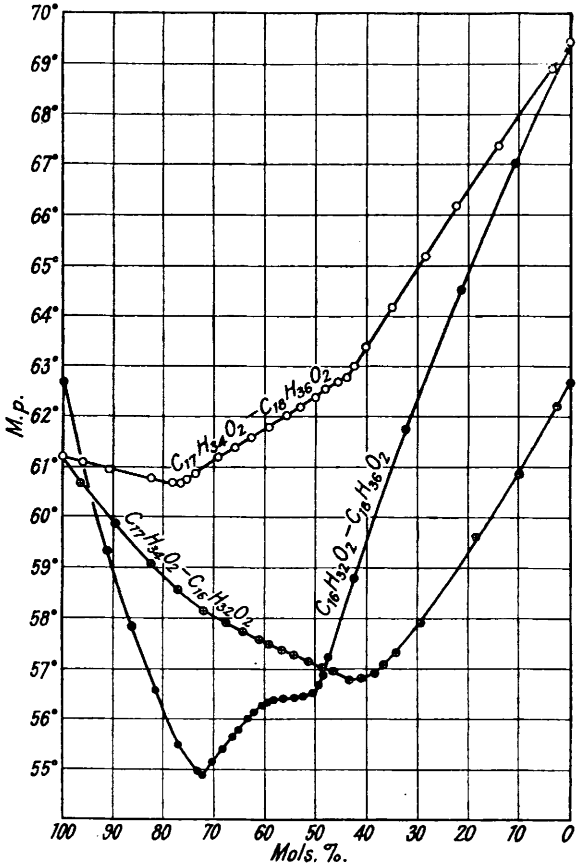
142. *Higher Aliphatic Compounds. Part VI. The Existence of Compounds in Binary Systems from Palmitic, Margaric, Stearic, Tricosanoic, and Tetracosanoic Acids.*

By J. C. Smith.

Several binary systems formed by even-numbered fatty acids have been investigated, and in each case there has been evidence of a molecular compound or of a " crystal compound " involving one molecule of each acid. The clearest case is that of palmitic and stearic acids (see fig.), although de Visser (*Rec. trav. chim.*, 1898, **17**, 182) did not recognise the significance of these results. Other examples of compound formation between " even " acids are given by Morgan and Bowen (*J. Soc. Chem. Ind.*, 1924, **43**, 346T), Bhatt and Watson (*J. Indian Inst. Sci.*, 1930, **13**, *A*, 141), and Piper, Chibnall, and Williams (*Biochem. J.*, 1934, **28**, 2182). Shriner, Fulton, and Burks (*J. Amer. Chem. Soc.*, 1933, **55**, 1494),



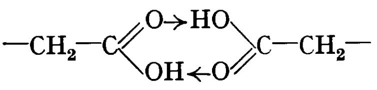
who investigated the systems of margaric acid with palmitic and with stearic acid, concluded that in " even–odd " systems no compounds were formed.

It seemed unlikely that the covalency forces would differ sufficiently to prevent compound formation between " odd " and " even " acids; nor would the dimensions of the respective crystal cells differ as much as in the pairs of " even " acids. Similarly, the m. p. of an " odd–even " compound should not be exceptionally low, and the compound should form solid solutions with each of the acids.

In the system of " odd–even " acids, tricosanoic acid–tetracosanoic acid (Chibnall, Piper, and Williams, *Biochem. J.*, 1936, **30**, 100; Ashton, Robinson, and Smith, this vol., p. 283), a curve can be drawn almost through the points to make a simple Type III system of solid solutions; but close inspection shows that the small but definite change in direction near the middle of the system is just what would occur if a compound was formed. Owing to lack of materials it was impossible to investigate the system further, and moreover, it was thought that more decisive evidence would be obtained from a study of acids of lower molecular weight.

The materials used by Shriner, Fulton, and Burks melted 1—2° below the accepted values, and these depressions may represent several units % of impurity. Actually, the effect of these impurities has been to smooth out and almost to obliterate the significant changes in the curves. In a similar way, Efremov (*Ann. Inst. Polyt. Ural*, 1927, **6**, 155), by using impure palmitic and stearic acids, completely missed the inflections characteristic of the " even–even " system. The systems formed by *pure* margaric acid show compound formation, the double molecules of palmitic acid (P_1–P_1), margaric acid (M_1–M_1), and stearic acid (S_1–S_1) giving place in mixtures to (M_1–P_1) and (M_1–S_1) " compounds." But the shape of the liquidus curves indicates that there may also be (M_3–P_1), (M_3–S_1), and (M_1–S_3) " compounds."

The view usually accepted (Sidgwick, *Ann. Reports*, 1933, **30**, 115) of the mode of association of carboxylic acids in the liquid state allows of the linking of only two molecules (see inset). A regular arrangement in the *crystal* of units of (M_1–M_1) and (M_1–S_1), perhaps alternate layers of these units, might be called for by the crystal symmetry, and the breaking up of this pattern might cause the liquidus curve to have a shape indicating apparent (M_3–S_1) units.



EXPERIMENTAL.

Purification of Materials.—Palmitic acid. The specimen described in Part I (J., 1931, 802) had f. p. and m. p. 62·67° ± 0·05° (m. p. in a capillary tube, 63·5°), and a new preparation gave the same values; de Visser (*loc. cit.*) gives m. p. 62·62° (cf. Francis and Collins, this vol., p. 138).

Stearic acid. Purified as in Part I, the substance had f. p. and m. p. 69·42° ± 0·05° (m. p., capillary tube, 70·5°); de Visser (*loc. cit.*) gives m. p. 69·32°.

Margaric acid. The specimen described in Part IV (J., 1933, 636) when tested with the thermometer used above had f. p. 61·17°, m. p. 61·19° ± 0·05° (m. p., capillary tube, 61·5—62°), and new specimens gave the same values. Garner and King (J., 1929, 1860) give f. p. 60·81°.

Measurement of Temperatures.—Anschütz thermometers were used to avoid correction for exposed stem. Thermometers used in this type of work need frequent standardisation, as heating above the range may cause a permanent expansion of the bulb and consequent low readings. There are also day-to-day variations of 0·01—0·02°.

Mixtures of Palmitic and Margaric Acids.—These all crystallised with very little supercooling; mixtures containing 40—70% of margaric acid gave better-defined crystals than were obtained from compositions just outside these limits. The m. p.'s (liquidus points) were taken with very slow heating of the melt, and are not more than 0·02° above the true liquidus points. Solidus points were not determined, but cooling curves for several of the mixtures showed that the whole process of solidification was completed within 0·5—1·0°. F. p.'s where determined were within 0·03° of the m. p.'s.

Mixtures of Margaric and Stearic Acids.—For mixtures containing 3—40% of margaric acid, varying m. p.'s were obtained unless the temperature of the bath was kept within 1° of that of the melt; in the rest of the system the behaviour was normal. Cooling curves failed to show a discontinuity or second arrest such as that which indicated the non-congruent m. p. of the compound formed from hexadecyl and octadecyl iodide (Part II, J., 1932, 740).

Palmitic Acid–Stearic Acid.—The curve in the figure is drawn from de Visser's data, by conversion of weight % into molecules %.

Tetracosanoic Acid.—A re-examination of the figures previously given (this vol., p. 285) showed that for the pure acid the m. p. had not been fully corrected, and that it should be 83·87° ± 0·05° (m. p. in a capillary tube 84—84·5°). For the mixtures with tricosanoic acid the values are as recorded.

Margaric–palmitic acid mixtures.

$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.
100·0	61·19°	72·1	58·11°	56·6	57·35°	43·5	56·76°	29·45	57·89°
96·5	60·67	67·75	57·89	54·3	57·25	41·2	56·80	18·7	59·59
89·6	59·85	64·2	57·70	51·5	57·12	38·55	56·89	9·9	60·84
82·35	59·06	61·1	57·56	48·9	57·00	36·8	57·06	2·5	62·18
77·1	58·54	59·3	57·47	46·7	56·93	34·2	57·31	0·0	62·67

Margaric–stearic acid mixtures.

$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.
100·0	61·19°	75·5	60·72°	59·3	61·77°	45·7	62·68°	28·5	65·16°
96·0	61·08	73·7	60·83	55·95	62·00	44·0	62·76	22·5	66·16
90·85	60·93	69·15	61·17	53·1	62·17	42·8	62·97	14·05	67·44
82·6	60·76	66·0	61·36	50·05	62·36	40·2	62·36	3·65	68·87
78·3	60·67	62·85	61·56	48·15	62·51	35·1	64·15	0·0	69·42
76·85	60·66								

The author's thanks are due to Miss P. C. Carey for the preparation of some of the margaric acid.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

[*Received, March* 19*th*, 1936.]