118. *The Dimorphism of Certain Aliphatic Compounds.*
Part II.

By JOHN WILLIAM COLE PHILLIPS and STANLEY AUGUSTUS
MUMFORD.

IN a previous paper (J., 1931, 1732) a thermal examination of the
ethyl esters of palmitic and stearic acids was reported, and in
agreement with Smith (*ibid.*, p. 802) it was found that the dimorphism
exhibited by these two esters was monotropic in character, the
transparent α-form first obtained when the liquid was cooled being
metastable and readily converted by further cooling into a more
opaque, higher-melting, stable β-modification with evolution of heat.
The transformation was found to be irreversible, and very much
more rapid with the palmitate than with the stearate.

It was further observed that, although the ethyl ester of margaric
acid also showed dimorphism, this, in contrast to that of the palmitate
and stearate, was enantiotropic, the transparent α-form, f. p. 25·2°,
obtained on solidification changing reversibly on further cooling
into an opaque β-modification,* at a transition temperature of 11—
12° (from the cooling curve). This has recently received confirm-
ation from Malkin's account (J., 1931, 2796) of his thermal and
X-ray examination of various higher aliphatic esters (compare
Nature, 1931, **127**, 126). This author records 25·0° as the setting
point of the α-form of ethyl margarate, and 9·5° as its transition
temperature; and the series of dimorphous ethyl esters has been
extended by his observation that ethyl nonadecoate sets at 35·5°
to a transparent solid and changes reversibly to an opaque form at
24·3—24·7°, whilst ethyl eicosoate solidifies to a metastable trans-
parent form at 40·5°, and is converted irreversibly into a stable
opaque modification, m. p. 41°, on further cooling.

From these facts, collected in Table I, it is evident that, although

* In the previous paper the low-temperature variety of ethyl margarate
was referred to as the γ-form, but as it appears to be crystallographically
similar to the β-forms of ethyl palmitate and stearate it is now termed the
β-modification.

TABLE I.

Dimorphism of the Ethyl Esters of the n-*Fatty Acids.*

Ester.	α-Form (transparent).	Transition.	Higher-melting β-form (opaque).
Palmitate	(metastable) f. p. 19·2° (a) 19·4 (b) 19·8 (c)	Monotropic (transition to β occurs at f. p. of α-form).	m. p. 24·1° (a) 24·18 (b) m. p.* 25 (b) 25 (c)
Margarate	(stable) f. p. 25·2 (a) 25·0 (c) m. p.* 25·8 (a) 28 (c)	Enantiotropic : Transition temp. = 11—12° (a) 9·5 (c)	—
Stearate	(metastable) f. p. 30·4 (a) 30·9 (b) 30·75 (c)	Monotropic (transition to β occurs slowly on further cooling).	m. p. 32·9 (a) 33·4 (b) m. p.* 34 (b) 34 (c) 33·5 (d)
Nonadecoate	(stable) f. p. 35·5 (c) m. p.* 37·5 (c) 37·5 (d)	Enantiotropic : Transition temp. = 24·5 (c)	—
Eicosoate	(metastable) f. p. 40·5 (c)	Monotropic (transition to opaque form occurs on further cooling).	m. p.* 41 (c) 42 (d)

References : (a) present authors; (b) Smith; (c) Malkin; (d) Levene and Taylor (*loc. cit.*).

(m. p.* indicates capillary m. p.)

alternation results when a comparison is made of the melting points of those modifications of the ethyl esters which are stable at the melting point, this is due to the circumstance that it is the β opaque forms of the esters of the even acids and the α transparent forms of those of the odd acids which are being compared. When the strictly comparable α-forms are alone taken into consideration, the alternation disappears, for, as pointed out by Malkin, the setting points of the α-forms of both odd and even esters lie on a smooth curve (see Fig. 2, B).

Malkin's summary (*loc. cit.*, p. 2800) of his thermal examination of the esters, however, fails to differentiate adequately between the monotropic dimorphism of the even and the enantiotropic dimorphism of the odd esters, and in particular, to indicate that the different stability of the transparent forms is due to the fact that those of the odd esters *are* the stable, but those of the even esters merely metastable, modifications in the vicinity of the setting point.

From Fig. 1, (ii), it will be seen that both cooling and heating curves of the ethyl esters of the odd acids show two distinct arrests, one at the setting point of the transparent α-form, and the other

at the temperature at which this changes reversibly into the opaque
β-modification, the α-form being stable between these two temper-
atures, and the β below the latter.   The change is definitely enantio-
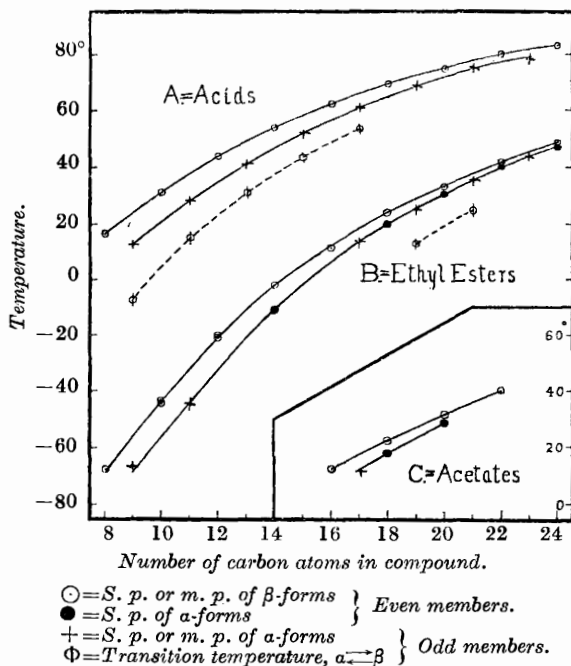tropic.

With the ethyl esters of the even acids, on the other hand [Fig.
1, (i)], only the cooling curves show two arrests; the first, as above,
is at the setting point of the transparent α-form, and the second

FIG. 1.

Cooling curves.   *Heating curves.*
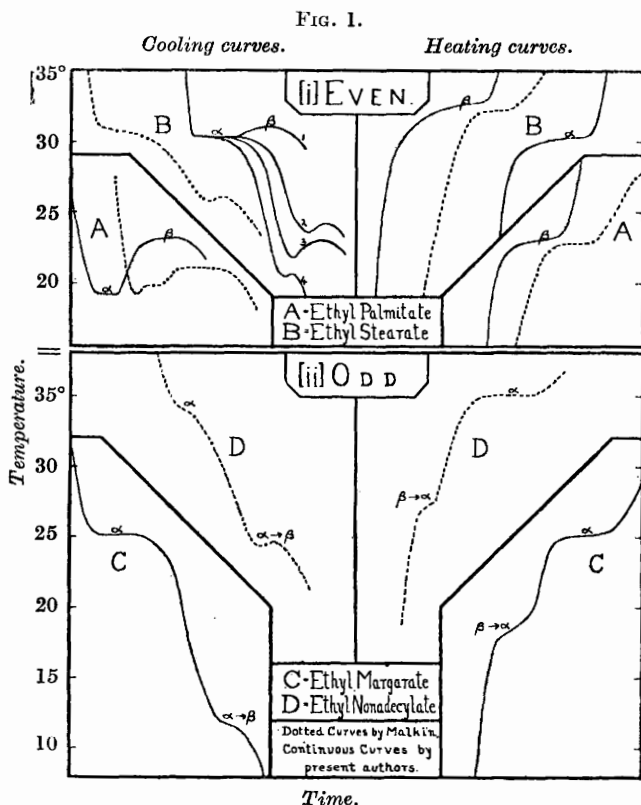
corresponds to a spontaneous and exothermic change into the stable,
opaque, and higher-melting β-modification.   In an ideal case these
two arrests are superimposed, the α- changing into the β-form
with rise of temperature above the setting point of the former.
This occurs, for example, with ethyl palmitate [A in Fig. 1, (i)],
and by regulating the rate of cooling and seeding with β-crystals,
this phenomenon can be induced with ethyl stearate also [curve
B (1), Fig. 1, (i)].   Normally, however, the cooling curve of the latter
compound resembles those of the esters of the odd acids in showing

arrests at two different temperatures [curves B (2)—(4), Fig. 1, (i)], the change from α to β being very slow, especially in the presence of traces of impurities (compare Smith, *loc. cit.*). With less pure specimens of ethyl palmitate a similar cooling curve may also be obtained. The temperature at which the second arrest occurs, however, cannot justifiably be termed a " transition " temperature, as is done by Malkin, for, apart from the fact that it varies considerably according to the conditions of the cooling, the heating curves

FIG. 2.

○ = S. p. or m. p. of β-forms } Even members.
● = S. p. of α-forms
+ = S. p. or m. p. of α-forms } Odd members.
Φ = Transition temperature, α ⇌ β

of these even esters show only one arrest, which occurs at the melting point of the higher-melting β-modification, providing the α ⟶ β-transformation has taken place to completion. If this change is slow, however, as with ethyl stearate, it is possible to solidify the ester and cool it to laboratory temperature in its metastable α-form, in which case, of course, the arrest in the heating curve occurs at the melting point of this α-modification [heating curve B, α, Fig. 1, (i)]. It is evident that we are here dealing with monotropic dimorphism.

From the X-ray spacing data of Malkin, the β-forms of both odd and even esters appear to be of the same crystallographic type and

to possess carbon chains tilted with respect to the planes formed by the terminal groups. They differ, however, in that the β even esters are stable up to their m. p.'s, whereas the β odd esters undergo transition into the corresponding α-forms some 10—15° below their m. p.'s. This difference, according to Malkin, is connected with the difference in the density of packing in the terminal planes between odd and even chains, the odd being separated by alternate loosely and closely packed planes and hence being less stable than the even, which are separated by similar closely packed planes. The α-forms of both even and odd esters, metastable in the case of the former, and stable down to the transition temperature in the case of the latter, give correspondingly longer spacings and appear to have vertical chains.

In extending these considerations to esters higher and lower in the series than those given in Table I, the variation of the rate of change from metastable to stable form in the case of even esters, and the extent to which this is influenced by impurities, has to be borne in mind. Since the change with ethyl palmitate is so very much more rapid than with ethyl stearate, it would be expected that isolation of the metastable α-forms of lower even esters might be a matter of difficulty. A preliminary thermal examination of the ethyl esters of myristic, lauric, and decoic acids appears to confirm this, and to indicate that only the stable β-forms are readily obtainable.

In the case of ethyl myristate, b. p. (uncorr.) 139·0° ± 0·4°/4 mm., prepared from the acid by the method of Whitby (J., 1926, 1458), the liquid supercooled to about 6° and then solidified in the opaque β-form, m. p. 12·3°, with rise of temperature, the f. p. of the ester (by seeding at 10·5°) being 11·7°; Garner and Rushbrooke (J., 1927, 1351) give 11·0° as the setting point. Two specimens of ethyl laurate were examined, b. p.'s 121·8° ± 0·2°/5 mm. and 121·7° ± 0·3°/5 mm., prepared respectively from lauronitrile by the imino-ether method, and from the acid as above, and both had f. p. − 2·0° (with supercooling to about − 4°); whilst that of the ethyl decoate, b. p. 96·5° ± 0·1°/5 mm., obtained from Kahlbaum and purified by fractionation, was − 20·5° (with supercooling to − 21·5°). Deffet (*Bull. Soc. chim. Belg.*, 1931, **40**, 385) gives − 19·9° as the f. p. of the latter ester. The cooling curves of the solid myristate and laurate showed no discontinuity, and the heating curves of all three esters only the one arrest at the m. p.

It will be seen from Fig. 2, B, that these freezing points lie on the curve obtained by plotting against the number of carbon atoms in the various compounds the m. p.'s of the β-forms of ethyl palmitate, stearate, and eicosoate (Table I), and the f. p.'s of ethyl

n-octoate ($-$ 44·75°, Timmermans, *Bull. Soc. chim. Belg.*, 1923, **31**, 389; $-$ 43·1°, Deffet, *loc. cit.*), and ethyl n-hexoate ($-$ 67·5°; Simon, *ibid.*, 1929, **38**, 47). The corresponding curve for the esters of the odd acids is incomplete, but it may be approximately outlined by plotting the setting points of ethyl margarate and nonadecoate (Table I), the m. p.'s of ethyl pentadecoate (14°; Le Sueur, *J.*, 1904, **85**, 827) and ethyl heneicosoate (45°; Levene and Taylor, *J. Biol. Chem.*, 1924, **59**, 905) and the f. p.'s of ethyl pelargonate ($-$ 44·45°; Timmermans, *loc. cit.*) and ethyl heptoate ($-$ 66·1°; Deffet, *loc. cit.*). The f. p.'s of the α-forms of the higher even esters fall satisfactorily on this odd-ester curve. It is of interest in this connexion that the f. p. recorded for ethyl laurate by Timmermans (*loc. cit.*), *viz.*, $-$ 10·65° (compare Görgey, *Annalen*, 1848, **66**, 303, who states that it solidifies at $-$ 10°), also lies close to this curve, and it is possible, therefore, that the solid obtained by these authors was the α-form of the ester. Nevertheless, the precise course of the lower part of the odd-ester curve is uncertain for the f. p. given by Deffet (*loc. cit.*) for ethyl pelargonate (*viz.*, $-$ 36·1°) is considerably higher than that of Timmermans (see above). This uncertainty, however, does not apply to the upper portion of the curve, and does not affect the general conclusions drawn from a survey of the f.-p. data, for the curve in question is, in any case, lower than, and distinct from, that of the even esters.

In contrast to these lower members, the change from α to β with the higher even esters will probably be as slow as, or even slower than, that with ethyl stearate. The closeness of the values given by Malkin for the setting point of the α- and the m. p. of the β-form of ethyl eiocosoate may, therefore, be in some measure due to incomplete conversion, for even with ethyl stearate the change takes a considerable time and in an m. p. determination carried out before all the ester is in the β-form the compound naturally shows signs of incipient fusion at the setting point of the α-variety. It is even possible, in certain cases, to realise a complete melting curve of the α-form (compare above).

In the case of the odd esters, such difficulties as these should not arise, and it is hoped to examine some of the other members in due course. Malkin records two spacings for ethyl heneicosoate, indicating the occurrence of dimorphism, but does not appear to have made a thermal examination of this ester.

The dimorphic peculiarities of the long-chain ethyl esters are paralleled by those of the acetates of the higher alcohols, at least so far as the even members are concerned. Thermal data for cetyl and octadecyl acetates are given in Fig. 3, from which it will be seen that they closely resemble their isomerides, ethyl palmitate and

stearate respectively. Their cooling curves show clearly how the
" transition " temperature, in the case of even esters, varies accord-
ing to the conditions of the experiment. With both compounds
the α-modification is sufficiently stable to be cooled to 12—15°
without undergoing transformation, and accordingly, as with
ethyl stearate, a melting curve of this form, as well as of the β,
can be obtained. The f. p.'s of the α- and m. p.'s of the β-forms of
these two esters are plotted against their carbon content in Fig. 2, C,
together with the m. p.'s of tetradecyl and eicosyl acetates (12—
13°, Krafft, *Ber.*, 1883, **16**, 1720; and 39·5—40·5°, Adam and

FIG. 3.

Cooling curves.   *Heating curves.*

H · CetylAcetate
J · Octadecyl Acetate

Time.
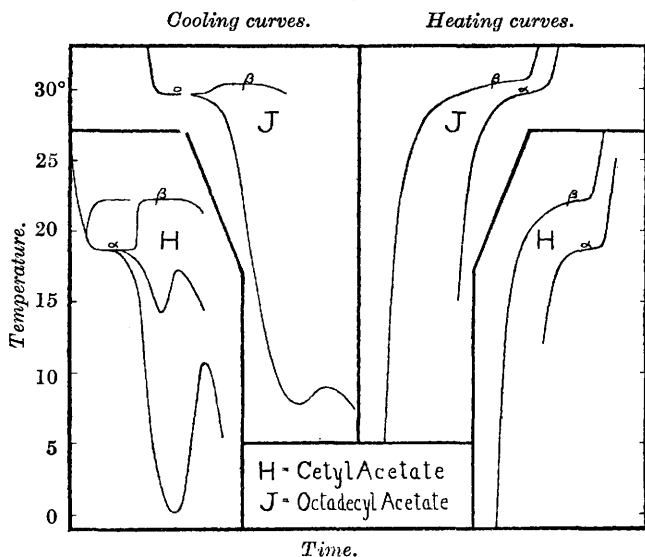
Dyer, J., 1925, **127**, 70, respectively). No data are available
regarding the odd esters of this series, apart from an m. p. of
pentadecyl acetate (10—11°; Panics, *Monatsh.*, 1894, **15**, 13), which
falls approximately on the freezing-point curve of the α-forms of the
above, but it seems probable that they will exhibit the enantiotropic
dimorphism of the odd ethyl esters, and this point is being investi-
gated.

Monotropic polymorphism has also been noted with, *inter alia*,
*i*sobutyl palmitate and stearate (Vorländer and Selke, *Z. physikal.
Chem.*, 1927, **129**, 435), diethyl cetylmalonate (present authors,
loc. cit.) and, of course, with many of the glycerides of the higher
even acids; and from the relationship of these compounds to the
monotropic esters discussed above, it seems possible that alternation

of dimorphic type may be found to be a more or less general character-
istic of series of aliphatic esters. The alternation in the case of the
methyl esters appears to be of a somewhat different kind, for evidence
of dimorphism has been found only with the esters of the odd acids
(Malkin, *loc. cit.*); but with the parent acids themselves a marked
resemblance to the ethyl ester series is apparent (Fig. 2). The
odd acids, as shown by Garner and his co-workers (J., 1924, **125**,
369, 881; 1925, **127**, 720; 1926, 2491), and confirmed by de Boer
(*Nature*, 1927, **119**, 50, 634), show enantiotropic dimorphism,
whilst as regards the even members, the latter author, from the
effect of temperature on the different sets of X-ray spacings observed
by Piper, Malkin, and Austin (J., 1926, 2310), concluded that they
had only monotropic modifications. At the same time, there are
several points of difference between the two series, notably in that
the enantiotropy of the odd acids is of a peculiar unilateral type in
the case of the higher members (Garner and King, J., 1929, 1849),
whilst the metastable modifications of the even acids appear to be
obtainable only by crystallisation from solvents, and to pass into
the corresponding stable forms on being heated to a more or less
definite " transition " temperature (Francis, Piper, and Malkin,
Proc. Roy. Soc., 1930, *A*, **128**, 214; Thibaud and La Tour, *Compt.
rend.*, 1930, **190**, 945). Two monotropic modifications have, how-
ever, been isolated in the case of an even member of the corresponding
unsaturated series, namely oleic acid, which can exist in a metastable,
transparent, acicular form, s. p. and m. p. 13·2°, and a stable opaque
variety, m. p. 16° (Kirschner, *Z. physiol. Chem.*, 1912, **79**, 759;
Bertram, *Rec. trav. chim.*, 1927, **46**, 397). It is also of interest to
recall that Tammann (*Z. anorg. Chem.*, 1920, **109**, 221) explained
the alternating melting points in the fatty-acid series on the assump-
tion that the even acids existed in two, but the odd in only one,
form, his evidence being that acetic acid was dimorphous, with a
triple point of 57·5° under 2330 kg./sq. cm., whereas formic acid
showed no such behaviour.

In conclusion, it would appear possible that a more or less similar
alternation of polymorphic type may likewise occur in other related
series of compounds. In the dibasic acid series, for example,
Caspari (J., 1929, 2709) isolated two modifications of azelaic acid,
but could only obtain one of suberic and sebacic acids, whilst La
Tour (*Compt. rend.*, 1930, **191**, 1348) found that succinic acid
exhibited enantiotropic dimorphism with a transition point some
50° below its m. p. With the alcohols, again, evidence has been
obtained from X-ray spacing data (Malkin, *J. Amer. Chem. Soc.*,
1930, **52**, 3739) of the existence of enantiotropy with the even, but
not the odd, members, and this has been confirmed thermally for

myristyl and cetyl alcohols by Garner and Rushbrooke and by the present authors respectively (*loc. cit.*).   With the halides, Deese (*J. Amer. Chem. Soc.*, 1931, **53**, 3673) records that *n*-amyl bromide exhibits a transition about 25° below its m. p., whereas the corresponding *n*-butyl and hexyl derivatives show no such behaviour; cetyl chloride (and possibly the bromide and iodide), on the other hand, shows monotropic dimorphism (present authors, *loc. cit.*). The available data for these and other series are, however, too scanty for further generalisation.