Summary

This article presents details concerning the preparation, analysis, properties and optical characteristics of certain salts of fluogermanic acid with nitrogen bases. All of these salts are soluble in water, but are hydrolyzed with separation of hydrated germanium dioxide. Hydrolysis is especially pronounced in the case of dimethylaniline fluogermanate as is evidenced by the round spots in the photomicrograph of the salt.

The analogy between fluogermanates and fluosilicates is shown by the formation of a dihydrate in the case of the hydroxylamine salts whereas the ammonium and hydrazine salts are anhydrous.

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x-Ray Studies of Fatty Acids[1,2]

BY F. B. SLAGLE AND EMIL OTT

Introduction

The long spacings of normal fatty acids have been measured by a series of investigators.[3] However, most of this work is not reliable, due in part to insufficient purity of the acids used. Due to the fact that we had a series of acids of exceptional purity available, it seemed worth while to repeat such measurements with increased accuracy. This was especially desirable in view of the study of mixtures of such acids which will be reported in a following paper.

Experimental Procedure

A. **Spectrograph.**—In all the work reported here a Bragg spectrograph (made in the Seeman Laboratory, Freiburg, i. Br.) with the approximate radius of 16.79 cm. was used. The adjustable front slit was set at 0.1 mm. during all of this work. Most of the measurements of the fatty acids were made by rotating the crystal at constant speed through the angle from 0 to ±10°, since we were only interested in the lower order reflections. The reflections were registered on Eastman x-ray films.

B. **x-Ray Source.**—x-Rays were obtained from a Seeman metal tube, using a tungsten filament and a copper target, the operating peak voltage being 40 kilovolts at 20 milliamperes. A nickel filter of 0.02 mm. thickness was used over the window of the tube at all times to cut out the β-radiation from the copper. The target of the tube was periodically cleaned, thus avoiding tungsten radiation, which under the worst conditions was found by spectrographic measurements to be less intense than the β-radiation from the copper after passing through the nickel filter. The β-radiation was never observed for the fatty acid reflections.

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(1) From a thesis submitted by F. B. Slagle, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Emil Ott and F. B. Slagle, compare preliminary note, *J. Phys. Chem.*, **37**, 257 (1933).

(3) Compare P. P. Ewald and C. Hermann, "Strukturbericht (1913–1928)," Akademische Verlagsgesellschaft, Leipzig, 1931, pp. 691–700.

C. Calibration of the Spectrograph.—Since the spectrograph was built with moderate precision only, it was found necessary to calibrate the instrument with utmost care in the angular range of the contemplated measurements. The reflections from mica do not completely cover this range when copper radiation is used, but the use of silver radiation eliminates this difficulty. It was found advisable to standardize the mica used against calcite, instead of using the mica values given by Siegbahn.[4] Actually we found appreciable deviation, which is to be expected in view of the chemical variations in mica. The fact that various micas have different *c*-spacings is also borne out by the work of Rinne[5] and Mauguin.[6]

The calibration of the spectrograph was then accomplished as follows. The first order reflection from the rhombohedral face of pure calcite (obtained from Dr. W. M. Thornton, Jr., of this Laboratory) is registered on a photographic film. The distance L between the corresponding reflections on either side of the primary beam is measured with a microcomparator to 0.01 mm. A correction for film shrinkage is obtained by imprinting on the undeveloped film in various places two points of known distance apart. This mode of measurement is applied in all cases. The third-order reflection of mica falls very close to the observed calcite reflection (Cu-radiation is used), and thus permits an accurate determination of the observed glancing angle Θ. From this third-order reflection, the other orders of mica are calculated according to Bragg's law. It is now possible to plot Θ against L. To obtain further calibration points the various reflections of mica are also obtained with silver radiation. We are thus enabled to obtain the Θ values of unknown substances by measurement of their L values.

The exact calculations of Θ used in this calibration should be given. The ordinary Bragg equation, $n\lambda = 2d \sin \Theta$ does not apply exactly when the index of refraction differs from unity. The corrected equation takes the form[4]

$$n\lambda = 2d\left(1 - \frac{4d^2}{n^2}\frac{\delta}{\lambda^2}\right)\sin \Theta$$

Siegbahn[4] gives the values of d from the rhombohedral face for calcite as calculated from the various orders, and it is observed that d becomes larger for the higher orders and approaches a constant value. The observed value for the first-order reflection of calcite is given as $d_1 = 3.02904$ Å.[4] From the ordinary Bragg's law ($n\lambda = 2d \sin \Theta$) we obtain the value of Θ for this first-order reflection. From the measurement of L, the effective radius, r, in the vicinity of the reflection is calculated. This value of r will be applicable to the third-order reflection of mica. Thus d_3 for mica is determined as 9.93447 Å. Knowing $\delta/\lambda^2 = 3.86 \times 10^{-6}$,[4] the true spacing d may be determined as follows

$$\text{since } d_n = d\left(1 - \frac{4d^2}{n^2}\frac{\delta}{\lambda^2}\right), \text{ it follows}$$

$$9.93447 = d(1 - (4d^2/9) \times 3.86 \times 10^{-6}) \text{ or}$$

$$d = 9.93615 \text{ Å}.$$

The value for any d_n may now be calculated, and by use of the ordinary Bragg's law again, the values of Θ may be calculated for any order and used in the calibration. Thus we obtain a plot of true angles against L.

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(4) Manne Siegbahn, "Spektroskopie der Röntgenstrahlen," Verlag Julius Springer, Berlin, 1931.

(5) F. Rinne, *Z. Krist.*, **59**, 230 (1924).

(6) Ch. Mauguin, *Compt. rend.*, **186**, 879 1131 (1928).

This calibration curve is used in the determination of the Θ values of the fatty acids. For the calculation of the *d* values, the corrected Bragg formula should be used (δ/λ^2 is not known). However, it is found that within the limits of the accuracy of the determinations, no systematic deviations are found when the ordinary Bragg's law is applied.

In cases with sharp lines the agreement for different orders is within one-tenth of one per cent. This accuracy is reproducible with different mountings of the sample, as well as with different chemical preparations. With broadened lines the accuracy is within five-tenths of one per cent. This precision appears to be higher than any previously obtained.

The values of the wave lengths used throughout this work are those given by Siegbahn.[4]

D. Measurement of Films.—On all of the pictures obtained from the fatty acids there were some strong lines (odd orders), and some weak lines (even orders). The accuracy of measurement of these lines depends on their strength and their sharpness. The strong, well-defined lines were measured with a microcomparator and the measurements could be checked to 0.01 mm. The weak lines were measured with a millimeter scale. The lines of intermediate strength were measured with either the microcomparator or the scale, depending upon the individual case.

In order to obtain the best value for each line, a series of measurements was taken on that line and the average value so obtained reported. All of the measurements of lines given in the tables to follow will be such average values. Those measurements which were made with the microcomparator will be marked (com.). All other lines were measured with the millimeter scale.

E. Preparation of Samples.—A short description of the three methods of preparing the samples is as follows:

(a) Crystallization from Acetone.—A few drops of an acetone solution of the pure acid were put on a glass plate and the acetone allowed to evaporate off. By regulating the rate of evaporation and the concentration of the acetone solution, it is very easy to obtain a uniform deposit on the plate of about 0.1 mm. in thickness.

(b) Melting on Glass Plate.—The technique for preparing samples by this method was more difficult. If a small amount of the acid is melted on a glass plate, it will persistently form a drop and not spread over the surface of the glass. If enough of the material is used a layer of the acid can be formed on the glass plate upon cooling, but such a layer will be very thick (about 1.0 mm.) and show very poor orientation. It was found necessary to form a much thinner film on the plate, causing longer exposure time. By spreading a small drop of the acid over the surface of the glass plate, and cooling rather rapidly (to avoid coalescence to a single drop) such thin films, of practically uniform thickness, can be deposited.

(c) Pressing of Solid Sample on Glass Plate.—If sufficient pressure is exerted upon a solid fatty acid it can be made to adhere to a glass plate. By pressing the acid between two glass plates it was found that the sample would spread to a uniform thickness. If the sample thus formed is thin, one of the glass plates can be removed so that all of the acid will remain in a thin film on the other glass plate. Samples prepared by this method are somewhat thicker than those prepared by the other methods and the reflection lines obtained are broadened.

F. Source of Acids.—The acids, C_{10} to C_{18}, used in this research were prepared by Dr. J. D. Meyer[7] and Dr. John Ruhoff under the direction of Prof. E. E. Reid. The

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[7] J. D. Meyer and E. E. Reid, THIS JOURNAL, **55**, 1574 (1933).

methods of preparation and purification are given in detail in dissertations submitted by them to the Johns Hopkins University in 1932. In addition the C_{19} acid was prepared by the author according to the same methods.

It is believed that the purity of these acids is 99.5% or better (judging from the cooling curves which were obtained), which appears to be purer than the acids used by the other investigators in this field.

G. x-Ray Measurements on the Pure Acids.—The pure acids ranging from C_{10} to C_{19} have been studied with samples prepared by the three methods given previously. All these pictures were taken at room temperature (23 to 28°) excepting for C_{10} and C_{11} which, due to their low melting points, were taken at a slightly lower temperature (20 to 22°) in order to be sure that the sample remained solid during the exposure. The effect of this temperature variation upon the spacing of the (001) planes is easily within experimental error. In the case of the hydrocarbons, Müller[8] found that the expansion along the *c*-axis between liquid air temperatures and room temperatures was so small as to be unmeasurable. Dr. D. A. Wilson of this Laboratory has, in the case of C_{15} acid, observed a slight variation in the spacing between -50 and $+25°$. This sample, which was prepared by crystallization from acetone, gave a spacing of 35.63 ± 0.05 Å. at 25°,

TABLE I

The letter A, B, C or D before each value stands for the modification as listed by Francis, Piper and Malkin. The values marked (*) will be explained in the discussion. The setting points given above are taken from the dissertation of Dr. J. D. Meyer, excepting for C_{19} which was determined by the author. Cooling curves for these acids are also given by Dr. Meyer.

Acid	Setting points	Melted	Acetone	Pressed	Piper's values
C_{10}	31.19	(C)23.02	(C)23.02	(C)22.95	......
C_{11}	27.77	(C)25.32	(C)25.40	(C)25.22	......
C_{12}	43.22	(C)27.18	(C)27.18	(C)27.31	(C)27.4
C_{13}	41.55	(A)34.92 (B)31.27	(A)34.92	(A)34.84	(A)35.3 (B)31.65
C_{14}	53.86	(C)31.44	(C)31.39	(C)31.26 36.64	......
C_{15}	52.26	(B)35.75 (A)39.88	(B)35.63	(B)35.67	(B)35.8 (A)40.0
C_{16}	61.82	(C)35.52	(C)35.47 (B)39.35	(C)35.53	(C)35.65 (B)39.1
C_{17}	60.66	(C)38.57	(B)39.98	(B)40.05 (D)32.85 (A)44.42	(B)40.5 (D)33.9 (C)38.6
C_{18}	68.82	(C)39.83	(C)39.62 (B)44.14 (A)46.15	(C)39.92 (B)44.14 (A)46.29	(C)39.95 (B)44.0 (A)46.6
C_{19}	67.64	......	(B)44.13	(B)44.37* (B)44.14*	(B)44.5

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[8] A. Müller, *Proc. Roy. Soc.* (London), **A127**, 417 (1930).

and a spacing of 35.19 ± 0.10 Å. at −50°. This change in spacing of 0.44 Å. corresponds to a temperature change of 75°, or a change of 0.00587 Å. per degree.

Table I gives the best value for the spacings obtained by the three methods of preparation together with the corresponding values reported by Francis, Piper and Malkin[9] and the setting points of the acids. Fig. 1 gives the plot of the spacings obtained for the pure fatty acids.

The following typical results will demonstrate the check obtained for the spacing from the successive orders (starting with the first order).

	C_{16} Acid melted on glass plate sin Θ/n	C_{13} Acid crystallized from acetone on glass plate sin Θ/n	C_{12} Acid pressed on glass plate sin Θ/n
	0.02167 (com)	0.02204 (com)	0.02815 (com)
	.02167 (com)	.02204	.02814
	.02166 (com)	.02203 (com)	.02819 (com)
	.02162 (wk)	.02202	.02817
	.02165 (com)		
	.02164		
Average	.02166	.02203	.02816
d	35.52 Å.	34.92 Å.	27.32 Å.

(com) = comparator measurement. (wk) = weak line.

A check was made on several acids to see how reproducible the results were. The samples were crystallized again on a glass plate, using the same method of crystallization and the sample remounted in the spectrograph. The values obtained with maximum deviations were

C_{10} (melted sample)	23.03 ± 0.03; 23.04 ± 0.04; 23.00 ± 0.06
C_{11} (melted sample)	25.31 ± 0.03; 25.30 ± 0.03; 25.27 ± 0.04; 25.32 ± 0.03; 25.34 ± 0.03
C_{12} (melted sample)	27.20 ± 0.01; 27.16 ± 0.02; 27.18 ± 0.02
C_{12} (pressed sample)	27.29 ± 0.02; 27.32 ± 0.03
C_{13} (melted)	34.91 ± 0.03; 34.92 ± 0.04
C_{16} (crystallized from acetone)	35.44 ± 0.07; 35.50 ± 0.06
C_{17} (crystallized from acetone)	39.98 ± 0.06; 39.98 ± 0.07
C_{18} (melted)	39.86 ± 0.04; 39.80 ± 0.06
C_{18} (crystallized from acetone)	39.62 ± 0.07; 39.62 ± 0.07
C_{19} (crystallized from acetone)	44.07 ± 0.07; 44.19 ± 0.10

Since the samples were prepared, using essentially the same methods, by two independent workers, samples of C_{12} and C_{13} were used to check the reproducibility of the chemical preparation.

	Sample I	Sample II
C_{12}	27.20 ± 0.01	27.18 ± 0.03; 27.16 ± 0.02
C_{13}	34.91 ± 0.02	34.02 ± 0.01

C_{11} was prepared by two entirely different methods: (1) by hydrogena-

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[9] F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A128**, 214 (1930).

tion of undecylenic acid and (2) by the alcohol–bromide–cyanide method from C_{10}. The results were

Hydrogenated Undecylenic	25.32 ± 0.03; 25.34 ± 0.03; 25.31 ± 0.03; 25.30 ± 0.03
Alcohol–Bromide–Cyanide	25.27 ± 0.04

The measurements for an entirely new modification of C_{14} acid are given. For the first five orders (fourth order is too weak for measurement), it is observed $\sin \Theta/n$ = 0.02103 (wk); 0.02103 (com), 0.02102 (wk) and 0.02094 (wk); average 0.02100; d = 36.64 Å.

This new modification of C_{14} was checked by preparing a new pressed sample which gave the value 36.64 Å., the maximum deviation being in both cases 0.05 Å.

Discussion of Results

From the data given it is seen that the results obtained for any one acid by a single method of preparation of the sample, except for the case of the pressed sample of C_{19}, give spacings which check within the experimental error. These results were not only reproducible with the same sample of the acid, but also with different samples of the acid prepared by the same methods by two independent investigators. It was also found in the case of undecylic acid (C_{11}) that the results were reproducible for two entirely different methods of preparation of the acid. This wide range of reproducibility, combined with the increased accuracy, permits the use of the reported substances as useful standards, where long spacings are desired.

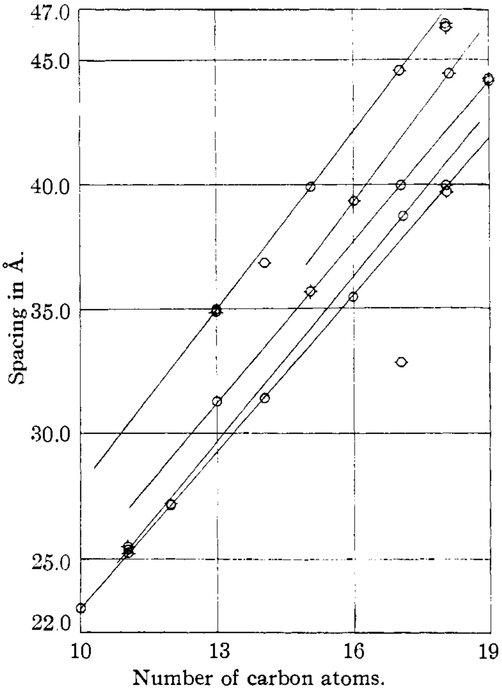

Fig. 1.—Pure acids: ○, melted sample; -○-, pressed sample; -⌽-, sample crystallized from acetone.

In Table I are given our values for the spacings of the pure acids as compared with those obtained by Francis, Piper, and Malkin.[9] In many cases there is a real difference which is sometimes as much as one per cent. In most cases our values are lower than those of Piper.

From the data given it is observed that there are deviations, which appear to be outside of the experimental error, between the spacings obtained for the same modification of a single acid, depending upon the method of preparation of the samples. Piper, Malkin and Austin[10] found similar variations for various long-chain compounds which in some cases were as much as one per cent. Their variations, in the case of fatty acids, were not more than one-half of one per cent., which is comparable with our findings.

If the values obtained from the melted samples and from those crystallized from acetone are compared, it is seen that the lower members of the fatty acid series check very well (except for C_{11}). The higher members (C_{14} and above) deviate giving a value for the melted sample which is higher than the acetone value. A possible explanation for these facts is as follows. The acetone samples were all obtained by evaporating the solutions at room temperature. For these samples the crystallization took place rather slowly, and there were no strains set up due to temperature changes on the solid after it was once formed. The samples crystallized from the melt were formed at their respective setting points, and then cooled to room temperature. In the case of the higher members of the series this crystallization took place very rapidly. The subsequent cooling of these samples gave additional strain, leading to a slightly different tilt of the chains.

The deviations between the pressed sample values and the melted or crystallized from acetone values do not show any regularity. Since these samples were prepared by exerting pressure on the solid acid, it was thought, in analogy to the explanation mentioned above, that the pressure might change the spacing slightly, and thus account for the observed variation. This point is very hard to test because of the difficulty in obtaining equal pressures on all portions of the acid. An attempt was made to test this theory, in the case of C_{19} acid. A pressed sample upon which very little pressure had been exerted gave a spacing of 44.37 Å. A pressed sample upon which much pressure had been exerted gave a spacing of 44.14 Å. This difference seems to be greater than the experimental error in the two measurements. The shift in the spacing is in the right direction, and would seem to substantiate the proposed explanation. This small variation with varying pressure might also be the cause for the decrease in sharpness of the reflections in the case of the pressed samples.

From an inspection of Fig. 1 it is seen that a plot of the spacing obtained against the carbon content of the acids gives a series of straight lines, as has already been known. According to the previous discussion, the spacings obtained from the samples which were crystallized from acetone are the most accurate values. If these spacings are considered, it is seen that the linear dependence with the carbon content is fulfilled, even with the increased accuracy obtained in this work. Also, as has already been

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[10] S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926).

known, the even and odd acids fall on separate lines. This indicates a different tilt in corresponding even and odd modifications. Malkin[11] has offered a simple explanation for this phenomenon. According to his picture there would also exist in the case of tilted chains a difference in packing of the end links of the chains of even and odd acids. This difference is supposed to account for the alternation in melting points. We find that the C_{11} acid, although belonging to a different line, lies nearly on the line connecting the C_{10} and C_{12} acids. This would indicate practically identical tilt of the chains, provided the end groups were arranged correspondingly. A very decided alternation in the melting points, however, forces us to assume a difference in the arrangement of the end groups.

We have further independent evidence of such a difference in arrangement. We observe that in all the modifications (A, B and C, as far as we could obtain them) of the acids, the even orders of the even acids are relatively stronger than the even ones in the odd series (of course in all these cases the even orders are always of lower intensity than the odd ones, in the range of orders studied by us). Since the relative strength of the orders is a function of the density along the chains, this means that the packing of end groups is different in odd and even cases.

Such difference in packing is further shown in the discovery of a new modification in the case of the C_{14} acid (pressed sample). The spacing of this modification does not seem to fit any previously known modification with sufficient accuracy. The most remarkable difference is, however, to be found in the intensity distribution. It is found: first order, weak; second order, strong; third order, weak; fourth order, indicated; fifth order, weak.

As a rule we observe fewer modifications than Francis, Piper and Malkin[9] with similar treatment. This was true especially of the D modification, which was never found except for C_{17} (pressed), where it was just indicated. It will be seen, in the following paper, that a larger number of modifications is readily obtained in the case of mixtures. In view of the high purity of our acid samples and measurable differences in spacings from other authors, this might suggest differences in composition as an explanation for the above phenomenon.

Summary

The interplanar distances of the (001) planes have been measured for the series of very pure normal fatty acids ranging from C_{10} to C_{19}.

The values thus obtained are of higher accuracy than of any similar previous measurements.

Depending upon the method of preparation of the sample slight variations in the spacings are observed.

The C_{19} acid was prepared as a part of this investigation.

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(11) T. Malkin, *Nature*, **127**, 126 (1931); T. Malkin, *J. Chem. Soc.*, 2796 (1931).

An entirely new modification of fatty acids was discovered in the case of the C_{14} acid.

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x-Ray Studies of Mixtures of Fatty Acids[1,2]

BY F. B. SLAGLE AND EMIL OTT

Introduction

x-Ray studies on well-defined mixtures of long chain compounds are relatively few. Most of the results available so far we owe to Piper and his co-workers.[3]

Since we had a series of unusually pure fatty acids available and since we are particularly interested in mixtures of long chain compounds from the standpoint of polymerization, this study was undertaken.

Experimental

I. Two-Component Mixtures of Fatty Acids

1. General. **(a) Preparation of Samples.**—All samples of the mixtures were prepared by the same method. In each case, samples of the acids were weighed out to 0.0001 g. The acids were then fused together in a watch glass and kept just above the melting point for some time. Continual stirring with a small glass rod assured thorough mixing of the several components. The entire mass was then solidified by rapid cooling.

The sample plates were prepared by melting and subsequent solidification of portions of these mixed samples on glass plates. Whenever a check was run on any sample, a second portion of the mixture was taken solidified on a glass plate, and then remounted in the spectrograph. The materials used and the x-ray technique are the same as used in the previous investigation.[4]

(b) Explanation of Tables.—Whenever the deviation for a value is listed, it will be the maximum deviation from the mean in Ångström units. Where more than one value is listed for a particular mixture, it is a check on the reproducibility of the result, unless otherwise explained. The final

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(1) From a thesis submitted by F. B. Slagle in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Emil Ott and F. B. Slagle, compare preliminary note, *J. Phys. Chem.*, **37**, 257 (1933).

(3) Hydrocarbons: S. H. Piper, D. Brown and S. Dyment, *J. Chem. Soc.*, **127**, 2194 (1925); G. L. Clark, *Nature*, **120**, 12 (1927); S. H. Piper, A. C. Chibnall, S. J. Hopkins, A. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2072 (1931). Acids: S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926); also F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A126**, 214 (1930).

(4) F. B. Slagle and Emil Ott, THIS JOURNAL, **55**, 4396 (1933).