The Higher n-Aliphatic Acids and their Methyl and Ethyl Esters

BY F. FRANCIS AND S. H. PIPER

Our investigations on the higher n-fatty acids have now been completed, and in this communication we give some additional and revised data for the acids with even carbon content from 14 to 38 and 46, and a redetermination of the crystal spacings of those containing an odd number from 17 to 25 and 29.

Some of the data for the ethyl esters previously published have been revised, and the crystal spacings redetermined of those of the acids containing an odd number of carbon atoms, and we have not described previously the constants of the methyl esters.

The complete data for the aliphatic acids afford a standard of comparison for those engaged on the study of either these derivatives or the n-primary alcohols isolated from natural sources.

The methods used for the synthesis of the higher members from behenic acid, and the precautions which have to be taken in their purification, have been published previously and are omitted from this communication.[1]

1. **Determination of Setting, Resolidification, Melting Points and Crystal Spacings.**—I. Setting or freezing points (s.p. in Tables I and II) can be determined by different observers to within ± 0.02° provided that 2–3 g. of material is available and a thermometer graduated to 0.1° is used; they are sensitive to the presence of about 0.1% of homologous impurities.

Acids, purified as far as possible by recrystallization, were converted into their ethyl esters. These were fractionated *in vacuo*, followed by recrystallization until their setting points ceased to rise after further purification. From these esters the acids, and, from the latter, the methyl esters, were prepared and also recrystallized until their s.p.'s were constant. It is these acids and esters whose setting points are given in Tables I and II.

The heats of crystallization of a considerable number of these substances have been determined by King and Garner and their results afford evidence on the question of impurities which will be discussed in a later communication.

With a few exceptions mentioned in the text, the impurities probably present in all the preparations described in this paper are of the order of a few parts per 1000. Behenic acid (obtained from erucic acid, s.p. 33.30°, by reduction) and its esters, however, are the purest materials we have succeeded in preparing, and the impurities probably present in these substances are of the order of a few parts per 10,000.

II. Melting points, determined in capillary tubes by the ordinary method, cannot be obtained with sufficient accuracy either for following the stages in the process of purification mentioned above, or for comparing the purity of different preparations of the same substance.

A more accurate method for the determination of these values in capillary tubes has been described,[2] but uniform results with different substances can best be obtained if the observation is made as follows on small quantities of material.

A fraction of a milligram of the substance is fused in a convenient position on the side of a tube 3–4 mm. in diameter, sealed at one end. The tube containing the material in the form of a circular or oval mass of crystals between 1.5 and 2.0 mm. in diameter is then placed in the bath, the crystals brought into the focus of the telescope and the observation of melting point and resolidification point (m.p. and r.p. in Tables I and II) made in the usual manner. If too large an amount has been taken, it may slide down the side of the tube as the melting point is reached, thus preventing the determination of the r.p. and the easy repetition of the observations.

Under these conditions, the melting point is observed more easily than when it is determined in a capillary tube filled in the usual manner, and high readings are largely, if not entirely, avoided.

III. Resolidification points (r.p.) are the temperatures at which the *partly* molten specimen in the capillary tube commences to resolidify when the temperature is lowered very slowly. If the apparatus previously mentioned is used for this determination, these values are found to be close to the s.p.; the extreme divergence is ± 0.2°, but is usually much less, and the error

(1) Francis, Collins and Piper, *Proc. Roy. Soc.* (London), **A158**, 691 (1937); Francis, King and Willis, *J. Chem. Soc.*, 999 (1937).

(2) Francis and Collins, *J. Chem. Soc.*, 137 (1936).

TABLE I

MELTING POINTS OF ACIDS OF EVEN CARBON CONTENT AND THEIR ESTERS

Carbon content of acid	Acids S. p.	Acids R. p.	Acids M. p.	Methyl esters β S. p.	Methyl esters β R. p.	Methyl esters β M. p.	Methyl esters γ M. p.	Ethyl esters α S. p.	Ethyl esters α R. p.	Ethyl esters α M. p.	Ethyl esters β S. p.	Ethyl esters γ M. p.
12	43.75(K)							−15.5(M)			−1.7	
14	53.65	53.9	54.4	18.37		18.8		4.45(M)			11.0(K)	
16	62.60	62.4	62.9	29.20			30.55	19.4			23.20	24.4
18	69.39	69.2	69.6	37.85	37.7	38.7[a]	39.1	31.05	30.95	31.4		33.9
20		74.9	75.35	45.41	45.2	45.8	46.6	40.36	40.15	40.54		41.65
22	79.70	79.6	79.95	51.84	51.7	52.7[a]	53.3	47.80	47.7	48.25		48.7
24	83.90	83.8	84.15	57.42	57.5	57.8	58.4	54.20	54.2	54.35		54.8
26	87.41	87.2	87.7	62.50	62.5	62.9	63.45	59.60	59.5	59.95		60.2
28		90.4	90.9		66.4	66.7	67.5	64.22	64.3	64.6		
30		93.2	93.6	70.3	70.4	70.8	71.7	68.30	68.35	68.45		
32		95.5	96.0		73.6	74.1	74.9	(72.0[b])	72.0	72.5		
34	98.00	97.8	98.2	77.0	76.9	77.2	77.9	75.30	75.2	75.4		
36	(99.7[b])	99.4	99.9		79.9	80.3	80.9	78.31	78.3	78.6		
38	(101.5[b])		101.6		82.3	82.7	83.1	(80.8[b])	80.3	80.55		
46		106.5	106.85		91.0	91.4	91.7	90.22	90.3	90.5		

[a] See text. [b] Interpolated values. M = Mumford and Phillips; K = King and Garner.

TABLE II

MELTING POINTS OF ACIDS WITH ODD CARBON CONTENT AND THEIR ESTERS

Carbon content of acid	Acids S. p.	Acids R. p.	Acids M. p.	Methyl esters β S. p.	Methyl esters β R. p.	Methyl esters β M. p.	Methyl esters γ M. p.	Ethyl esters S. P. from graph esters even acids	Ethyl esters R. p.	Ethyl esters M. p.
17	60.81(K)	60.85	61.3		28.1	28.6	29.7	25.4 (25.15 K)	25.4	25.7
19	68.8(Kc)	68.2	68.65	38.64(K)	38.4	38.9	39.3	35.95 (36.05K)	35.8	36.1
21	73.5(Kc)	73.7	74.3		46.6	47.2	47.6	44.18	43.95	44.5
23	78.69(K)	78.4	79.1		53.5	54.0	54.4	51.05	51.1	51.4
25	82.91(K)	82.7	83.5		59.2	59.5	60.0	56.9	56.85	57.15
29		89.7	90.3		68.3	68.8		66.35	66.3	66.6

K = King and Garner observed, Kc calculated.

in the observation, like that of the m.p., is ± 0.05°. When a sufficient amount of substance is not available for the determination of its s.p. the approximation to it obtained from the r.p. is of importance, and for this reason these values are recorded for all the preparations described in this communication.

IV. To obtain X-ray photographs, flakes of the material are pressed in a thin layer onto a glass strip 5 mm. × 1 cm., using the minimum pressure necessary to cause adhesion. Heavy pressure or rubbing tends to distort the crystals, causing broad lines in the reflections. The plate is mounted vertically with its coated face in the axis of rotation of the X-ray spectrometer, and parallel to a narrow beam of X-rays passing through the spectrometer slits. The beam is supplied by any suitable tube with a copper anti-cathode and is filtered by a thin nickel foil. The specimen is rocked to and fro by a cam mechanism, and the reflections are recorded on a strip of photographic plate or film placed perpendicular to the X-ray beam and 5 cm. from the rotation axis of the spectrometer. Reflections are

recorded on both sides of the central beam, and the angle of rock is varied to suit the type of record required—about 10° for poor material, 20° for good. The spacings are calculated in the usual way from the Bragg law $n\lambda = 2d \sin\theta$, and are given in Tables III and IV.

Exposure times vary from one hour to six or more with a Phillips type of tube running at 10 m.a.

2. The Acids: Even Carbon Content

(i) A consideration of the differences between the s.p.'s of pairs of acids with even carbon content, which will be mentioned later, led to a re-investigation of that with 20 atoms. It was prepared from a very pure specimen of its ethyl ester, and the values for the r.p. and m.p. were found to be higher than those previously obtained. The crystals of the acid from benzene gave a remarkably good X-ray photograph from which the B spacing of 48.45 Å. was obtained, but when crystallized from acetic acid, the resulting crystals showed the C spacing, 44.15 Å., together with the B. This is the only case we have come

across in which both B and C forms came down from the solution of a pure acid, and consequently it modifies our previous statement, that pure acids with an even carbon content crystallized from acetic acid, show the C spacing only (Table III, cols. 2, 3). Acids with an odd number of carbon atoms give the same B spacing irrespective of the solvent used in their preparation (Table IV, col. 2). The relationship between the B and C spacings and the carbon contents of the even acids is linear.

(ii) When the s.p.'s of these acids—or if these are unknown, their respective r.p.'s—are plotted against their carbon content from 12 to 24 and extrapolated to 46, they fall on a smooth graph. Only small amounts of the esters of the acid C_{36} and still less of C_{38} were available, and in consequence the acids obtained from them, and particularly the latter, could not be purified as satisfactorily as all the other members of the series. The acid C_{36} gave an m.p. of 99.9° and r.p. of 99.4°, and the value for the s.p. from the graph is 99.7°. The observed m.p. of C_{38} is 101.6°, but the r.p. is 1.5° below this temperature, thus showing clearly the presence of impurities. From the graph the s.p. is 101.5°.

(iii) When the differences between the s.p.'s of pairs of acids with even carbon content are plotted against that of the intermediate acid from $C_{16}-C_{14}$ to $C_{38}-C_{36}$, the values fall within experimental error on a smooth graph. The differences between the corresponding m.p.'s determined in a capillary tube are very close and in many cases identical with the above data.

(iv) Usually the identity of one of the *n*-aliphatic acids, *isolated from natural sources*, is determined by comparing its m.p. and that of either its methyl or ethyl ester with the corresponding data for the synthetic derivatives; a determination of either the acid alone or one of its esters can be misleading. Identity, however, can be established with certainty from the m.p. and r.p. of the acid, and a measurement of the crystal spacings of a specimen obtained by crystallization from benzene and another from acetic acid. These spacings are not very sensitive to the presence of small amounts of impurities of the order of 1–2%, but the effect of these on the m.p. or r.p. can be detected and has been previously discussed.[1]

(v) The m.p.'s and crystal spacings of some of the higher synthetic *n-primary alcohols* have

been described[1] but the most satisfactory method for establishing the identity of such substances *isolated from natural sources* consists in investigating the *n*-acids obtained from them by oxidation, since the constants for these derivatives are better established than those for the alcohols.

3. Acids: Odd Carbon Content

The number of acids containing an odd carbon content which have been investigated up to the present is considerably smaller than those with an even, and it is known that when the s.p.'s of the former are plotted against their respective carbon content, the resulting graph lies below that of the latter. The extent of this divergence from the graph of the even members is as follows: C_{17} 5.3°, C_{19} 4.0°, C_{21} 3.5°, C_{23} 3.2°, C_{25} 2.6° and C_{29} 2.0°.

The constants of these acids prepared from highly purified esters are given in Table II and their B crystal spacings in Table IV. The relationship between the latter and the carbon content of the acid is linear.

TABLE III

ACIDS OF EVEN CARBON CONTENT. CRYSTAL SPACINGS, Å.

Carbon content of acid	Acid B	C	Methyl ester	Ethyl esters B
14		31.60		
16	39.1	35.60	43.45	
18	43.75	39.75	47.95	25.80
20	48.45	44.15	52.30	
22	52.95	48.3	57.02	29.90
24	57.75	52.6	61.70	32.15
26	62.2	56.25	66.15	34.45
28	67.15	61.05	70.80	36.65
30	71.4	65.2	75.25	38.75
32	76.3	69.25	79.95	41.1
34	80.5	73.3	84.15	43.45
36	85.25	78.1	89.30	46.3
38	90.0	82.1	93.00	48.05
46	108.2	99.05	121.7(?)	57.45

TABLE IV

ACIDS OF ODD CARBON CONTENT AND THEIR ESTERS CRYSTAL SPACINGS, Å.

Carbon content of acid	Acid B	Methyl ester	Ethyl ester
17	40.45	46.3	24.75
19	44.50	50.8	26.95
21	49.25	55.25	29.35
23	53.40	60.0	31.50
25	57.65	64.55	33.60
29	66.35	73.75	38.1

4. The Methyl Esters

(i) The methyl esters of the aliphatic acids were prepared by the usual method from the acids

F. FRANCIS AND S. H. PIPER

whose constants are given in this communication, and Schering-Kahlbaum purest methyl alcohol (b. p. 63.8–64.0°). They were recrystallized either from benzene or glacial acetic acid, and their m.p.'s, etc., are given in Tables I and II. The crystal spacings of these derivatives, calculated from remarkably good photographs showing a large number of orders, are accurate to ± 0.1%, Tables III, IV. These spacings, plotted against carbon content, fall accurately on two straight lines, those for the acids containing an odd number of carbon atoms lying about 0.5 Å. above those of the even. This has been noticed previously by Malkin.[3]
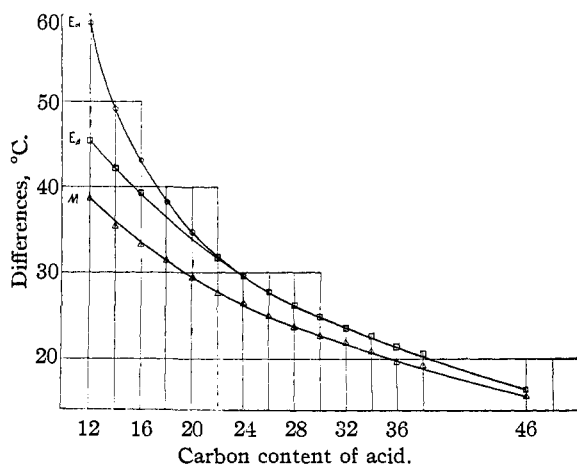

Fig. 1.—Differences between setting points of acids and esters: $E\alpha$ ○, α-ethyl; $E\beta$ □, β-ethyl esters; M △, methyl esters.

(ii) When the s.p.'s of the lower methyl esters were determined, they were found to behave in a manner that had not been observed in any of the other series. For instance, if molten methyl palmitate is allowed to cool at room temperatures, the temperature falls below the s.p. and then when crystallization takes place rises, in the ordinary way, to 28.95°, but after an interval there is a further rise to 29.20°; similarly with methyl stearate and behenate, where the two temperatures are 37.37 and 37.80° for the former and 51.65 and 51.84° for the latter. King and Garner noticed this behavior and the s.p. recorded by these observers was the higher of the two values.[4]

In order to obtain comparable results, the atmosphere around the specimens was maintained at a temperature of 18–20° below their respective s.p.'s.

(3) Malkin, J. Chem. Soc., 2796 (1931).
(4) King and Garner, J. Chem. Soc., 1372 (1936).

When the values for the s.p.'s of the esters of the even-membered acids are plotted against carbon content from C_{14} to C_{38} and extrapolated to C_{46}, they fall with great regularity on a smooth graph.

(iii) In the case of the methyl esters of the acids with an odd number of carbon atoms, the graph constructed as above lies below that for the even in the case of the lower members, but the r.p. of C_{29} ester coincides with it. The extent of the divergence from the graph of the even members is as follows: C_{17} 5.3°, C_{19} 3.0°, C_{21} 2.0°, C_{23} 1.3°, C_{25} 1.0°.

When the differences between the s.p.'s of even-membered acids and those of their methyl esters are plotted against the carbon content of the former from C_{12} to C_{36} and extrapolated to C_{46} they fall on a smooth graph (see M, Fig. 1).

The corresponding data for the methyl esters of the odd acids from C_{17} to C_{29} lie on a second graph.

(iv). **Dimorphism of the Methyl Esters.**— The m.p.'s of the methyl esters of the even series from C_{16} to C_{36} (Table I, col. 8) lie between 1.0 and 1.5° above their respective r.p.'s (Table I, col. 5), but if the determination is made on that modification which separates on crystallization and before the temperature has fallen more than 1° or so, it is found that in most cases a lower m.p. is obtained, which is about 0.5° above the r.p. (Table I, col. 7). In Table I we have classified as β esters those whose s.p.'s have been determined and whose m.p.'s appear to be the lower of the two values determined as above, although in some cases, marked with a cross, the latter may correspond to a mixture of β-γ esters. The γ esters are those with the higher m.p. A similar classification is made of the methyl esters of acids containing an odd number of carbon atoms, Table II.

The resolidification of the molten esters is very slow and in the case of the lower members the r.p. cannot be observed in a capillary tube with any degree of certainty. The velocity of the change, however, increases as the series is ascended, but it never appears to be as great as that of the corresponding ethyl esters. The phenomena observed during the determination of s.p., and mentioned previously, may be due to this small velocity of crystallization, or to the existence of two modifications of the ester, that with the lower m.p. changing to the higher with heat evolution.

(v) In addition to the two m.p.'s of what we

have termed the β- and γ-modifications, there is another phenomenon which can be observed if the molten ester is allowed to cool to a few degrees below its r.p. and the temperature then slowly raised. Under these conditions the solid ester illuminated by transmitted light is translucent, and in the case of the esters of C_{20}, C_{24}, C_{26}, C_{28}, C_{32} and C_{36}, the specimen suddenly becomes opaque at temperatures between 0.4 and 0.7° below the m.p. of the γ-modification. In the case of C_{22}, however, the change takes place at 0.4° below the m.p. of the β-form and 1.0° below that of the γ. This may be due to the formation of liquid crystals, but at a later date we hope to explore these and other changes that we have observed in the solid esters of acids containing an odd or even number of carbon atoms, by the determination of crystal spacings at various temperatures.

5. The Ethyl Esters

When the s.p.'s of what we have classified as the α-ethyl esters, Table I, col. 9, of the acids with even carbon content from C_{16} to C_{38} and extrapolated to C_{46} are plotted against these contents, the values lie with great regularity on a smooth graph. That there is no alteration in this series between the esters of the even and odd numbered acids is seen in the close correspondence between the observed values in Table II, col. 10, and those obtained by interpolation from the graph of the esters of the even acids in col. 9.

When the differences between the s.p.'s of the acids and their α-ethyl esters are plotted against the carbon content of the parent acid, the values lie on a smooth graph from C_{16} to C_{38} and extrapolated to C_{46}, and on this also lie the extrapolated values for C_{14} and C_{12} described by Mumford and Phillips.[5] It is possible—as indicated in Fig. 1—

(5) Mumford and Phillips, *Rec. trav. chim.*, **52**, 183 (1933).

that the differences of the β-ethyl esters and their corresponding acids for C_{12} to C_{16} fall on a second graph which joins the above at C_{22}, that is, the esters of the acids with higher carbon content than C_{22}, or possibly C_{24}, exist in one form which may correspond to either the α- or β-modifications of the lower members. They are classified as the former in Table I.

The crystal spacings of the specimens of the ethyl esters of the acids with an odd number of carbon atoms are accurate to 0.1%. The relationship between these and the carbon content of the acid is linear, and 0.1 Å. above that for the esters of the even-membered acids.

The dimorphism of the lower ethyl esters of the acids with even carbon content and the m.p.'s of the unstable modifications have been described in a previous communication,[1] but no phenomenon similar to this has been observed with certainty in the corresponding esters of the acids with an odd carbon content.

Summary

In this communication revised data are given for the setting or freezing, melting, and resolidification points, and the crystal spacings of the *n*-fatty acids and their methyl and ethyl esters. The acids are those with even carbon content from 14 to 36 and 46, and some of the odd from 17 to 25 and 29. These substances have been ·purified by a combination of fractional distillation *in vacuo*, followed by recrystallization until their setting points ceased to rise. Some observations are also included on the dimorphism which occurs in the methyl and ethyl esters.