Found	Found	Formula	Calcd.	Found	B. p., uncor. at 1.95 mm.	Per cent. present
Normal Series								
n-Decanoic, Capric	31.19[21]	30.9		$C_{10}H_{20}O_2$			79	0.3
n-Dodecanoic, Lauric	43.75[20]	42.9		$C_{12}H_{24}O_2$			104.5	.4
n-Tetradecanoic, Myristic	54.4[20]	54.1		$C_{14}H_{28}O_2$			128.5	2.8
n-Hexadecanoic, Palmitic	62.9[20]	62.4		$C_{16}H_{32}O_2$			150	2.8
n-Octadecanoic, Stearic	69.6[20]	69.2		$C_{18}H_{36}O_2$			170	0.2
n-Eicosanoic, Arachidic	75.35[20]	74.3	110.3	$C_{20}H_{40}O_2$			188	.6
n-Docosanoic, Behenic	79.95[20]	78.3	112.7	$C_{22}H_{44}O_2$			205.5	0.4
n-Tetracosanoic, Lignoceric	84.15[20]	83.7	113.7	$C_{24}H_{48}O_2$			222	1.2
n-Hexacosanoic, Cerotic	87.7[20]	86.8		$C_{28}H_{52}O_2$			237	0.8
Optically Active Hydroxy Series								
2-Hydroxytetradecanoic, α-OH-myristic	81.5–82[25b]	88.5	...	$C_{14}H_{28}O_3$	244.36	246.5	146.5	0.2
2-Hydroxyhexadecanoic, α-OH-palmitic	86–87[15] 86.16 ± 0.05[24b]	93.6	...	$C_{16}H_{32}O_3$	272.42	272.5	166.5	4.0
Iso Series								
8-Methylnonanoic, Isocapric		..	103.1	$C_{10}H_{20}O_2$	172.26	...	75	0.1
10-Methylundecanoic, Isolauric		41.2	108.0	$C_{12}H_{24}O_2$	200.31	200.8	100.5	.4
12-Methyltridecanoic, Isomyristic	50.5–51.5[26]	53.3	107.3	$C_{14}H_{28}O_2$	228.36	228.5	124.5	2.8
14-Methylpentadecanoic, Isopalmitic	61.8–62.4[26]	62.4	102.1	$C_{16}H_{32}O_2$	256.42	256.1	146.5	5.8
16-Methylheptadecanoic, Isostearic	67.6–68.2[26]	69.5	107.3	$C_{18}H_{36}O_2$	284.47	284.2	166.5	4.0
18-Methylnonadecanoic, Isoarachidic		75.3	105.1	$C_{20}H_{40}O_2$	312.52	312.6	185	5.0
20-Methylheneicosanoic, Isobehenic		79.4	108.4	$C_{22}H_{44}O_2$	340.57	340.4	202.5	4.0
22-Methyltricosanoic, Isolignoceric		83.1	110.5	$C_{24}H_{48}O_2$	368.62	370.4	219	2.8
24-Methylpentacosanoic, Isocerotic		86.9	112.1	$C_{26}H_{52}O_2$	396.68	396.9	234	3.6
26-Methylheptacosanoic, Isomontanic		89.3	...	$C_{28}H_{56}O_2$	424.73	...	248	0.8
Dextrorotatory *Anteiso* Series								
6-Methyloctanoic		..	89.7	$C_9H_{18}O_2$	158.23	...	60	0.1
8-Methyldecanoic		−18.5	87.1	$C_{11}H_{22}O_2$	186.29	190.2	88	.6
10-Methyldodecanoic		6.2	92.4	$C_{13}H_{26}O_2$	214.34	214.5	112.5	1.0
12-Methyltetradecanoic		23.0	86.4	$C_{15}H_{30}O_2$	242.39	242.3	136	4.8
14-Methylhexadecanoic		36.8	90.9	$C_{17}H_{34}O_2$	270.44	270.7	156.5	3.6
16-Methyloctadecanoic	49.9–50.6[37b]	46.8	93.2	$C_{19}H_{38}O_2$	298.49	299.4	176	4.8
18-Methyleicosanoic		55.6	94.1	$C_{21}H_{42}O_2$	326.55	326.1	194	5.6
20-Methyldecosanoic		62.1	99.9	$C_{23}H_{46}O_2$	354.60	353.8	211	3.6
22-Methyltetracosanoic		67.8	101.5	$C_{25}H_{50}O_2$	382.65	382.3	227	7.0
24-Methylhexacosanoic		72.9	104.5	$C_{27}H_{54}O_2$	410.70	410.6	241.5	5.2
28-Methyltriacontanoic		80.7	107.0	$C_{31}H_{62}O_2$	466.81	...	266	1.0[c]

[a] Temperatures of complete melting were determined by the method of Francis and Piper.[20] [b] *dl*-Isomer. [c] Includes C_{29} and C_{30} fractions from which pure acids were not isolated.

molecular weight of 300 for the acids. The 12% loss was due mainly to adsorption of colored constituents on the clay.

Fractional distillation of the mixed methyl esters yielded 328 g. (81%) of distillate and 53 g. (13%) of residue, leaving 24 g. (6%) not recovered. This 6% loss (material not condensed by a water-cooled condenser) probably represents extensive decomposition of the methyl esters of oxygenated acids, in view of the fact that the methyl esters of acids of normal oxygen content are thermally stable and distill without decomposition. The boiling points (uncorrected) at 1.95 mm. pressure and an estimate of the relative proportions of the various methyl esters in the 81% distillate are listed in Table I. The proportions are expressed volumetrically and are uncorrected for the presence of volatile products of decomposition.

The differences in the boiling points of the various methyl esters are due chiefly to differences in molecular weight and to a smaller extent to structural differences. The mixture was initially separated by distillation into a series of fractions differing from each other by one —CH_2— unit. Fractions corresponding to acids of odd carbon content each yielded an *anteiso* acid. Fractions corresponding to acids of even carbon content

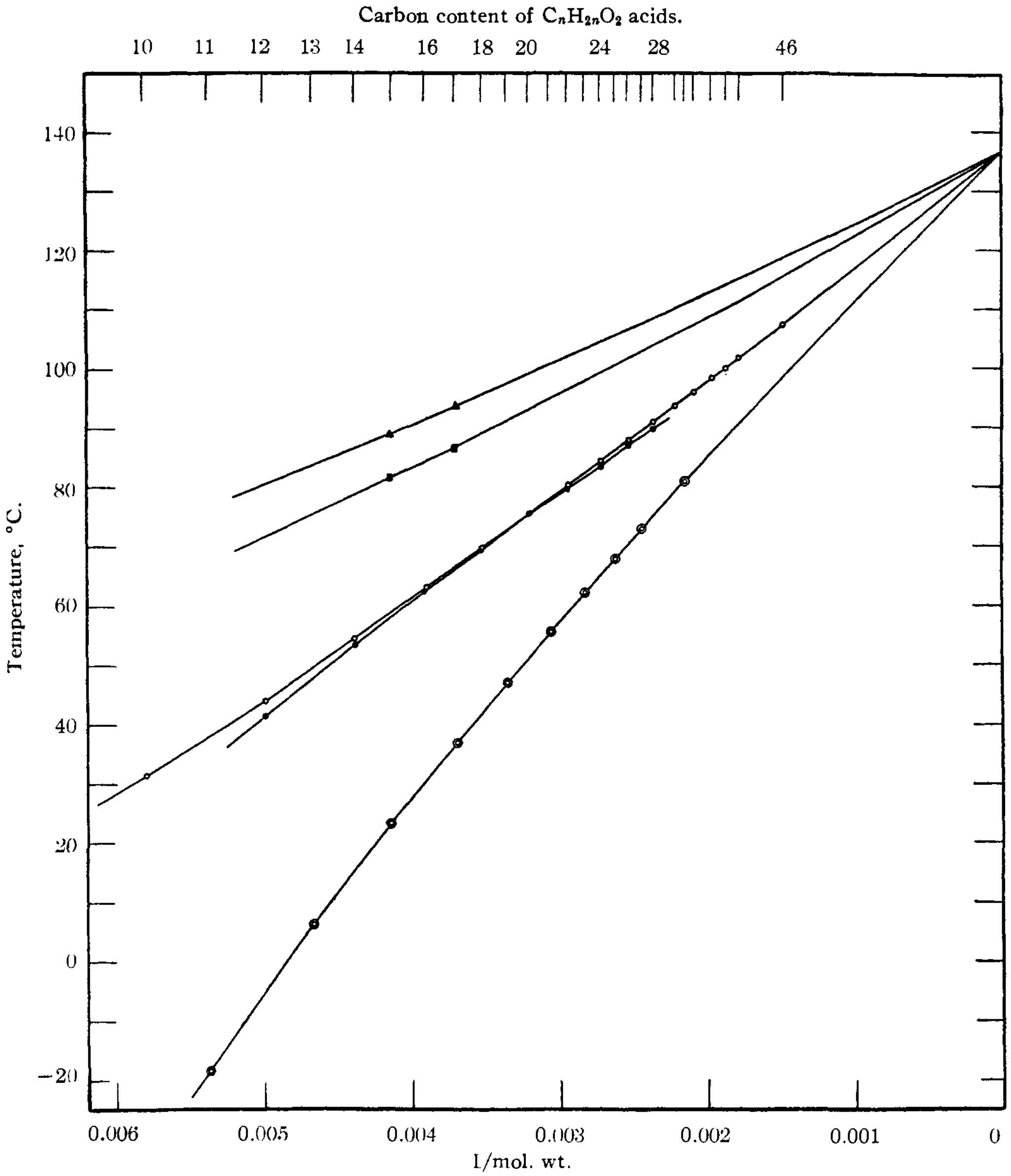

Fig. 1.—Melting points of fatty acids: ⊙—⊙, *anteiso* acids; ●—●, iso acids; ⊙—⊙, normal acids[20,21]; ▲—▲, stereoisomeric 2-hydroxy acids; ■—■, synthetic 2-hydroxy acids.[24,25]

each yielded a normal acid, an iso acid and in two instances a 2-hydroxy acid with two fewer carbon atoms. In order effectively to separate the corresponding normal and iso acid esters, by means described below, it was necessary to remove the 2-hydroxy acids. This was done by fractional crystallization of the free acids from petroleum ether, in which the 2-hydroxy acids are nearly insoluble. Final traces of the 2-hydroxy acids were destroyed by oxidation with potassium permanganate, after which the residual normal acid and iso acid were reësterified.

As a means of improving the separation of binary mixtures of fatty acids by distillation, Axe and Bratton[17] suggested extending the mixture with a hydrocarbon diluent. This procedure has been successfully applied to the purification and/or separation of the methyl esters of all of the degras acids except the 2-hydroxy acids. Methyl esters have the advantage of co-distilling with the hydrocarbon diluent at their normal boiling points, whereas the fatty acids form minimum boiling azeotropic mixtures with hydrocarbons.

The boiling points of the methyl esters of the normal acids are only 3–4° higher than the boiling points of the methyl esters of the iso acids. Their separation is further complicated by the fact that

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(17) Axe and Bratton, This Journal, **59**, 1424 (1937).

some of the normal acids are present in very small proportions. By means of the technique of extended distillation it has been possible to isolate both the iso and normal acids, although in some cases the latter have not been obtained in completely pure condition.

The various acids were recovered from the purified ester fractions and recrystallized to constant melting point from acetone or petroleum ether.

Identification and Proof of Homology

Each of the acidic constituents falls naturally into one of four groups characterized by a distinctive crystal habit (Plates I–IV).[18] In addition, the boiling points of the methyl esters (Table I) and the melting points of the fatty acids (Table I) of the members of each group lie on smooth curves when arranged in order of increasing molecular weight. Above C_{10} in the fatty acid series it appears that molecular weight is the major variable affecting the melting points (Fig. 1). The melting point curves are nearly linear with respect to reciprocal molecular weights and converge at infinite molecular weight at about 136.5°.

It has not been feasible separately to identify each individual constituent, but rather to determine the identity of at least one member of each group and establish the homologous relationship within each group by a determination of the actual relationship between two or more adjacent members.

Normal Fatty Acid Series.—This series contained all even members from C_{10} to C_{26}. All but C_{14} and C_{16} are minor components. Both identity and homology followed from a direct comparison, by means of mixed melting points, with authentic specimens.[19] Because of the relative difficulty of isolation, the melting points (Table I) are lower by 0.3–1.7° than the best reported values.[20,21] The normal acids crystallize in characteristic thin plates appearing as equilateral parallelograms with an acute angle of approx. 55°. Representative photomicrographs are shown in Plate I. Shead[22] established the suitability of the angular constants of microcrystalline profiles and silhouettes for the identification of substances. The profile angle of the normal fatty acids is unrelated to chain length but is a characteristic property of the even or odd members of the series. The normal fatty acids crystallize in the monoclinic system.[23]

Optically Active 2-Hydroxy Acid Series.—Only the C_{14} and C_{16} members were isolated. Higher homologs, if present, did not survive distillation of the methyl esters. Kuwata[5] found the C_{16} member, 2-hydroxyhexadecanoic acid, to be levorotatory, $[\alpha]_D$ -1.0 (*c*, 5.2 in alcohol), and identified it by oxidation to *n*-pentadecanoic acid as an optical isomer of *dl*-2-hydroxyhexadecanoic acid. Similarly, oxidation of our 2-hydroxyhexadecanoic acid yielded *n*-pentadecanoic acid, m. p. 52.4°; Meyer and Reid,[21] 52.26°. Oxidation of our 2-hydroxytetradecanoic acid yielded *n*-tridecanoic acid, m. p. 41.3°; Meyer and Reid,[21] 41.55°. Optical rotations were not determined. However, the melting points in the following tabulation indicate that these acids are distinct from the synthetic acids and hence must be optical isomers.

	2-Hydroxyhexadecanoic acid			2-Hydroxytetradecanoic acid	
	Kuwata[5]	Present study	Synthetic[24]	Present study	Synthetic[25]
M. p. of acid, °C.	86–87	93.6	86.16 ± 0.05	88.5	81.5–82
M. p. of methyl ester, °C.	45–46	45.6	57.5 (s.p.)	...	...
Neut. eq. of acid	...	272.5	272.4 (calcd.)	246.4	244.4 (calcd.)

The 2-hydroxy acids crystallize in clusters of radiating fibers. Photomicrographs are shown in Plate II.

Homology in this series is such that higher homologs cannot be derived from lower homologs by known chain building processes involving the carboxyl group. The question arises as to whether these hydroxy acids might be intermediates in the biosynthesis of normal acids or *vice versa*.

Iso Acid Series.—All even members from C_{10} to C_{28} were isolated. Their melting points (Table I) lie very close to the melting points of the corresponding normal acids. However, mixed melting points with normal acids are depressed 10–15°. Furthermore, the crystal habits of the normal and iso acids are dissimilar. The latter crystallize in thin plates appearing as elongated parallelograms with a characteristic profile angle of approximately 75° (Plate III). The ratio of length to width increases greatly as the series is ascended so that the higher members appear to the naked eye as fine needles.

Fordyce and Johnson[26] synthesized a series of iso acids but did not give sufficient physical data for a rigorous comparison.

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(18) The photomicrographs were made at 860 diameters with cardioid illumination. Crystals were prepared by dissolving sufficient fatty acid in Mineral Seal Oil (Viscosity at 100°F., 5.2 Centistokes) for slight crystallization to occur at room temperature. Crystals of the normal and iso acids were prepared in small beakers and transferred to slides for observation. The 2-hydroxy and *anteiso* acids were prepared for observation as follows: A drop of the crystal slurry was placed on a slide, and as the cover glass was pressed down, a concentration gradient was produced, assuring that some part of the slide would have optimum density. The acid was then redissolved by warming. By means of a movable stage crystallization could be followed from the center outward. In addition to the still photographs shown here, action photographs of the crystallization of the *anteiso* acids were made.

(19) Authentic normal acids were obtained as follows: C_{12} from coconut oil, C_{14} to C_{22} from hydrogenated sardine oil.

(20) Francis and Piper, THIS JOURNAL, **61**, 577 (1939).

(21) Meyer and Reid, *ibid.*, **55**, 1577 (1933).

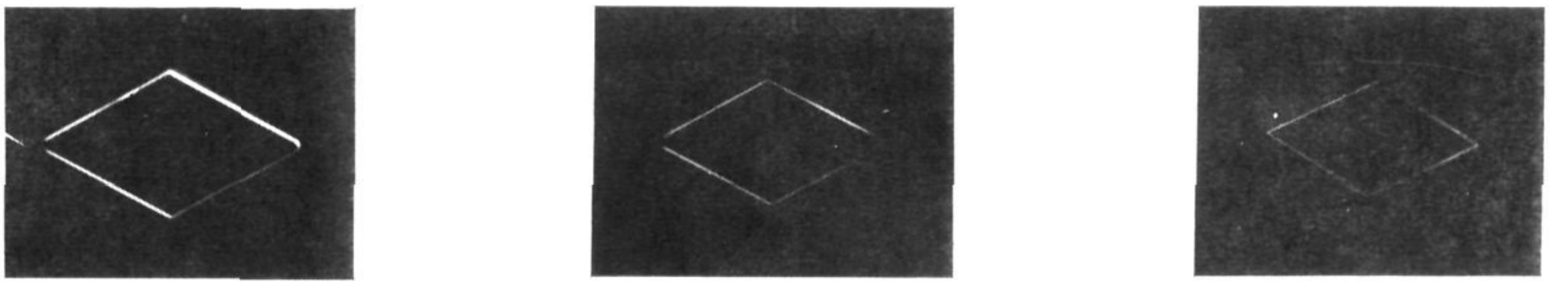
(22) Shead, *Ind. Eng. Chem., Anal. Ed.*, **29**, 496 (1937).

(23) Muller, *Nature*, **116**, 45 (1925).

(24) Mendel and Coops, *Rec. trav. chim.*, **58**, 1133 (1939).

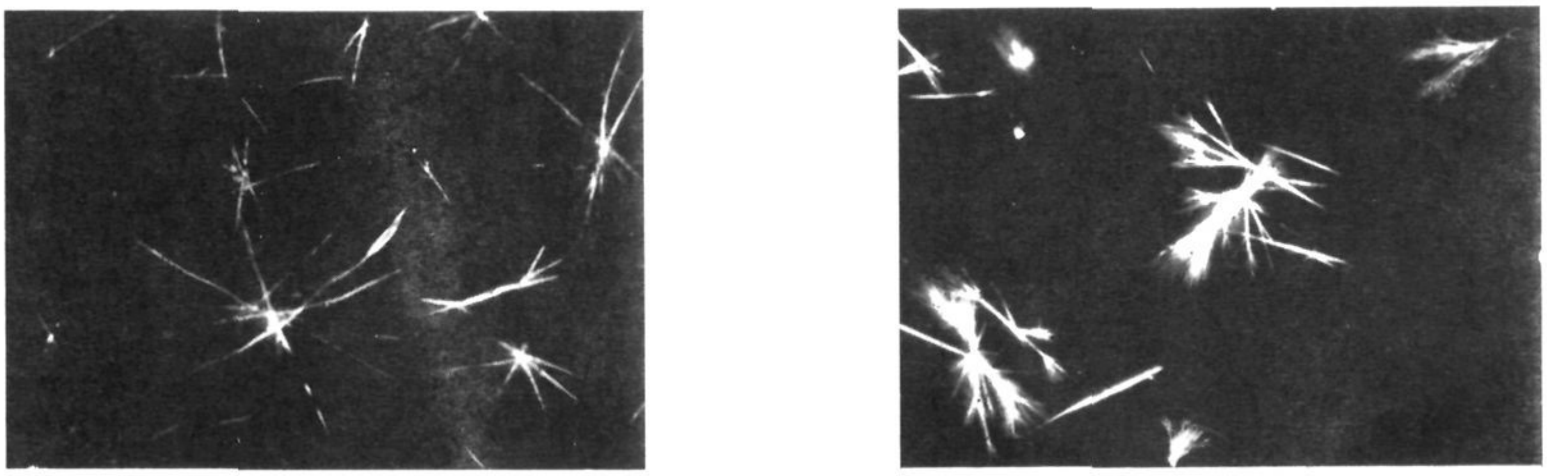
(25) Le Sueur, *J. Chem. Soc.*, **87**, 1903 (1905).

(26) Fordyce and Johnson, THIS JOURNAL, **55**, 3368 (1933).



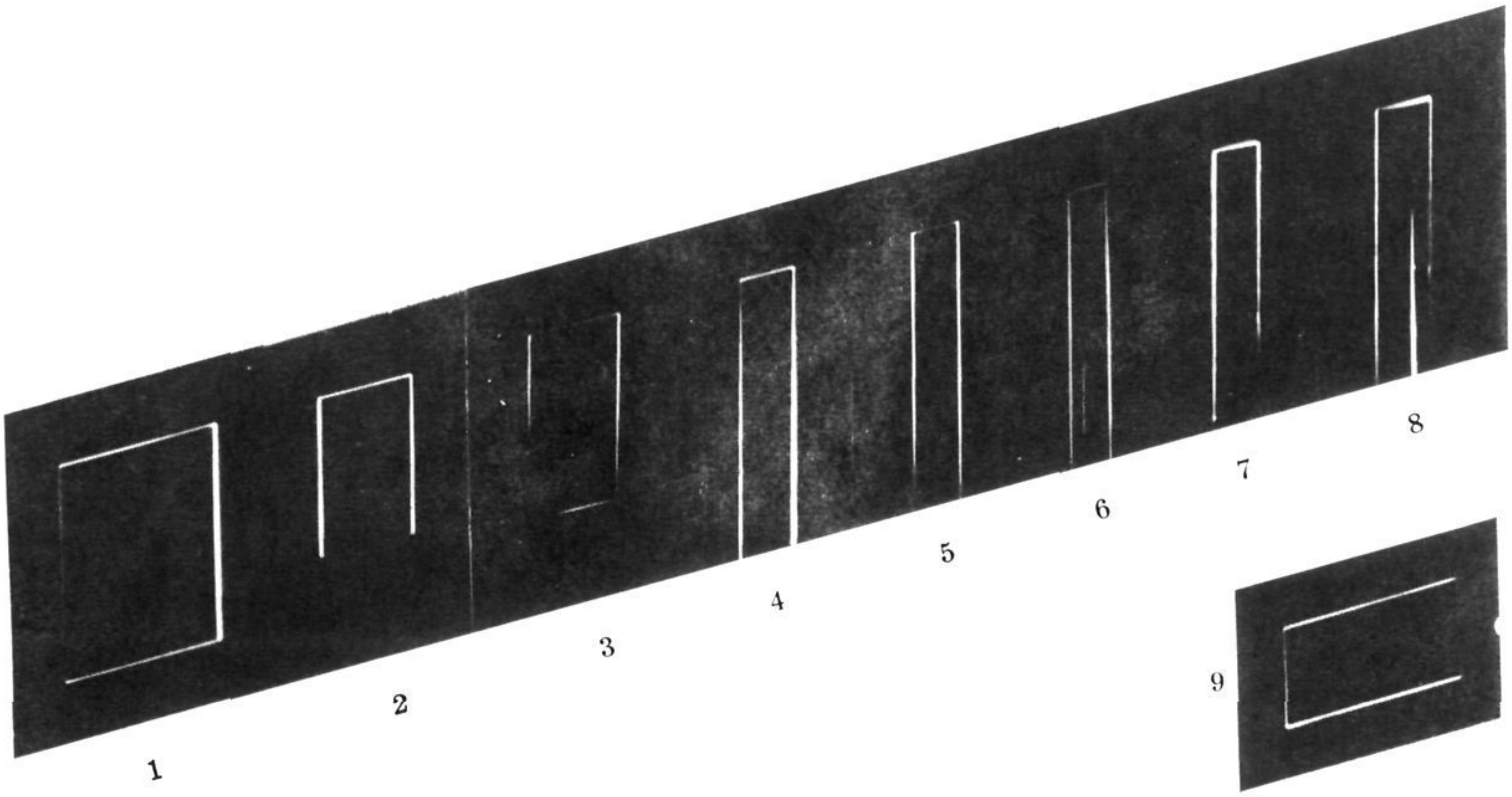
Myristic Palmitic Lignoceric

Plate I.—Normal acids.



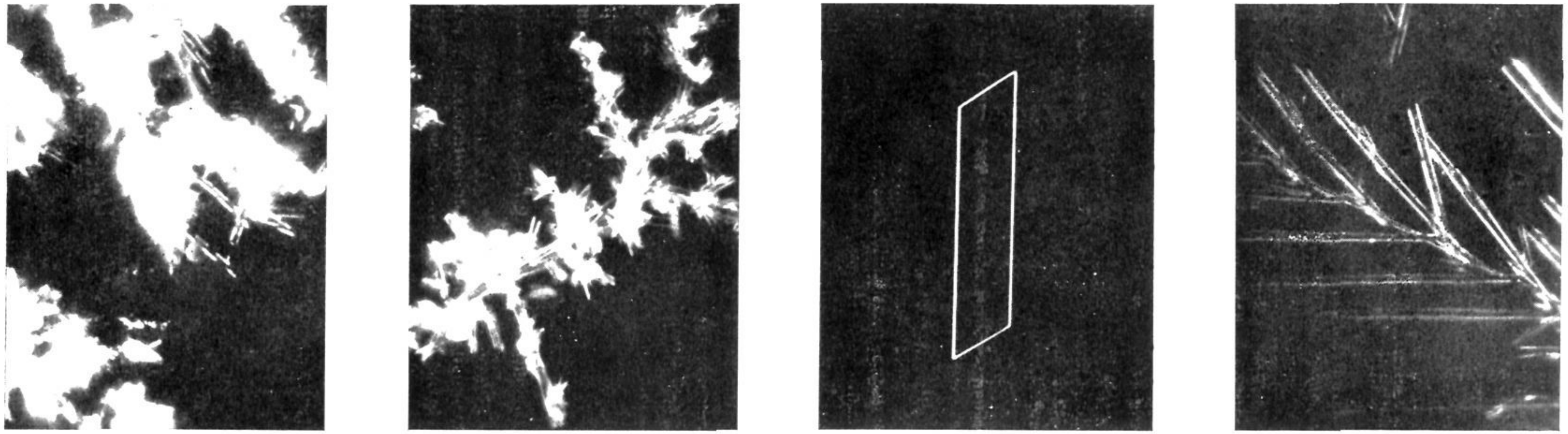
2-Hydroxymyristic 2-Hydroxypalmitic

Plate II.—Hydroxy acids.

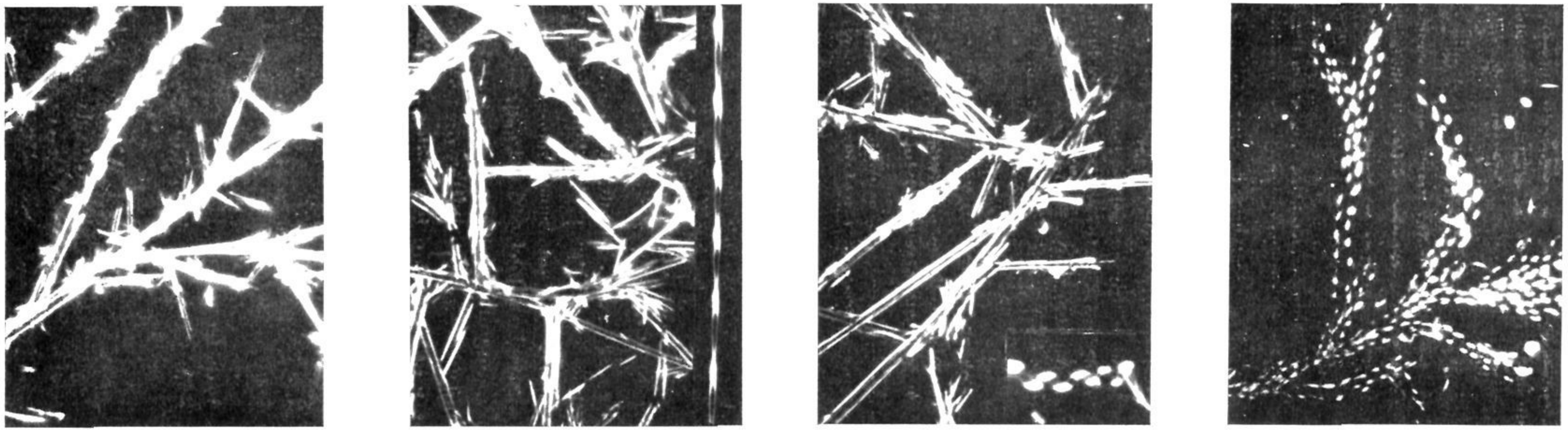


1, Isolauric
2, Isomyristic
3, Isopalmitic
4, Isostearic
5, Isoarachidic
6, Isobehenic
7, Isolignoceric
8, Isocerotic
9, 17-Methyloctadecanoic

Plate III.—Iso acids.



d-14-Methylhexadecanoic *d*-16-Methyloctadecanoic *dl*-16-Methyloctadecanoic *d*-18-Methyleicosanoic



d-20-Methyldocosanoic *d*-22-Methyltetracosanoic *d*-24-Methylhexacosanoic *d*-28-Methyltriacontanoic

Plate IV.—*Anteiso* acids.

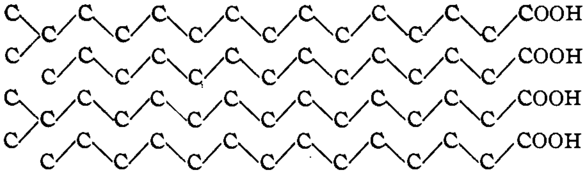
Acid	Melting point, °C. Synthetic[26]	From degras
Isomyristic	50.5-51.5	53.3
Isopalmitic	61.8-62.4	62.4
Isostearic	67.6-68.2	69.5

Recently Cason[27] undertook the synthesis of a series of methyloctadecanoic acids. The first member of this series to be reported was the iso acid, 17-methyloctadecanoic acid. By application of the nitrile synthesis to the C_{18} acid, m. p. 69.5° from degras, a C_{19} acid was obtained which proved to be identical with Cason's 17-methyloctadecanoic acid. Mixed melting points of the acid and derivatives were not depressed.

	Melting point, °C.	
	Cason's iso-C_{19}[27]	C_{19} from degras C_{18}
Acid	67.3-67.8	66.9
Amide	100.2-101.3	101.2
Tribromoanilide	112-112.5	112.1

The homologous relationship of adjacent members was established by obtaining isostearic acid from the C_{16} member by twice applying the nitrile synthesis. The intermediate 15-methylhexadecanoic acid melts at 60.2°; the corresponding amide melts at 99.3°.

An easier clue to homology, and incidentally to structure, was found in the behavior of binary mixtures of the iso acids with normal acids. The well-known fact that solidification point curves of binary mixtures of adjacent even-numbered normal fatty acids exhibit *two* transitions has been explained[28] on the basis of intermolecular compound formation. The solidification point[29] curve for mixtures of palmitic acid and isopalmitic acid exhibits only *one* transition (Fig. 2). The non-occurrence of compound formation in this case must be attributed to interference from the methyl side chain of isopalmitic acid. However, such interference does not occur if the chain length of the normal acid does not exceed the length of the unbranched portion of the iso acid. This can be illustrated by a simple diagram in which the carbon chain is represented as a coplanar zigzag.[30,31] The next higher normal acid will not fit into the available space. This is illustrated by the binary solidification point curves (Fig. 3). The lower pair involve isostearic acid which is known to be branched at the 16th carbon atom. The systems with heptadecanoic acid and hexadecanoic (palmitic) acid



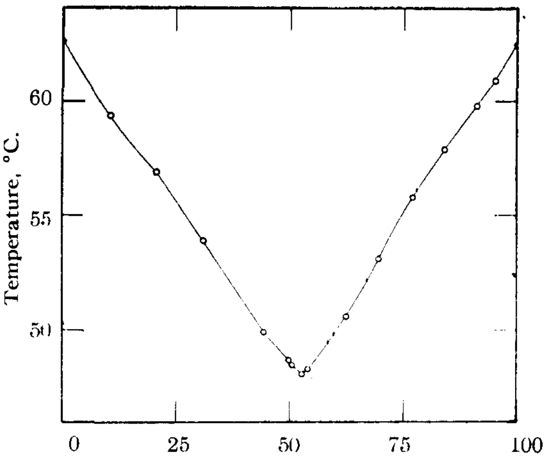


Fig. 2.—Solidification point curve; 14-methylpentadecanoic (isopalmitic) acid-hexadecanoic (palmitic) acid.

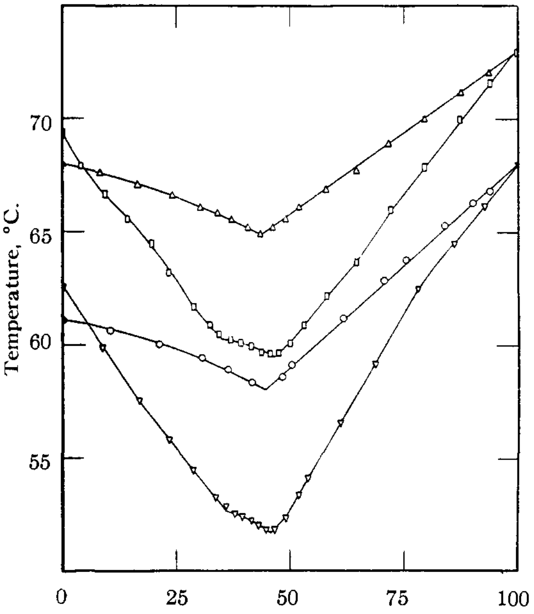


Fig. 3.—Solidification point curves: △—△, 18-methylnonadecanoic (isoarachidic) acid-nonadecanoic acid; □—□, 18-methylnonadecanoic acid-octadecanoic (stearic) acid; ○—○, 16-methylheptadecanoic (isostearic) acid-heptadecanoic (margaric) acid; ▽—▽, 16-methylheptadecanoic acid-hexadecanoic (palmitic) acid.

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(27) Cason, THIS JOURNAL, **64**, 1106 (1942).

(28) Francis, Collins and Piper, *Proc. Roy. Soc.* (London), **A158**, 710 (1937).

(29) By using a thermometer with a short bulb and a 50-ml. beaker with a valley pressed in the side-wall, solidification points reproducible to 0.1° can be determined with as little as 0.1 g. of fatty acid. The rate of cooling is controlled by proximity to a low-heat hot-plate. The specimen is stirred by rotating the thermometer. For a series of determinations 0.1 to 0.2 g. of an acid is weighed into the modified beaker and incremental additions of the other acid are made. Thorough mixing is assured by adding and carefully evaporating a few drops of acetone after each addition. Any acid adhering to the thermometer is rinsed into the beaker with acetone. The volatility of acids below C_{14} may introduce appreciable error.

(30) Piper, Malkin and Austin, *J. Chem. Soc.*, 2310 (1926).

(31) Müller and Shearer, *ibid.*, **123**, 3159 (1923).

exhibit, respectively, *one* and *two* transitions. The upper pair of curves involve the C_{20} branched acid. Its systems with nonadecanoic acid and octadecanoic (stearic) acid exhibit, respectively, *one* and *two* transitions. Hence, the C_{20} acid is branched at the 18th carbon atom and must be 18-methylnonadecanoic (isoarachidic) acid.

Dextrorotatory *Anteiso* Series.—The unique feature of this series is that the members contain odd numbers (C_9–C_{31}) of carbon atoms. The *anteiso* series differs from the iso series in that the end group is *s*-butyl instead of isopropyl.

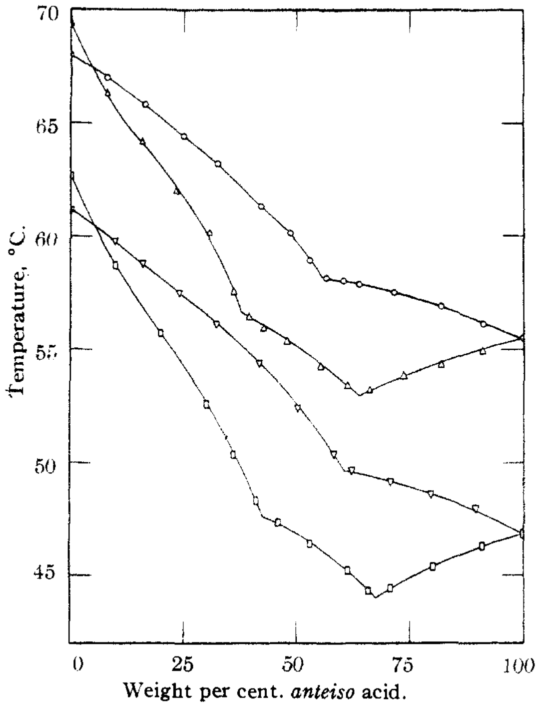
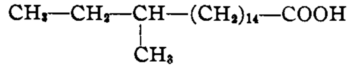


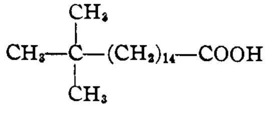
Fig. 4.—Solidification point curves: ○—○, *d*-18-methyleicosanoic acid–nonadecanoic acid; △—△, *d*-18-methyleicosanoic acid–octadecanoic (stearic) acid; ▽—▽, *d*-16-methyloctadecanoic acid–heptadecanoic (margaric) acid; □—□, *d*-16-methyloctadecanoic acid–hexadecanoic (palmitic) acid.

Binary solidification point curves with normal acids (Fig. 4) show that the C_{19} and C_{21} members are branched at the 16th and 18th carbon atoms, respectively. The possible structures for the C_{19} member are (I) *d*-, *l*-, and *dl*-16-methyloctadecanoic acid

I 

$$CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}(CH_2)_{14}{-}COOH$$

and (II) 16,16-dimethylheptadecanoic acid.

II 

$$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}(CH_2)_{14}{-}COOH$$

The optically inactive possibilities were eliminated by determination of the optical rotations[32] tabulated below.

Acid	Concn., g./100 ml.	Obs. rotation 2-dm. tube	$[\alpha]^{26}D$
12-methyltetradecanoic	88.2 (pure subs.)	+23.9 ± 0.15°	+4.7°
14-methylhexadecanoic	20.04 (in acetone)	+ 5.8 ± 0.15°	+5.0°
16-methyloctadecanoic	20.40 (in acetone)	+ 5.4 ± 0.15°	+4.6°

According to the rule of Boys,[33] the absolute configuration of these acids must be the same as the absolute configuration of levorotatory *d*-2-methylbutanol-1 from fusel oil, *i. e.*, the *d*-configuration. This is further substantiated by the fact that the acids obtained from levorotatory *d*-2-methylbutanol-1 by oxidation and by the nitrile synthesis are dextrorotatory. Molecular rotations, except for the lowest homolog in which the carboxyl group is attached directly to the asymmetric carbon atom, are strikingly uniform. The rotations of the C_{17} and C_{19} *anteiso* acids are not strictly comparable since these were measured in acetone solution.

Acid	Specific rotation	Molecular rotation
d-2-Methylbutanoic[34]	$[\alpha]D$ +17.5°	+17.85°
d-3-Methylpentanoic[35]	$[\alpha]D$ + 8.92°	+10.35°
d-4-Methylhexanoic[36]	$[\alpha]^{20}D$ + 8.44°	+10.98°
d-12-Methyltetradecanoic	$[\alpha]^{26}D$ + 4.7°	+11.37°

The asymmetry of the natural *anteiso* acids is reflected in their curious crystal habit (Plate IV). These acids crystallize from solution in mineral oil in a tubular form which is generated by the counterclockwise spiral growth of a very thin and quite narrow ribbon. The diameter of the tubes is on the order of one micron. A frequent variation of the tubular form is an open helical coil appearing in some of the photomicrographs as parallel rows of alternating dashes. A rare modification appears as a ribbon twisted along its major axis.

Comparison of *dl*- and *d*-16-Methyloctadecanoic Acid.—Cason and Prout[37] synthesized and characterized *dl*-16-methyloctadecanoic acid. Close similarity with *d*-16-methyloctadecanoic acid is suggested by the following comparison.

	16-Methyloctadecanoic *dl*	*d*
Acid, m. p., °C.	49.9[a]	46.8
Acid, s. p., °C.	48.6[a]	46.8
Amide, m. p., °C.	92.5–93.0[37]	93.3
Tribromoanilide, m. p., °C.	106.2–106.9[37]	108.4
Acid, $n^{55}D$	1.4400[37]	1.4400[b]

[a] Specimen supplied by Cason. [b] Determined by Cason.

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[32] Optical rotations were determined by Dr. W. E. Militzer, University of Nebraska, using a Bates type saccharimeter.

[33] Boys, *Proc. Roy. Soc.* (London), **A144**, 655, 675 (1934).

[34] Marckwald, *Ber.*, **32**, 1093 (1899).

[35] Marckwald and Nolda, *ibid.*, **42**, 1590 (1909).

[36] Welt, *Compt. rend.*, **119**, 855 (1894).

[37] Cason and Prout, THIS JOURNAL, **66**, 49 (1944).

Mixed melting points were not noticeably depressed. Crystal habits, however, are distinctly different (Plate IV).

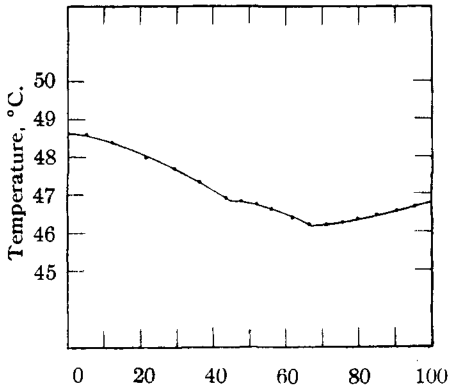

Fig. 5.—Solidification point curve: *d*-16-methyloctadecanoic acid–*dl*-16-methyloctadecanoic acid.

The binary solidification point curve of the *dl* and dextro acids (Fig. 5) shows that the *dl* acid exists as a *dl* compound. Further compound formation of the type d_3l or d_2l is evident in the mid-portion of the curve. From the flatness of the curves it can be concluded that the compounds are largely dissociated.

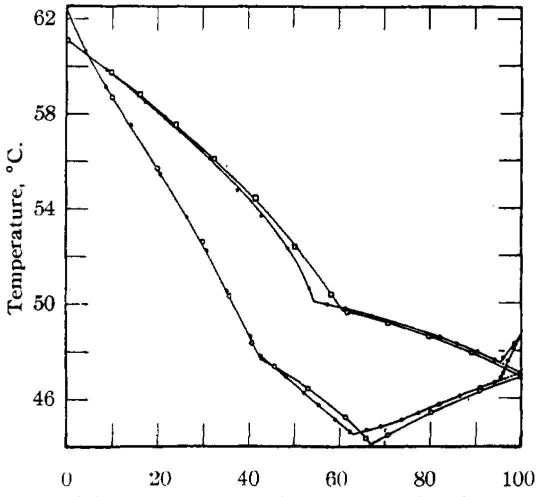

Fig. 6.—Solidification point curves: □—□, *dl*-16-methyloctadecanoic acid–heptadecanoic (margaric) acid; ○—○, *dl*-16-methyloctadecanoic acid–hexadecanoic (palmitic) acid; □ --□, *d*-16-methyloctadecanoic acid–heptadecanoic acid; ○ –○, *d*-16-methyloctadecanoic acid–hexadecanoic acid.

Binary solidification point curves of the *dl* acid with normal acids (Fig. 6) offer a further test and verification of the validity of the new method of locating a side chain. Quantitative interpretation of the curves is limited by the non-ideal nature of fatty acid mixtures. It appears that the first effect of a normal acid on the *dl* acid is to cause dissociation of the *dl* compound. The resulting mixture of stereoisomers is almost indistinguishable from the dextrorotatory acid in behavior with normal acids.

Amides of Fatty Acids.—In order to more completely characterize the new fatty acids reported in this paper the amides have been prepared. Melting points are listed in Table I. The melting points of the iso amides and *anteiso* amides, plotted against the number of carbon atoms in the molecule, have been observed to lie on parallel curves which exhibit minima approximately at each fifth carbon atom (Fig. 7). Timmermans[40] associates periodic minima in the properties of an homologous series with a spiral arrangement of the carbon atoms in the chain. The occurrence

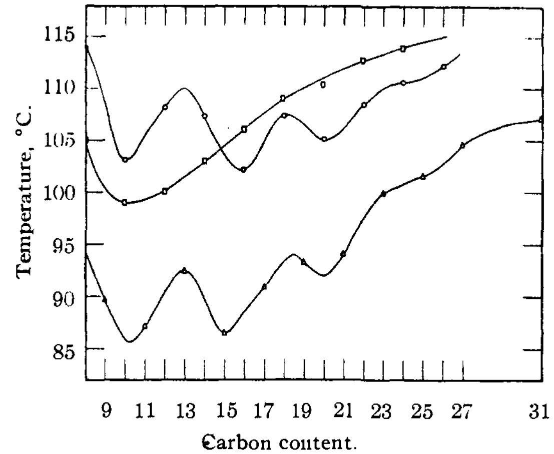

Fig. 7.—Melting points of amides: ○—○, amides of iso acids, from degras acids except C_8, Levene and Allen,[38] m. p. 114°; □—□, amides of normal acids[39]; △—△, amides of dextrorotatory *anteiso* acids.

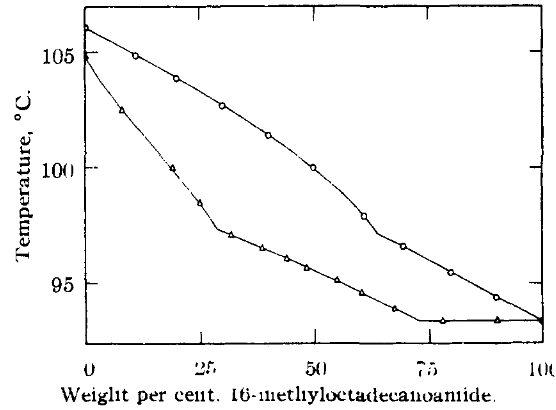

Fig. 8.—Solidification point curves: ○—○, *d*-16-methyloctadecanoamide–heptadecanoamide; △—△, *d*-16-methyloctadecanoamide–hexadecanoamide.

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(38) Levene and Allen, *J. Biol. Chem.*, **27**, 443 (1916).

(39) Robertson, *J. Chem. Soc.*, **115**, 1210 (1919).

(40) Timmermans, *Bull. soc. chim. Belg.*, **35**, 282, 1126 (1926).

of periodic repetition of melting point minima is unprecedented.[41]

It is of interest that the amides associate in the same manner as the fatty acids and may be used in place of the fatty acids for the determination of structures. Solidification point curves are shown in Fig. 8 for the amides of the fatty acids whose solidification point curves appear as the lower pair in Fig. 4.

Acknowledgment.—The writer is indebted to Dr. James Cason, Vanderbilt University, for generously supplying samples of *dl*-16- and 17-methyloctadecanoic acids and derivatives, and to Dr. W. E. Militzer, University of Nebraska, for determining optical rotations.

Summary

Thirty-two of the acidic constituents of degras have been isolated and identified. These include: (1) nine normal fatty acids, C_{10} to C_{26}; (2) two optically active 2-hydroxy acids, C_{14} and C_{16}; (3) ten iso acids, C_{10} to C_{28}; (4) eleven dextrorotatory *anteiso* acids, C_9 to C_{27} and C_{31}.

Dark field photomicrographs of representative members of each of the four series have been prepared.

A new method of structure elucidation applicable to acids or amides with simple branched chains is based on the number of transitions appearing in the solidification point curves of binary mixtures of the branched acid or amide with normal fatty acids or amides.

WHITING, INDIANA RECEIVED OCTOBER 19, 1944

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[41] Gilman, "Organic Chemistry," 2d ed., John Wiley & Sons, Inc., New York, N. Y., 1943, Vol. II, p. 1730.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A Spectrophotometric Study of the Anhydro Base of Viridine Green

BY TERRELL L. HILL,[1] GERALD E. K. BRANCH AND MORRIS PATAPOFF

Introduction

In a solution of N,N'-diphenyl-*p*,*p*'-diaminotriphenylmethyl chloride in methyl alcohol the following triphenylmethane derivatives can exist

I $(C_6H_5NHC_6H_4)(C_6H_5)C{=}C_6H_4{=}N^+HC_6H_5$
II $(C_6H_5NHC_6H_4)(C_6H_5)C{=}C_6H_4{=}NC_6H_5$
III $(C_6H_5N^+H_2C_6H_4)(C_6H_5NHC_6H_4)(C_6H_5)COCH_3$
IV $(C_6H_5NHC_6H_4)_2(C_6H_5)COCH_3$

II is the conjugate base of I. It is called the Homolka base, or better the anhydro base, since it is the anhydride of the color base. IV is the pseudo base of I in the methanol system, just as the carbinol is the pseudo base in the water system. It is a methyl ether. III is the conjugate acid of IV.

Equilibria between I and II, and between III and IV are very rapid, since the reactions are simple neutralizations. But the reversible reactions of I or II to III or IV are slower. I is stable with respect to III, and IV is stable with respect to II. Hence II and III are metastable compounds, and they can exist in appreciable concentrations only because they are formed by reactions that are faster than those by which equilibria are achieved.

I is green, II is red, and III and IV are colorless. Hence many of the reactions between these compounds can be studied colorimetrically.

In our work we started with a solid preparation of the bases. This solid contained a much larger proportion of the anhydro base than corresponds to equilibrium. This material we shall call the red solid in the rest of this article. Since we had a method of analyzing the red solid for anhydro base the colorless pseudo bases present were not objectionable.

The anhydro base polymerizes or resinifies slowly when dissolved in a solvent with which it cannot combine to form an ether. It is much more stable as the red solid, though even in this form it gradually deteriorates.

The anhydro base was first prepared by Baeyer and Villiger[2] by evaporating a brown ethereal solution obtained by shaking a salt of the dye with a mixture of aqueous sodium hydroxide and ether. Prepared in this way it is contaminated with colored polymers or resins. These impurities are to a great extent avoided when the anhydro base is formed in a methanol solution of the dye, transferred by extraction methods to an inert solvent from which it can be precipitated without concentrating the solution. Such methods allow the formation of pseudo bases much more than the method of Baeyer and Villiger does.

Preparation and Analysis

The chloride of the dye was prepared in a way that is essentially that first used by Meldola.[3]

Diphenylamine and aluminum chloride in the ratio of 17 to 13 by weight were mixed in a large container. An amount of benzotrichloride equal to half of the diphenylamine in moles was added. When this mixture was warmed the reaction started and proceeded to completion with some violence. The reaction product was washed with warm dilute aqueous hydrochloric acid, and then dried with hot toluene. The residue was dissolved in methyl alcohol, and aqueous sodium hydroxide, carbon tetrachloride and water were added in the order given. The red carbon tetrachloride layer was repeatedly washed with water and dried with sodium sulfate. From this solution the chloride was precipitated with a little less hydrochloric

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[1] This paper has been constructed from portions of a Thesis presented by T. L. Hill, in partial fulfillment of the requirements for the Ph.D. degree at the University of California.

[2] Baeyer and Villiger, *Ber.*, **37**, 2866 (1904).

[3] Meldola, *J. Chem. Soc.*, **41**, 189 (1882).