CXI.—*Higher Aliphatic Compounds. Part I. The Systems Ethyl Palmitate–Ethyl Stearate and Hexadecyl Alcohol–Octadecyl Alcohol.*

By John Charles Smith.

During the preparation of cetyl iodide for another investigation (Smith, this vol., p. 251) the necessity for a revision of the criteria of purity of this halide, and indeed of higher aliphatic compounds in general, became evident. De Visser (*Rec. trav. chim.*, 1897, **17**, 182) purified palmitic and stearic acids and mapped their binary system. Carlinfanti and Levi-Malvano (*Gazzetta*, 1909, **39**, 353) generally confirmed his figures and concluded that the system showed the existence of a molecular compound which formed solid solutions with each of the pure acids. Efremov (*Ann. Inst. Polyt. Ural*, 1927, **6**, 155), using less pure acids (m. p.'s 59·2° and 67·8° respectively), found no evidence of the molecular compound, and described the system as an unbroken series of solid solutions exhibiting a minimum (Type III of Roozeboom, *Z. physikal. Chem.*, 1899, **30**, 385).

It is now found that hexadecyl and octadecyl alcohols form a system of Type III. Both ethyl palmitate and ethyl stearate are dimorphous, and in mixtures the lower-melting forms give an unbroken series of solid solutions without minimum or maximum (Type I of Roozeboom).

All the substances were purified exhaustively by at least two methods, and in each case the different processes led to final products of identical freezing point. The results show the inadvisability of relying on melting points in capillary tubes as criteria of purity, especially for cetyl alcohol, in which a 15% admixture of octadecanol lowers the m. p. by only 0·7°, and a 30% admixture raises it again to that of the pure substance.

EXPERIMENTAL.

Purification of Materials.—Palmitic acid. Kahlbaum's acid (f. p. 60·9°, 40 g.) was recrystallised five times from 95% ethyl alcohol (f. p. raised to 62·2°) and then ten times from pure benzene. The product (8 g.) had f. p. and m. p. 62·66° * (m. p. in capillary tube 63·5°), unchanged by two further crystallisations from benzene and one from ligroin (De Visser, *loc. cit.*, gives m. p. 62·618° ; Stratton and Partington, *Phil. Mag.*, 1924, **48**, 1085, f. p. 62·25°, m. p. 62·65°).

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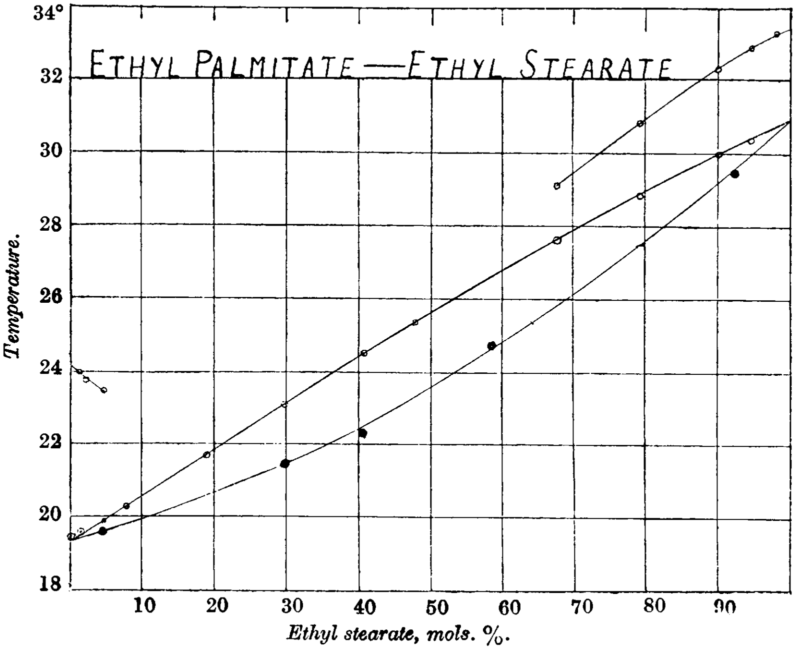
* F. p.'s and m. p.'s were taken in apparatus of the Beckmann type with standardised thermometers, and are correct to ± 0·04°.

Ethyl palmitate. Palmitic acid (m. p. 62·66°) yielded this ester, which, crystallised from absolute alcohol or ligroin, melted at 24·18°. Commercial "purified" palmitic acid (m. p. 52—54°) was esterified and the product fractionated (12 mm.) until no further change in the m. p. (24·18°) was effected. Some of the rejected fractions were recrystallised from alcohol or ligroin to constant m. p., 24·18° (capillary tube 25°), and finally, ester of this m. p. was hydrolysed (aqueous-alcoholic potassium hydroxide solution) to palmitic acid (once recrystallised from alcohol) of f. p. 62·65°.

FIG. 1.



When the liquid ester is cooled, it crystallises in large transparent plates (f. p. and m. p. 19·40°), but on stirring, these change rapidly to fine, opaque crystals, while the temperature rises to about 23°; on heating these melt at 24·18°. When the ester is quite pure, it is difficult to keep the lower-melting crystals long enough for a determination of the f. p. From the curve for mixtures of ethyl palmitate and ethyl stearate (see Fig. 1), the f. p. of the former would appear to be 19·3° instead of the value 19·4° actually observed. The higher-melting form does not crystallise rapidly enough for its f. p. to be determined in the ordinary way.

Ethyl palmitate made from crude palmitic acid may have m. p.'s as low as 18° and 22° owing to the presence of impurities other than ethyl stearate (Heinz, *J. pr. Chem.*, 1855, **66**, 37, gives m. p. 24·2°; Adam, *Proc. Roy. Soc.*, 1922, **101**, 471, gives 25·5°).

Cetyl alcohol. Crude cetyl alcohol (f. p. 47·3°) was distilled at 12 mm. from a Claisen flask. The distillate was fractionated (0·2—0·4 mm.) through a 60 × 3 cm. column of Raschig rings, and the distillate collected in three or four fractions without interruption of the boiling. Although the pressure remained nearly constant (McLeod gauge), the b. p. varied from 125° to 140° according to the rate of distillation. (Cetyl alcohol does not " wet " glass, and the mercury thread of the thermometer must be outside the column.) The f. p.'s of the first fractions were always much lower than those of the other fractions, showing the greater effect of the lower alcohols than of octadecyl alcohol on the f. p. of cetyl alcohol. In both the sixth and the seventh distillations the main fractions froze at 49·27° (m. p. capillary tube 50°). Fractions melting above 48·6° (90% cetyl alcohol) were easily recrystallised from methyl alcohol, the solid separating in a crystalline form instead of as a soft curd, and the f. p. was raised to 49·27°, unchanged by recrystallisation from benzene.

Ethyl palmitate (m. p. 24·18°), when reduced with sodium and alcohol, the reaction product being distilled with superheated steam, gave cetyl alcohol of constant f. p. 49·27°. Even with the purest alcohol, the rise to the maximum f. p. is very slow above 49·22°.

In the literature values from f. p. 46·30° to m. p. (capillary tube) 51° are found. Krafft (*Ber.*, 1883, **16**, 1721) gives m. p. 49·5°; Scheuble and Loebl (*Monatsh.*, 1904, **25**, 346) 49·3° (sharp); Adam (*loc. cit.*) 50°.

The method recommended for purification of commercial cetyl alcohol is therefore distillation (at 1—15 mm.) until the main fraction freezes at 48·6° (90%), followed by crystallisation from methyl alcohol.

Stearic acid. Kahlbaum's acid (f. p. 67·8°, 20 g.) crystallised seven times from 95% alcohol gave 5 g. of acid (f. p. 69·30°), and this after three crystallisations from benzene had constant f. p. and m. p. 69·41° (m. p. capillary tube 70·5°). Other specimens of stearic acid were purified similarly to products of identical f. p. (De Visser, *loc. cit.*, gives m. p. 69·320°; Schiff, *Annalen*, 1883, **223**, 264, 69·4—69·5°; Dubowitz, *Chem.-Ztg.*, 1930, **54**, 814, 69·7°.)

Ethyl stearate. Stearic acid (f. p. 69·41°) yielded ethyl stearate of f. p. 30·92°, unchanged by crystallisation from ethyl alcohol or ligroin. It crystallises in large transparent plates like those of ethyl palmitate, and if rubbed with the thermometer they change slowly to fine crystals of m. p. 33·4°. On standing, the clear solid of m. p. 30·9° becomes opaque, changing to the higher-melting form, although with impure specimens the change may take some hours. This form will grow slowly if the liquid is seeded and kept at 32—33° ; it seems to be deposited directly from alcoholic solutions. In capillary tubes, the two forms of crystal melt at 32·5° and 34° respectively (Erdmann and Bedford, *Ber.*, 1909, **42**, 1332, give 33·7°. As with ethyl palmitate, the lower-melting form is not mentioned in the literature).

Commercial "purified" stearic acid (m. p. 53—56°) was converted to ethyl stearate (m. p. 23·2°), which was fractionated (at 1 mm.) until the main fraction froze at 28·6°, and then crystallised from alcohol containing 0·3% of sulphuric acid. (In the absence of acid, solutions of impure ester deposit a soft curd and are difficult to filter.) Crystallisation from alcohol or ligroin gave a final product of f. p. 30·92°, and higher m. p. 33·4°, but during the purification of five fractions the f. p. always passed through a maximum at 31·05° (higher m. p. 33·2°). Material of f. p. 31·05° was precipitated from the mother-liquor as a soft curd changing to hard crystals in a minute or two, and further purification gave products which immediately deposited crystals from alcoholic solution. The ester was contaminated apparently with some substance with which it could form solid solutions exhibiting a maximum m. p.

Octadecyl alcohol. Ethyl stearate (f. p. 30·92°, 18 g.) on reduction * (sodium 9 g., ethyl alcohol 80 c.c., dried with calcium) gave 9 g. of the alcohol (60% yield). Distilled with superheated steam and dried, the substance froze at 57·84°. Crystallisation once from methyl alcohol or twice from benzene raised the f. p. to 57·95° (m. p. 58·0° ; capillary tube 58·5°).

Stearic acid (f. p. 67·8°) was esterified, and the product (distilled at 10 mm. without fractionation) was reduced in quantities of 50 g. (yields 32 g. and 34 g., *i.e.*, 74% and 79%, of crude alcohol, f. p. 57·3° and 57·4° respectively). Crystallised four times from methyl alcohol and then four times from benzene, the substance froze at 57·93° (Levene, West, and van der Scheer, *J. Biol. Chem.*, 1914, **30**, 521, give m. p. 58·5°).

Stearic acid (f. p. 67·8°) was esterified with *n*-butyl alcohol (b. p. 116·4—117·8°/754 mm.), and the product (b. p. 180—185°/1 mm.) froze at 25·9°. Recrystallised once from ether, it had f. p. 26·3° and m. p. (capillary tube) 27°, but was not further purified. Only

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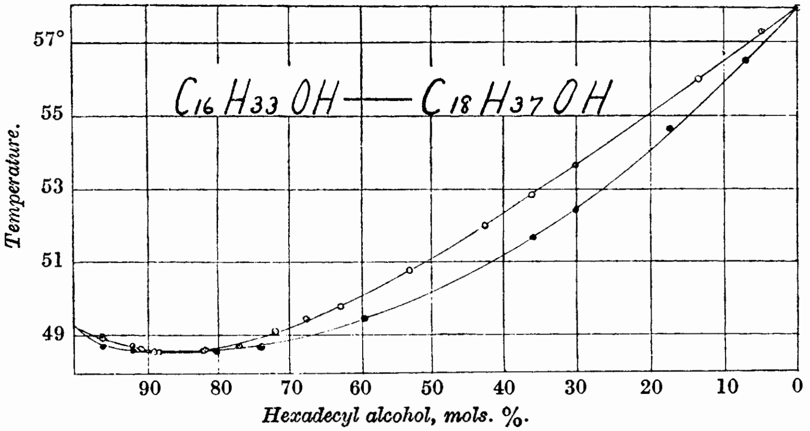
* The author is indebted to Mrs. G. M. Robinson, M.Sc., for advice on the reduction of esters.

one crystalline form of this ester was observed. (Vorländer and Selke, *Z. physikal. Chem.*, 1927, **129,** 452, give m. p. 28°.) Reduction of this crude ester by sodium and ethyl alcohol gave 32 g. (yield, 80%) of octadecyl alcohol, so this alternative method offers no advantage.

Mixtures of Ethyl Palmitate and Ethyl Stearate.—The mixtures crystallised rapidly in large transparent plates, but on standing a few hours mixtures near the extreme compositions changed so that the m. p. became much higher than the original f. p. These new m. p.'s corresponded to the higher m. p.'s of the esters themselves, and lay on curves forming part of a new system which could not be completely realised.

FIG. 2.



Points on the solidus curve (see Fig. 1) could be obtained with an accuracy of only 0·1—0·2°. The liquidus curve, if the composition is plotted as per cent. by *weight*, is almost a straight line.

Stearate, mols. %.	F. p.	Higher m. p.	Stearate, mols. %.	F. p.	Higher m. p.
100·0	30·92°	33·4°	29·7	23·1°	—
99·6	30·87	—	18·95	21·71	—
98·3	30·72	33·32	7·8	20·27	—
94·6	30·36	32·90	4·65	19·87	23·47°
90·0	30·00	32·32	2·16	19·60	23·77
79·0	28·83	30·81	1·05	19·47	23·97
67·5	27·67	29·13	0·83	19·41	24·02
47·9	25·37	—	0·00	19·40	24·17
40·5	24·50	—			

Solidus Curve.

Ethyl stearate, % ...	92·3	79·0	58·5	40·5	29·7	4·65
Temp.	29·5°	27·5°	24·75°	22·3°	21·5°	19·55°

Mixtures of Hexadecyl and Octadecyl Alcohols.—In order to obtain consistent values for the f. p.'s of mixtures of these alcohols, the supercooling of the melt should not exceed 0·1° and the outer bath should be about 0·5° below that of the melt. With only slight precipitation of solid, constant f. p. values are obtained, which are within 0·03° of the m. p. (obtained by raising the temperature of the bath 2° above the f. p.). On the cetyl alcohol side of the curve the initial values of the f. p. may be as much as 0·2° below the final. The data are plotted in Fig. 2.

Liquidus curve.

$C_{16}H_{33}\cdot OH$, mols. %	100	96·3	96·0	93·6	91·2	88·7	87·35	81·95	81·75	77·1	72·2	67·95	63·3	53·5	43·2	36·5	30·6	13·55	4·7	0·0
Temp.	49·27°	48·87°	48·98°	48·71°	48·64°	48·57°	48·55°	48·59°	48·63°	48·72°	49·12°	49·45°	49·8°	50·79°	51·98°	52·86°	53·63°	56·01°	57·36°	57·95°

Solidus curve.

$C_{16}H_{33}\cdot OH$, mols. %	96·3	93·6	80·3	74·1	60·0	36·5	30·6	17·5	7·0
Temp.	48·82°	48·65°	48·55°	48·7°	49·5°	51·65°	52·4°	54·65°	56·5°

Part II, to be published shortly, will deal with cetyl and octadecyl iodides, and with hexadecane and octadecane.

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THE DYSON PERRINS LABORATORY,
OXFORD.

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