CCLXXXVI. MELTING-POINTS AND LONG CRYSTAL SPACINGS OF THE HIGHER PRIMARY ALCOHOLS AND *n*-FATTY ACIDS¹.

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IN previous papers dealing with the metabolism of paraffins in the plant we have pointed out the necessity of gaining some insight into the constitution of the mixed primary alcohols and fatty acids which invariably accompany them in plant waxes. With this end in view we have obtained, by isolation from waxes or by synthesis, a series of primary alcohols, acetates, *n*-fatty acids and ethyl esters of 26–36 carbon atoms of a degree of purity satisfying the requirements of X-ray analysis. These products are described in the present paper, as also are certain synthetic mixtures which we have found of great use in elucidating the composition of the naturally occurring alcohols and acids.

To save space in this and the following communications we shall frequently allude in the text to a long straight-chain compound, whatever its nature, by the letter C with a subscript denoting the number of carbon atoms in the chain. Thus, *n*-triacontanoic acid will be written C₃₀ acid, and the corresponding alcohol C₃₀ alcohol. In the Tables, for the same reason, and where no confusion is likely to arise, we simply state the number of carbon atoms in the chain. Thus an equimolar mixture of *n*-octacosanoic, *n*-triacontanoic and *n*-dotriacontanoic acids will be described as equimolar 28+30+32 acids.

EXPERIMENTAL.

Preparation of the higher primary alcohols and n-fatty acids.

The isolation of *n*-hexacosanol from cocksfoot has already been described [Pollard *et al.*, 1931]. This alcohol and its derivatives have been further purified in the following way. 6.9 g. of the acetate were recrystallised first from light petroleum (b.p. 40–60°) and then from acetone. 3.8 g. of this material (m.p. 60–60.2°) were saponified in the usual way to recover the alcohol, which melted at 79.5–79.8°. 2.0 g. of the alcohol were oxidised to *n*-hexacosanoic acid [Pollard *et al.*, 1931], the ethyl ester of which was distilled at 145°/0.03 mm. Crystallised from acetone this melted at 60.1–60.2°, and the recovered acid after two crystallisations from acetone at room temperature and two from acetone at 37°

¹ The melting-points recorded in this paper were obtained by the method described by Piper *et al.* [1931] and are corrected.

melted at 87.8–88.0°. Another sample (3 g.) of the alcohol was converted *via* the iodide and the nitrile into *n*-heptacosanoic acid, the ethyl ester of which was distilled at 150–155°/0.08 mm. Crystallised from acetone this melted at 62.5–62.6°, and the recovered acid, after crystallisation from acetone at 37° melted at 87.5–87.7°. The ester (0.2 g.) was reduced with sodium (0.1 g.) in dry ethyl alcohol (1 ml.) to *n*-heptacosanol. Acid formed by saponification was removed as the calcium soap and the alcohol crystallised first from ethyl alcohol and then from acetone, m.p. 81.2–81.6°. The yield was poor (17 mg.).

The preparations of *n*-octacosanol from wheat, and of the corresponding acid have already been described [Pollard *et al.*, 1933]. The alcohol (2 g.) was converted *via* the iodide and the nitrile into *n*-nonacosanoic acid. The ester (1.5 g.) was distilled (160–165°/0.05 mm.) and after crystallisation from acetone melted at 66.7–66.8°. The recovered acid, after two crystallisations from acetone at 37°, melted at 90.6–90.8°. The ester (0.5 g.) on reduction with sodium gave *n*-nonacosanol, m.p. 84.6–85°, in poor yield (46 mg.).

The preparation of *n*-triacontanol from lucerne and of its corresponding acid has already been described [Chibnall *et al.*, 1933]. The alcohol (0.5 g.) was converted *via* the iodide and nitrile into *n*-hentriacontanoic acid, which was crystallised from acetone at 37°. The yield was 0.26 g. and the melting-point 93.0–93.2°.

n-Dotriacontanoic acid was prepared by Clemmensen reduction of synthetic 13-keto-*n*-dotriacontanoic acid [Chibnall *et al.*, 1934]. 1.4 g. of *n*-triacontanol were converted into the iodide, which was recrystallised from ethyl alcohol, m.p. 72.8–73.2°. The iodide (0.3 g.) was converted *via* the nitrile into *n*-penta-*n*-triacontanoic acid, which was recrystallised repeatedly from benzene and then sublimed *in vacuo* at 130°. It melted at 98.3–98.5°. Another sample of the iodide (1.3 g.) was converted into *n*-hexatriacontanoic acid, using butyl alcohol in the malonic ester condensation [Bleyburg and Ulrich, 1931]. The crude acid (0.6 g.) was esterified and the product distilled at 0.01 mm. The purified ester melted at 78.5–78.7° and the recovered acid after two crystallisations from acetone at 37° melted at 100.1–100.3°. The ester (0.22 g.) was reduced with sodium to *n*-hexatriacontanol. The yield was poor, and the product after sublimation *in vacuo* melted at 93.2–93.6°. This is nearly 1° lower than the extrapolated value and the material was impure.

As is to be expected, the solubility of all these products decreases with increase in chain length; this is very marked in the case of the acids and especially so in the case of the alcohols. Thus all the esters and acetates are fairly soluble even at room temperature in most organic solvents. In the cases of the acids and alcohols those with 26 carbon atoms are soluble at room temperature only in chloroform and benzene, but are soluble in most organic solvents at the boiling-point; whereas those with 36 carbon atoms are insoluble in all cold solvents and are soluble only with difficulty in boiling solvents other than chloroform and benzene.

The alcohols are markedly less soluble than the corresponding acids, and our experience suggests that odd-number acids are more soluble than even.

The sodium and potassium soaps on the contrary become increasingly soluble in organic solvents with increase in chain length; those of the higher members being soluble to an appreciable extent in boiling acetone and fairly freely soluble in boiling benzene. The calcium soaps are slightly soluble in boiling alcohol or acetone but are nearly insoluble in boiling benzene. We have already called attention to this change in the solubilities of the higher soaps when discussing the separation of the constituent alcohols and acids of the wax coccerin [Chibnall *et al.*, 1934].

According to our experience long-chain alcohols prepared by saponification of waxes can only be obtained completely free from calcium soaps by a slow process of extraction with acetone at 40° or with boiling ether, in which the soaps are completely insoluble.

Mixtures of known composition.

Owing to the impossibility of complete separation of the constituents of many mixtures of aliphatic compounds the only way to establish the composition of mixed wax products is to compare their behaviour with that of similar synthetic mixtures. It is only possible to prepare a limited number of the latter, and it has been our endeavour to select such as will allow of generalisations. Thus we have prepared series of mixtures of varying composition, of pairs of alcohols, acids, acetates and esters, and have attempted to predict from the observations made on these what will be the behaviour of other pairs of similar composition but different chain lengths. We have carried out the same process for a limited number of triple mixtures, but here the generalisation is more difficult and uncertain.

The mixtures were prepared from pure synthetic standards by the method used by Piper *et al.* [1931] for mixtures of paraffins. As the products (10–20 mg.) were obtained by crystallisation from a small volume of acetone it follows that when one component is added only in small amount, *e.g.* 1–5 %, the mixture may contain a little less than this proportion. Also the constitution of the mixed crystals deposited from solution will vary during the process of crystallisation and there may sometimes be an appreciable difference in the spacings of the top and bottom fractions when quantities of more than a few mg. are crystallised. To meet this difficulty and at the same time to suit the small quantity of material available we have produced very small amounts of the mixed crystals and endeavoured to take photographs with the X-ray beam covering the whole of the specimen. Though there is still some uncertainty in the exact percentage composition of the mixture, the spacing is a mean for the specimen concerned, and it must be emphasised that these mixtures have been made with the express object of obtaining the general form of the melting-point and crystal spacing curves, which are used later to interpret the composition of naturally occurring mixtures of similar components. Accuracy of the same order as that obtained by de Visser [1898] or Smith [1931], in which each sample was prepared by melting together weighed amounts of the two components, is neither claimed nor considered necessary in the present work since we have been concerned with establishing the actual presence in bulk of the main constituents of natural waxes, rather than in estimating the exact percentages in which they occur.

Crystalline forms and long crystal spacings.

The external crystalline form of substances of the long-chain aliphatic series has been discussed by Gascard [1921]. All the acids, esters, alcohols and acetates we have examined behave in the manner he describes. When crystallised from appropriate solvents, the pure material separates in rhombs showing sharp acute angles and clean straight cleavages.

The crystal forms of both binary and ternary mixtures are in general similar to those of the pure products; the rhombs still have sharp acute angles and straight cleavage edges, but the latter are perhaps a little more broken. In the case of the mixed acids the plates are often so thin that they tend to curl up so that a small aggregate of crystals, when viewed under low magnification, exhibits a fern-leaf structure. Mixed acetates are difficult to obtain in good crystalline

form, and on filtration they pack down to a mass of fine lamellae with edges that are very much broken. Gascard [1921] recognised that regularity of shape is no criterion of purity when the contamination is due to an homologous substance.

Aliphatic compounds may appear in various crystalline modifications due to a variation in the angle of tilt between the crystal planes and the molecule, and the spacing of a particular compound varies directly with the sine of the angle of tilt. The crystal forms important in this work are described as A, B and C. A forms have a vertical chain, B a chain tilted at about $63-60^\circ$ to the flake surface and C a chain with a tilt in the neighbourhood of 53° . For our purpose it is convenient to list the forms in terms of angular inclination of the molecule rather than stability. The various α forms (the most stable forms) discussed in the literature may or may not have vertical chains according to the nature of the compound and its chain length. The alcohol and ester crystal modifications are described by Malkin [1930; 1931], the *n*-fatty acids by Francis *et al.* [1930], the long-chain paraffins by Piper *et al.* [1931] and are briefly summarised below.

Long spacings of all substances in one series which crystallise in the A form, when plotted against the number of carbon atoms in the chain, lie on a single straight line for both odd and even chains. Odd-number alcohols and paraffins and all acid soaps crystallise only in the A form. No odd- or even-number acid of chain length greater than 18 has been found to occur in this modification, and pure esters only adopt it at temperatures near the melting-point. Even-number paraffins of 24 or more carbon atoms when melted usually recrystallise in the A form and always adopt it at temperatures near the melting-point. Odd- and even-number acids, even-number alcohols and all esters crystallise from most organic solvents in the B form and in most cases adopt either an A or C form at high temperatures. The presence of impurity frequently causes a substance, which would normally crystallise as a B modification, to adopt the A or C form. The appearance of both A and B, or B and C forms on the same plate is, in our experience, always an indication of impurity if the material has been crystallised from solution.

The nature of the solvent may have a direct effect upon the crystal form assumed. It is therefore advisable to employ standard solvents. We have used warm acetone for acids and alcohols and warm light petroleum for esters and acetates. The crystallographic data we have tabulated are valid for these solvents, but modifications might have to be introduced if other solvents were employed. For example, one of our natural alcohols crystallised from light petroleum appeared in both A and B forms, the latter being predominant, whilst from benzene-alcohol A form crystals alone were deposited.

The spacings have been obtained in the same way as for paraffins [Piper *et al.*, 1931]. To reduce exposure times the distance plate-specimen has been decreased to 5 cm. and for fairly pure specimens the rocking angle of the specimen holder increased to 22° . This allows the registration of the high order ($n+2$) [Pollard *et al.*, 1933]. This order of reflection is not obtained sharply in poor crystals and to save time the angle of rock is limited to 11° for the exposures of mixtures.

It is of course possible accurately to measure the spacing of a specimen from a single order by employing a comparison reflection from a known standard. This may mean a saving in time, but in our experience the appearance of the different orders can be so suggestive that it is worth the extra time to register the complete series.

In previous work we have insisted upon a large number of orders of reflection as a criterion of purity. It is difficult to lay down any exact guide for the actual number of orders that should be measurable for a standard exposure, for this will vary with the nature of the material and also with its chain length. Roughly speaking, however, good crystals of substances of chain length 24 or more should give a series of orders filling the whole angle of rock of 11° . The exposure times vary; paraffins require half the exposures of active group compounds, and it is necessary to remember that each series has a characteristic intensity fluctuation; acids and alcohols for instance have the first few even orders weak and the odd strong, but strong even and weak odd for high orders.

The melting-points and long crystal spacings of the higher primary alcohols and acetates (Table I).

The melting-points of the odd- and even-number primary alcohols lie on one smooth curve, a feature characteristic of substances melting from the A form. This curve follows on that of the lower members described by Malkin [1930]. The melting-points are sharp, and setting-points are readily obtained without leaving a nucleus, the material separating in very small needle-shaped crystals. Only B form spacings of even-number alcohols are included in Table I. The A spacing of the pure even-chain substance only appears at high temperatures, and when an A spacing is recorded at room temperature it will be from an impure specimen. The A spacings we require for the construction of graphs have been obtained by extrapolation from the straight line on which the spacings of the odd-number alcohols lie, since the latter only crystallise in this form.

Table I. *Melting-points and long crystal spacings of the higher primary alcohols.*

No. of carbon atoms	Source	M.P. ° C.	S.P. ° C.	Crystal spacings in Å.		Acetate M.P. ° C.
				Series No.	A B	
26	Cocksfoot	79.5-79.8	79.1	B 257	— 57.95	60.0-60.1
27	From C ₂₆	81.2-81.6	81.0	B 316	72.95 —	—
28	Wheat	83.2-83.4	82.8	B 256	— 62.15	64.6-64.8
29	From C ₂₈	84.6-85.0	84.1	B 230	78.0 —	—
30	Lucerne	86.3-86.5	85.9	B 259	— 66.53	69.1-69.2
32	Synthetic*	89.3-89.5	88.9	B 348	— 71.0	72.6-72.8
34	Reduction of cocceryl alcohol	91.9-92.2	91.6	B 266	— 74.64	75.5-75.8
36	From C ₃₄ †	93.2-93.6	92.6	B 317	— 80.28	—

* Sample kindly provided by Prof. Francis.

† Impure, see text.

The melting-points of the acetates also fall on a smooth curve for the odd- and even-number series. Transitions similar to those described for the paraffins [Piper *et al.*, 1931] were observed in all cases, but the temperatures at which they occurred both on heating and cooling were not accurately reproducible, and the effect of impurity in the form of another acetate was not marked; we have therefore purposely omitted further reference to them. Also, since sufficient data to decide the nature of the polymorphism of acetates are not yet available, the spacing results obtained have not so far proved of value and are not recorded.

The melting-points and long crystal spacings of the higher n-fatty acids and ethyl esters.

The melting-points fall on two smooth curves, one for the odd- and the other for the even-number acids. The setting-points are sharp, the material separating in long needles which grow from the bottom of the melt to the top. It is however necessary to leave a nucleus to prevent supercooling. The melting-points of the ethyl esters lie on one smooth curve, as was found for the lower members of the series by Francis *et al.* [1930] and by Levene and Taylor [1924]. Sharp setting-points are obtained with a nucleus, the material separating in long needles. Transitions on heating and cooling similar to those described for the paraffins were also observed, but as in the case of the acetates the temperatures at which they occurred were not as reproducible as with the paraffins and were not markedly affected by the presence of another ester. Details are therefore omitted.

Table II. *Melting-points and long crystal spacings of the higher n-fatty acids and ethyl esters.*

No. of carbon atoms	Source of acid	M.P. ° C.	S.P. (with nucleus) ° C.	Crystal spacings in Å.		Ethyl esters M.P. ° C.	Crystal spacings in Å.	
				Series No.	B		Series No.	B
26	C ₂₆ primary alcohol	87.8- 88.0	87.5	B 239	62.0	60.1-60.2	B 37	34.4
27	"	87.5- 87.7	87.0	B 188	61.95	62.5-62.6	B 231	35.7
28	C ₂₈ primary alcohol	90.8- 91.1	90.5	B 262	66.76	64.7-64.8	B 218	36.4
29	"	90.6- 90.8	90.3	B 202	66.21	66.7-66.8	B 222	38.1
30	C ₃₀ primary alcohol	93.6- 93.9	93.4	B 238	71.4	68.8-68.9	B 219	38.8
	Synthetic*	93.8- 94.0	93.6	B 235	71.4	—	—	—
31	C ₃₀ primary alcohol	93.0- 93.2	92.6	B 223	70.44	—	—	—
32	Synthetic	96.1- 96.3	95.5	B 279	76.12	72.6-72.7	B 312	41.1
34	C ₃₄ primary alcohol	98.3- 98.5	97.8	B 272	80.4	75.6-75.8	B 347	43.5
35	"	98.3- 98.5	98.0	B 314	78.75	—	—	—
36	"	100.1-100.3	99.7	B 275	85.34	78.4-78.6	—	—

* Sample kindly provided by Mrs G. M. Robinson.

The B spacings alone are recorded for the acids, as these are used in identifications. Francis *et al.* [1930] considered that correct values for both B and C spacings and the melting-point were necessary to establish the purity of an acid. In the light of further experience we are now able to reduce these criteria to a correct melting-point and the appearance of the B spacing alone, giving a good reflection of order ($n+2$). We rarely use the C spacings for identifications and therefore have not attempted to measure them with high accuracy. Both melting-points and spacings are in good accord with those of Francis *et al.* [1930] when the latter are corrected for a consistent error making them about 0.5 % too high. They also agree with measurements made on synthetic material prepared in Prof. Francis's laboratory. The results and the corrected data for acids 14-26 are to be published later.

Spacings of ethyl esters are also given in Table II. These agree well with those for the esters 14-26 of Francis *et al.* [1930] and of Malkin [1931] for the lower members.

*Melting-points of binary mixtures of even-number alcohols,
acetates, acids and ethyl esters.*

Alcohols. The melting-point curve for mixtures of *n*-hexacosanol and *n*-octacosanol is similar to that obtained by Smith [1931] for *n*-hexadecanol and *n*-octadecanol, giving only a slight depression of up to 0.5° when 5–30 % of the higher component is present. The setting-points, even without a nucleus, are sharp and within 0.3° of the melting-point, the material separating in all cases in very small needles.

Table III. *Melting-points and long crystal spacings of mixtures of
n-hexacosanol and n-octacosanol.*

Percentage composition		M.P. ° C.	Crystal spacings in Å.			Remarks	Acetates M.P. ° C.
C ₂₆	C ₂₈		Series No.	A	B		
100	0	79.5–79.8	B 257	—	57.95	B form only	60.0–60.1
95	5	79.2–79.5	B 248	70.53	—	A form only	—
90	10	79.1–79.3	B 249	71.1	—	—	60.2–60.4
75	25	79.2–79.4	B 250	72.7	—	—	60.6–60.8
60	40	79.5–79.7	B 251	73.1	—	—	61.8–62.0
50	50	79.9–80.2	B 252	73.5	—	—	62.3–62.4
40	60	80.6–80.9	B 278	74.6	—	—	62.6–62.8
30	70	81.2–81.5	B 277	75.4	—	—	63.4–63.6
25	75	81.2–81.6	B 253	75.2	—	—	63.4–63.6
20	80	81.6–81.9	B 276	75.75	—	B form disappears	—
10	90	82.2–82.4	B 254	75.4	62.25	—	64.3–64.4
5	95	82.6–82.8	B 255	75.4	62.5	A form appears	—
0	100	83.2–83.4	B 256	—	62.18	B form only	64.6–64.8

Acids. As in the case of the standard acids it is necessary to leave a nucleus to obtain the setting-point without supercooling. With small additions of the other acid (1–2.5 %) the material separates in large needles similar to those of the pure acids, but with the grosser mixtures the material separates in amorphous form, an observation which will disclose at once the approximate purity of a sample of naturally occurring fatty acid.

Table IV. *Melting-points and long crystal spacings of mixtures of
n-octacosanoic and n-triacontanoic acids.*

Percentage composition		M.P. ° C.	S.P. (with nucleus) ° C.	Crystal spacings in Å.			Remarks
C ₂₈	C ₃₀			Series No.	B	C	
100	0	90.8–91.1	90.5	B 262	66.76	—	—
97.5	2.5	90.4–90.6	89.8	B 280	67.54	61.32	C form appears
95	5	90.0–90.2	89.7	B 281	68.1	61.5	—
90	10	88.7–88.9	88.3	B 320	68.7	63.9	—
75	25	86.6–86.8	86.0	B 283	71.35	—	C form has disappeared
70	30	86.3–86.5	85.7	B 322	69.5	—	—
60	40	86.7–86.9	86.2	B 323	70.2	—	—
50	50	87.1–87.3	86.7	B 319	69.16	—	—
40	60	87.6–87.8	87.1	B 324	70.8	—	—
25	75	89.8–90.1	89.3	B 285	71.0	—	—
20	80	—	—	B 326	71.6	65.5	C form appears
10	90	92.0–92.2	91.6	B 327	72.4	65.4	—
5	95	92.6–92.8	92.2	B 287	71.4	—	—
2.5	97.5	93.1–93.3	92.7	B 288	71.9	—	—
0	100	93.8–94.0	93.6	B 235	71.4	—	—

Table V. *Melting-points and long crystal spacings of mixtures of ethyl n-hexadecanoate and ethyl n-octadecanoate.*

Percentage composition		M.P. ° C.	Crystal spacings in Å.			Remarks
C ₂₆	C ₂₈		Series No.	A	B	
100	0	60.1-60.2	B 37	—	34.4	B form only
99	1	60.1-60.2	B 309	—	34.5	
97.5	2.5	60.1-60.3	B 308	—	34.55	
95	5	60.2-60.4	B 306	—	34.7	
90	10	60.4-60.6	B 305	—	34.95	
80	20	60.9-61.0	B 304	38.9	35.75	A form appears
70	30	61.3-61.4	—	—	—	—
60	40	61.7-61.8	B 302	40.3	36.5	—
50	50	62.1-62.3	B 301	40.3	—	B form disappears
40	60	62.6-62.8	B 300	40.5	—	—
20	80	63.6-63.7	B 298	40.1	—	—
10	90	64.2-64.3	B 297	40.0	—	—
5	95	64.4-64.5	B 296	39.9	—	A form appears
2.5	97.5	64.5-64.6	B 295	—	36.9	B form only
1	99	64.6-64.7	B 294	—	36.4	
0	100	64.7-64.8	B 218	—	36.4	

The mixed melting-point curves. For the construction of the melting-point curves of binary mixtures of acids we have used the classical values of de Visser [1898] for the setting-points of mixed stearic and palmitic acids and our own

Fig. 1.

Fig. 2.

observations on the melting-points of mixtures of *n*-octacosanoic and *n*-triacon-tanoic acids. The curve for the latter pair approximates in form to de Visser's setting-point curve, both having a maximum depression at about 70 % of the

lower component. There are two inflections in de Visser's curve at about 60 and 50 % of the palmitic acid. Our melting-point curve also shows a kink between 40 and 50 % of the lower component, corresponding to the 50 % inflection on de Visser's setting-point curve. If large enough amounts of the C_{28} and C_{30} acids had been available to observe setting-points without previous crystallisation from a solvent it is probable that the inflections would have been more marked. We have assumed that all binary acid mixtures have a maximum depression at a composition containing 70 % of the lower constituent. We have determined the melting-points of equimolar mixtures of several other pairs of acids (Table VI) and the depressions of these equimolar melting-points lie on a smooth curve when plotted against the mean chain length. We have assumed that the maximum depressions occurring at 70 % of the lower component will lie on a similar curve. We have taken the maximum depressions observed for the acids (16+18 and 28+30), and drawn a smooth curve passing through these two points and parallel with the equimolar depression curve. From this graph we obtain the maximum depressions for all neighbouring pairs of acids. We have thus four points to construct each of the curves given in Fig. 1, *viz.* the melting-points of the pure components, of the equimolar mixtures and of the mixtures of maximum depression. We consider these curves to be sufficiently accurate for our purpose.

The mixed melting-point curves for the alcohol pairs were constructed in the same way (Fig. 2). The ester and acetate mixed melting-point curves are practically linear between the melting-points of the two constituents and offer no difficulty.

*The long crystal spacing curves of binary mixtures of even-number
alcohols, acids and ethyl esters.*

We give the spacing composition curves for one pair each of alcohols and acids. As with the paraffins [Piper *et al.*, 1931], we assume that the curves are similar for all pairs of a given type, only raised or lowered in the scale of ordinates to lie between the spacings of the pure components.

Alcohols. The tendency is for crystallisation to occur in the A form. When 5 % of the long chain has been added to the short the B form has disappeared, but at the other end B and A spacings appear together for 5 and 10 % contamination. The A form alone appears at 20 % of the short chain in the long. Between the extreme compositions in which the A form exists there is a fairly uniform rise in spacing from the low end to about equimolar proportions. Above equimolar concentrations the spacing approximates to that of the higher-melting component. Spacings are correct to about 0.5 %.

Acids. Crystallisation under the conditions laid down above produces the B modification. Both B and C spacings occur simultaneously between 2.5 and 10 % at the top end of the curve and between 10 and 20 % at the short end, but C spacings alone were not observed, though they can be obtained by melting the substance [Piper *et al.*, 1926]. The variations in the B spacings follow a similar course to those of the alcohols. It should be mentioned that mixtures of about equimolar proportions do not give consistent spacing values. The results agree with the previously published data of Piper *et al.* [1926], Francis *et al.* [1930] and Ott and Slagel [1933]. These last workers found the spacing of a binary mixture to depend on the history of the specimen, and that in many cases it changed with age as the specimen passed into a more stable modification. An all-round accuracy of more than 1–2 % is not claimed for these measurements.

Between the compositions at which the C form disappears the photographs are generally poor, they show few orders and broad diffuse lines.

Ethyl esters. The substances begin to crystallise in the A form at a contamination of 5 % at the long end. At the short end the A form first appears for a 20 % addition of the long chain. The A spacing of the mixture is sensibly

Fig. 3.

Fig. 4.

constant over the whole range of concentrations for which it occurs, whilst the B spacing of the shorter component tends to increase with contamination. At the long end of the curve the B spacing is approximately constant.

Melting-points and long crystal spacings of ternary mixtures.

All the melting-points and spacings observed for ternary mixtures are recorded in Table VII. The following useful generalisations are drawn from the results shown in this Table, and in the previous Tables on binary mixtures.

(1) Acetates and esters have melting-points determined by the mean molecular weight and exhibit no appreciable depression. This behaviour is strictly analogous to that of the paraffins [Piper *et al.*, 1931].

Table VI. *Melting-points of equimolar mixtures.*

Composition	Acids M.P. ° C.	Ethyl esters M.P. ° C.	Alcohols M.P. ° C.	Acetates M.P. ° C.	Paraffins M.P. ° C.
24 + 26	79.8*	(57)	(76)	—	—
26 + 28	83.5	62.3	80.2	62.4	59.1
28 + 30	87.3	66.9	83.6	67.4	(63.6)
30 + 32	90.2	71	(86.7)	(70.8)	(67.8)
32 + 34	93.1	74.5	(89.6)	(74.3)	(71.3)
27 + 28	(87.6)	—	81.6	—	—
27 + 29	(85.2)	—	81.7	—	—

Data in brackets are extrapolated.

* Francis *et al.* [1930].Table VII. *Melting-points and long crystal spacings of ternary equimolar mixtures.*

Composition	Acids		Alcohols		Ethyl esters M.P. ° C.	Acetates M.P. ° C.	Paraffins M.P. ° C.
	M.P. ° C.	Crystal spacing Å.	M.P. ° C.	Crystal spacing Å.			
24 + 26 + 28	(79.8)	(69.4)	(76.5)	(72)	(60.2)	(60.2)	(56.6)
26 + 28 + 30	83.4	(73.2)	80.7	77.05	64.9	64.4	61.8
28 + 30 + 32	87	77.6	(84.0)	(82.5)	68.5	(68.8)	(65.8)
30 + 32 + 34	90	81.6	(87.1)	(87.5)	72.7	(72.5)	(69.7)
32 + 34 + 36	92.8	85.65	(89.9)	(92)	75.7	(75.8)	(72.8)

Data in brackets are extrapolated.

(2) Table VI shows that equimolar binary mixtures of alcohols melt about 0.2–0.4° above, and of acids about 3.4–4.5° below, that of the lower component. Addition of the next higher even-number component to make equimolar ternary mixtures raises the melting-point of the alcohols by about 0.5°, and lowers that of the acids a further 0.2–0.3°.

(3) The B spacing of the highest-melting acid in a ternary mixture will appear alone if this acid constitutes 20 % or more of the whole. This fact is valuable, since it allows one to fix a lower limit for the amount of the longest chain in such a mixture. If the longest chain only constitutes 10 % or less of the whole the spacing appears to be near to the B of the intermediate chain. The measurements in such cases should give a value for the spacing agreeing to within about 1 or 2 % with that of the pure material.

(4) Ternary mixtures of alcohols in which no single component is present to an amount of more than 75 % will crystallise in the A form. Since the chains in this form are vertical one might expect the spacing to have a mean value, but the figures do not lend much support to this view. In the one case where a single component constituted 80 % of the whole its approximate B spacing was obtained.

(5) The X-ray photographs of quite complicated mixtures of alcohols are often very good, showing many sharp orders. In view of this fact it is well to state that the numerical value of an A spacing of an even-number alcohol must never be used alone as identification, for the fact that an even-number alcohol has crystallised in this form is proof of contamination. Acid and ester mixtures however give photographs whose appearance (few diffuse orders) easily distinguishes them from pure material.

Francis *et al.* [1930] drew attention to the appearance of the longer spacings in equimolar mixed binary ethyl esters, and Malkin [1931] explained that they were due to the appearance of the A form. Both A and B spacings remain sensibly constant over the ranges of composition in which they appear alone,

and hence are not a great help in fixing percentage compositions. But it is useful to remember that mixtures containing from 20 to 95 % of the longer component give the longer A spacing. The A spacing of a pure ethyl ester is only obtained at high temperatures and its appearance at room temperature is definite proof of contamination.

Calculation of the data in Table VIII.

The depressions of the equimolar melting-points (Table VII) of ternary mixtures below the melting-point of the mean component, when plotted against the mean chain length lie on a smooth curve. We have also made a few ternary mixtures of varying proportions. The results have been extrapolated in the manner described below and are shown in Table VIII.

Table VIII. *Triple non-equimolar mixtures.*

(All data are extrapolated except those in heavy type.)

Composition	Acids		Alcohols		Ethyl esters	Acetates	Paraffins
	M.P. ° C.	Spacing Å.	M.P. ° C.	Spacing Å.	M.P. ° C.	M.P. ° C.	M.P. ° C.
40 % 24 + 40 % 26 + 20 % 28	79	67	76.1	70.3	59	59	55.3
40 % 26 + 40 % 28 + 20 % 30	83.2	71.6	80.4	75.75	63.8	63.8	60.3
40 % 28 + 40 % 30 + 20 % 32	86.6	76	83.9	81.25	68	68	64.8
40 % 30 + 40 % 32 + 20 % 34	89.7	80.5	86.9	86.25	72.1	72.1	68.7
40 % 32 + 40 % 34 + 20 % 36	92.5	85	89.8	91.25	—	—	—
20 % 24 + 40 % 26 + 40 % 28	81	67	78.3	73.8	61	61	57.4
20 % 26 + 40 % 28 + 40 % 30	84.8	71.7	82.3	78.9	65.5	65.5	62.1
20 % 28 + 40 % 30 + 40 % 32	87.9	76	85.6	84.4	69.5	69.5	66.5
20 % 30 + 40 % 32 + 40 % 34	91.1	80.5	88.2	89.4	73.2	73.2	70
20 % 32 + 40 % 34 + 40 % 36	93.7	85	91.2	94.5	—	—	—
10 % 24 + 80 % 26 + 10 % 28	82.9	62	77.8	58.9	60.2	60.2	56.6
10 % 26 + 80 % 28 + 10 % 30	86.5	67	81.9	63.2	64.8	64.8	61.5
			B form				
10 % 28 + 80 % 30 + 10 % 32	89.7	71.5	85.3	67.5	68.9	68.9	65.8
10 % 30 + 80 % 32 + 10 % 34	92.4	76	88.2	71.6	72.7	72.7	69.7
10 % 32 + 80 % 34 + 10 % 36	95.1	80.5	91.5	75.6	—	—	—

If we select say the mixture 20 % C₂₆ + 40 % C₂₈ + 40 % C₃₀ acids we note that the melting-point of 84.8° is 6.3° below that of the mean component. We assume that this melting-point difference varies with mean chain lengths in the same way as the equimolar differences, since the ternary equimolar depression of melting-point for a mean chain length 28 is 7.7°. The difference between the two depressions is 1.4°. We now assume that the melting-point depression in any mixture of three neighbouring even-number acids of this composition will lie on a curve similar to that for the equimolar depressions, but converging on it at the long-chain end. The same reasoning is assumed to apply to mixtures of different proportions and also to mixtures of other substances. By constructing these curves we have been able to compile the melting-points in Table VIII.

The spacing values of the acids follow from generalisation 4 above. For the alcohols we note that in 20 % C₂₆ + 40 % C₂₈ + 40 % C₃₀ the spacing of 78.9 Å. is 3.4 Å. higher than the A spacing of the component of mean chain length. Here we assume that the difference will be constant for alcohol mixtures of this percentage composition but differing in mean chain length, and we apply the same rule to alcohol mixtures of any other compositions of which we have prepared a specimen.

Use of the mixed melting-point and mixed crystal spacing data in interpreting the composition of unknown mixtures.

In interpreting the composition of wax alcohols and acids we make use of the series of curves of mixed melting-points for acids, alcohols and esters, and the corresponding spacing data. In the case of the alcohols we first endeavour to find a binary mixture whose characteristics are as close as possible to those of our mixture. For this purpose the melting-point of the derived paraffin (or acetate) is first compared with the standard paraffin (or acetate) curves, and the constitution of the binary mixture having the same melting-point is found. Since these standard curves are linear this corresponding binary mixture is unique, giving at once the mean chain length and hence the molecular weight of the paraffin (or acetate) under investigation. The mean molecular weight so obtained will be sufficiently correct, even if there are more than two constituents of the unknown mixture.

The standard curves for acids show a large and those for alcohols a small depression. In general therefore both the melting-point of the alcohol itself and that of the derived acid will correspond to two or more possible binary mixtures. Thus the melting-points of the alcohols or of the acids alone are insufficient to fix the composition of a binary mixture. However, when they are set out on the appropriate standard curves it is immediately possible to see if a binary mixture of the proportions demanded by the acetate melting-point will correspond. It is surprising how often a reasonable fit is obtained for the three quantities, though more often it is necessary to assume the presence of at least a small amount of a third component. Where a binary mixture is suspected we seek confirmation from the spacing data.

The process can be followed from the example given below. The columns headed "corresponding mixture" contain the binary mixtures found from the standard curves.

Lac wax fraction 5.

	M.P. ° C.	Corresponding mixture	Spacing	Corresponding mixture
Alcohol	82.0	80 % C ₂₈ + 20 % C ₂₆	79.5	50 % C ₃₀ + 50 % C ₂₈
Derived acetate	65.6	20 % C ₃₀ + 80 % C ₂₈	—	—
Derived acid	85.3	10 % C ₂₈ + 90 % C ₂₆	71.6	A little high for B form of C ₃₀
		or 65 % C ₂₈ + 35 % C ₂₆		
Derived paraffin	62.3	20 % C ₃₀ + 80 % C ₂₈	—	—

The derived acid spacing requires the presence of C₃₀ and no binary mixture suits the whole of the data. Therefore the mixture is at least ternary and the amount of C₃₀ cannot be less than 20 % (generalisation 3). The derived acetate and paraffin both require the same mixture, so we can assume our mixture to have a mean chain length of 28.4. The A spacing of the C₂₈ alcohol is 75.5 Å., or 4 Å. less than that observed, and the corresponding mixture suggests equal proportions of alcohols. Since the 50 % C₃₀ + 50 % C₂₈ gives too high a molecular weight, as well as being out of accord with the other observations, we expect to have some C₂₆ in the mixture. We tried a synthetic mixture of 40 % C₃₀ + 40 % C₂₈ + 20 % C₂₆ and obtained the correspondence shown below.

	Alcohol		Derived acid		Acetate	Derived paraffin
	M.P. ° C.	Spacing Å.	M.P. ° C.	Spacing Å.	M.P. ° C.	M.P. ° C.
Lac alcohol fraction 5	82	79.5	85.3	71.6	65.6	62.3
Synthetic 20 % C ₂₆ + 40 % C ₂₈ + 40 % C ₃₀	82.3	78.9	84.8	71.7	65.6	62.1

The agreement throughout is good and the proportions suggested must be close to the true composition of the alcohol. It is to be remembered that we only suggest a constitution accounting for the bulk of the mixture; there may well be small percentages of alcohols above and below those given.

For estimating the composition of the mixed free acids occurring in waxes we have usually made use of the mixed melting-points, the mixed spacings and the acid values, for in this range the acid value and mixed ester melting-points appear to possess about the same order of accuracy in assessing the mean molecular weight. Further the mixed ester spacings are not very helpful in suggesting the percentage composition of a mixture, and to save labour we have in many cases refrained from preparing the esters. The data are used in the manner described for alcohols.

SUMMARY.

Several pure alcohols, acids, acetates and ethyl esters of from 26 to 36 carbon atoms have been prepared, and their melting-points and long crystal spacings have been measured and recorded.

Several binary and ternary mixtures of known compositions have been prepared from them and their melting-points and crystal spacings recorded.

Methods have been devised for extending the observations made on a limited number of synthetic mixtures to cover a much larger number which have not been specifically prepared. It is shown how the data so obtained may be used to determine, within limits, the composition of the mixed alcohols and acids present in waxes.

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