the molecular size. Semiquinoids are radicals in which one electron is shared by two atoms which possess each a septet of electrons, alternately supplemented to an octet by the odd electron. Several cases are made accessible to a potentiometric study by the application of an organic solvent, acetic acid. Stable and titrable semiquinoids could be demonstrated in the following classes of organic substances: the alkylated diamines, the phenylated diamines, phenazine and many of its derivatives except those containing an amino group, and γ,γ'-dipyridyl and the quaternary ammonium base derived from it.

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The Ternary System: Palmitic, Margaric and Stearic Acids

BY R. L. SHRINER, J. M. FULTON AND D. BURKS, JR.

The occurrence of palmitic and stearic acids as constituents of many oils, fats and waxes is well established. Margaric acid, the intermediate C_{17} acid, has been reported in numerous natural products[1] but many investigators have denied that this odd carbon acid exists in nature.[2]

The difficulty in establishing the presence of margaric acid in mixtures of fatty acids arises from the fact that the freezing point curves for palmitic and stearic acids indicate compound formation.[3] This compound of approximately equimolecular amounts of palmitic and stearic acids melts at nearly the same temperature as margaric acid. Moreover, the equimolecular mixture of palmitic and stearic acids is stated not to be separable by fractional crystallization.[4] Even the status of margaric acid prepared by some synthetic methods has been questioned. This is of importance because of the proposed use of the synthetic glyceryl trimargarate (Intarvin) as a food for diabetics.

The purpose of the present investigation was to make a complete study of the ternary system composed of mixtures of palmitic, margaric and stearic acids. Such a study would not only indicate the possible compounds formed between these acids but also show the effect of the addition of margaric acid to the compound of palmitic and stearic acids. Com-

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(1) A review to 1912 is given by Bömer and Limprich, *Z. Untersuch. Nahr. Genus.*, **23**, 641 (1912); Hébert, *Bull. soc. chim.*, [IV] **11**, 612 (1912); [IV] **13**, 1039 (1913); Klimont, Meisl and Mayer. *Monatsh.*, **35**, 1115 (1914); **36**, 281 (1915); Jacobson and Holmes, THIS JOURNAL, **38**, 485 (1916); Lipp and Kovács, *J. prakt. Chem.*, **99**, 243 (1919); Lipp and Casimer, *ibid.*, **99**, 256 (1919); Dunbar and Brunneweis, THIS JOURNAL, **42**, 658 (1920); Trillet, *Ann. Physik*, **6**, 1 (1925); Sekito, *Z. physiol. Chem.*, **199**, 225 (1931).

(2) Heintz, *Pogg. Ann.*, **84**, 238 (1851); **87**, 21 (1852); **87**, 553 (1852); **102**, 257 (1857); Heiduschka and Felser, *Z. Untersuch. Nahr. Genus.*, **38**, 241 (1919); Heiduschka and Luft, *Arch. Pharm.*, **257**, 33 (1919); Holde, *Ber.*, **34**, 2402 (1901); **35**, 4306 (1902); **38**, 1247 (1905).

(3) De Visser, *Rec. trav. chim.*, **17**, 182 (1898).

(4) De Visser, *ibid.*, **17**, 346 (1898); Heintz, *Pogg. Ann.*, **102**, 257 (1857)

pound formation has been reported for mixtures of *n*-eicosanoic and stearic,[5] lignoceric and stearic, and lignoceric and palmitic acids,[6] but in all these cases pairs of acids containing an even number of carbon atoms have been involved. No information is available on the behavior of mixtures of higher fatty acids with odd and even numbers of carbon atoms other than occasional mixed melting points.

Experimental

Palmitic Acid.—One hundred grams of crude bayberry wax was placed in a three-liter round-bottomed flask. To this was added two liters of ethyl alcohol and 30 g. of sodium hydroxide dissolved in 50 cc. of water. The mixture was refluxed vigorously for two hours. Alcohol was distilled until foaming interfered. The contents of the flask were then placed in a porcelain evaporating dish and evaporated to dryness on a steam-bath.

The sodium salt was powdered and washed with two 800-cc. portions of ether. The salt was then dissolved in six liters of hot water and the solution filtered. The hot solution was acidified with sulfuric acid. On cooling the acid solidified and was removed. The crude cake was melted and washed with 500 cc. of 2% warm sodium bicarbonate solution. The solid cake obtained on cooling was recrystallized from 400 cc. of acetone with the aid of norite. The first crop of material weighed 70 g. and melted at 55°. This material was then recrystallized from acetone six times, after which no further change in melting point or neutral equivalent took place. Colorless crystals were obtained, m. p. (capillary tube) 62.2–62.4°. A determination of the neutral equivalent gave the value 256.0; calcd. for $C_{16}H_{32}O_2$: 256.2.

Margaric Acid.—This acid has been prepared by the oxidation of diheptadecyl ketone produced by the distillation of barium stearate.[7] This method obviously yields a mixture of margaric and stearic acids. Le Sueur[8] oxidized heptadecyl aldehyde obtained from α-hydroxystearic acid. Margaric acid may also be obtained from the latter by direct oxidation[9] or by heating silver stearate with iodine and fusion of the heptadecyl alcohol with alkali.[10]

An attempt was made to prepare margaric acid by treating cetylmagnesium bromide with carbon dioxide.[11] The product obtained by this procedure melted at 59–60° and consisted of beautiful lustrous plates. Examination showed, however, that this material was not pure margaric acid at all but contained over 41% dicetyl, $C_{32}H_{66}$, and considerable cetyl alcohol. Treatment of this mixture with alkalies and extraction of the solution with ether or benzene failed to remove all the impurities because of the soapy nature of the solutions. Margaric acid having the correct neutral equivalent and melting point could not be obtained from this mixture.

In order to obtain margaric acid of unquestionable purity it was synthesized by the following series of reactions: cetyl alcohol $\longrightarrow$ cetyl bromide $\longrightarrow$ cetyl cyanide $\longrightarrow$ margaric acid. This method has been used before[12] and yields margaric acid which cannot be contaminated with palmitic or stearic acids since each of the intermediates may be carefully purified.

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(5) Morgan and Bowen, *J. Soc. Chem. Ind.*, **43**, 346 (1924).

(6) Meyer, Brod and Soyka, *Monatsh.*, **34**, 1127 (1913); Meyer and Beer, *ibid.*, **34**, 1202 (1913).

(7) (a) Krafft, *Ber.*, **12**, 1668 (1879); **15**, 1687 (1882); (b) Meyer and Beer, *Monatsh.*, **33**, 311 (1912).

(8) Le Sueur, *J. Chem. Soc.*, **85**, 827 (1904); **87**, 1888 (1905).

(9) Levene and West, *J. Biol. Chem.*, **16**, 475 (1913).

(10) Heiduschka and Ripper, *Ber.*, **56**, 1736 (1923).

(11) Ruttan, *Intern. Congr. App. Chem. Appendix*, **25**, 431 (1912).

(12) Heintz, Ref. 2; Köhler, *Jahresb.*, **9**, 579 (1856); Becker, *Ann.*, **102**, 209 (1857); v. Braun and Sobecki, *Ber.*, **44**, 1464 (1911); Holde, Ref. 2; Levene and Taylor, *J. Biol. Chem.*, **59**, 905 (1924).

Preparation of Cetyl Bromide.—One hundred and ninety grams of cetyl alcohol was placed in a 3-liter, round-bottomed flask. To this was added 350 g. of hydrobromic–sulfuric acid mixture made by passing sulfur dioxide through a mixture of 165 g. of bromine and 190 g. of cracked ice. Fifty-five grams of concentrated sulfuric acid was added to the above mixture. The mixture was then refluxed as vigorously as possible for twelve to fifteen hours.

The reaction mixture was cooled and the layers separated. The top layer was dissolved in ether and washed with water five times. The ether solution of cetyl bromide was dried with calcium chloride and the ether distilled. The oil remaining was distilled *in vacuo* and the fraction which boiled from 150–190° (2–3 mm.) was collected.

Refractionation gave pure cetyl bromide boiling at 165–170° (2–3 mm.), yield 160 g., 54% of the theoretical.

Preparation of Cetyl Cyanide.—A mixture of 152 g. of cetyl bromide, 40 g. of potassium cyanide and 5 g. of potassium iodide in 1500 cc. of 95% ethyl alcohol was refluxed for fifty-five hours. The solution was diluted with 500 cc. of water and cooled. The cetyl cyanide was separated and washed with 250 cc. of cold 50% sulfuric acid, then with water and 2% sodium bicarbonate solution. Vacuum distillation gave 100 g. of material boiling from 170–180 at 2 mm. (80% of the theoretical). The crude distillate was dissolved in warm acetone and the solution cooled in ice. Pure colorless crystals of cetyl cyanide separated;[13] m. p. 29.5–30°; d^{35}_{35} 0.8306; n^{35}_{D} 1.4451; yield 40% of the theoretical.

Hydrolysis of Cetyl Cyanide to Margaric Acid.—The cetyl cyanide (50 g.) was hydrolyzed by refluxing with 25 g. of sodium hydroxide in 95% alcohol for ten hours. About one-half the alcohol used for hydrolysis was distilled and the solution was cooled in an ice-salt bath. The sodium salt was filtered and washed with cold acetone and alcohol. The salt was suspended in hot water and acidified with 15% hydrochloric acid. The mixture was cooled and the acid separated as a solid cake. It was filtered and washed with a large volume of warm water.

The acid, when cooled, melted at 56–57.5°. Recrystallization from ligroin gave colorless crystals, m. p. 59.9–60° (capillary tube); yield 39 g. Determination of the neutral equivalent gave 272.6; calcd. for $C_{17}H_{34}O_2$, 270.2.

Stearic Acid.—Eastman stearic acid was found to be quite pure. It was recrystallized three times from acetone; m. p. 69.6–69.8° (capillary tube). The neutral equivalent was 285.0; calcd. for $C_{18}H_{36}O_2$, 284.3. Further recrystallization did not change these values.

Determination of Freezing Points.—The freezing points of the mixtures were determined in the apparatus similar to that used for determination of molecular weights by the freezing point method. In order to secure supercooling of the samples it was found necessary to maintain the outside constant temperature bath 3° below the freezing point of the particular sample used. The degree of supercooling of the sample permitted was 0.2–0.3°. If a greater degree of undercooling took place the sample was melted and the determination repeated. A Bureau of Standards thermometer calibrated to 0.1° was used which permitted estimations of the temperature to 0.05°. In each determination a plot of time *vs.* temperature was made and from this curve the true freezing point was obtained corrected for the degree of undercooling by extrapolation. All mixtures were made up determinately by weighing the amounts of each component The data obtained are summarized in Tables I–IV and represent true freezing points in which the solid and liquid phases are in equilibrium. Each freezing point given is the result of several readings, and the maximum error in reproduction of the freezing points was 0.05°. It should be noted that the freezing points in Tables I–IV represent definite temperatures and are quite different from the usual capillary melting

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(13) Phillips and Mumford, *J. Chem. Soc.*, 1732 (1931).

point ranges given in the above experimental part and which are ordinarily quoted as criteria of purity.

FREEZING POINTS OF BINARY MIXTURES

TABLE I

(Data plotted in Curve I)

Palmitic, mole	Stearic, mole	Freezing point, °C.
0.0	1.0	68.40
.1	0.9	66.25
.2	.8	63.65
.3	.7	61.20
.4	.6	58.15
.5	.5	55.90
.6	.4	55.40
.7	.3	54.00
.8	.2	54.85
.9	.1	57.50
1.0	.0	60.70
.47	.53	56.10
.75	.25	53.95
.725	.275	53.60

TABLE II

(Data plotted in Curve II)

Palmitic, mole	Margaric, mole	Freezing point, °C.
0.0	1.0	59.35
.1	0.9	58.10
.2	.8	56.95
.3	.7	56.35
.4	.6	55.85
.5	.5	55.50
.6	.4	55.30
.7	.3	55.95
.8	.2	57.15
.9	.1	58.80
1.0	.0	60.70

TABLE III

(Data plotted in Curve III)

Margaric, mole	Stearic, mole	Freezing point, °C.
0.0	1.0	68.40
.1	0.9	66.90
.2	.8	65.30
.3	.7	63.75
.4	.6	62.30
.5	.5	61.40
.6	.4	60.65
.7	.3	59.95
.8	.2	59.35
.9	.1	59.30
1.0	.0	59.35

TABLE IV

FREEZING POINTS OF TERNARY MIXTURES

Palmitic, mole	Margaric, mole	Stearic, mole	Freezing point, °C.
0.8	0.1	0.1	56.00
.6	.2	.2	53.65
.4	.3	.3	55.40
.2	.4	.4	58.00
.2	.2	.6	60.10
.3	.3	.4	56.60
.4	.4	.2	55.05
.2	.6	.2	56.95
.3	.4	.3	56.25
.4	.2	.4	55.70
.6	.1	.3	54.40
.7	.1	.2	53.50
.6	.3	.1	54.20
.4	.1	.5	56.00
.7	.2	.1	54.50

Discussion

Curve I, which shows the freezing points of mixtures of palmitic and stearic acids, possesses a transition point which clearly indicates the formation of a compound. Since the compound decomposes at or near its melting point it is difficult to state its exact composition but it appears to be very close to an equimolecular mixture of the two acids. The eutectic temperature for palmitic and stearic acids is 53.6°, at a composition of 0.725 mole of palmitic and 0.275 mole of stearic acid. This value was first obtained graphically and then checked experimentally. The time-temperature curves were carefully studied to see if a second halt or transition temperature could be observed but none could be found with certainty.

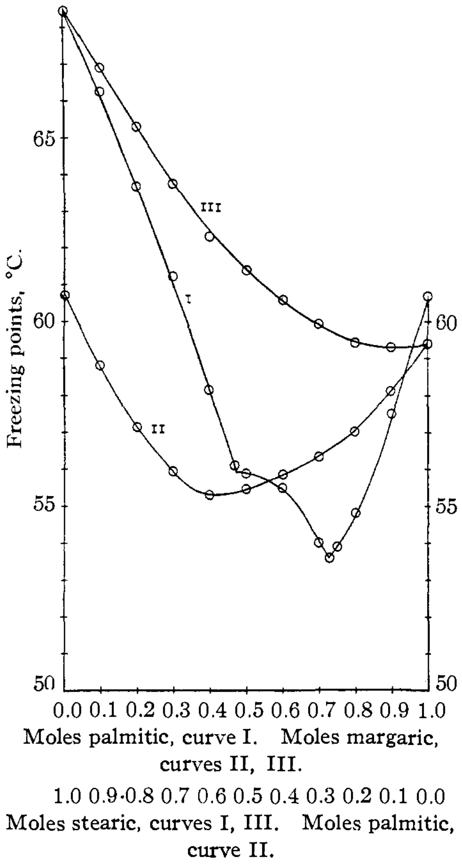

Fig. 1.

Curves II and III show no indication of compound formation between the C_{16} and C_{17} acids or C_{17} and C_{18} acids, respectively. No definite eutectics are formed and Curves II and III belong to the case in which continuous mixed crystals are formed in the solid phase.[14] This fact indicates that the separation of margaric acid from palmitic acid and especially from stearic acid would be very difficult.

The ternary mixtures were plotted according to the method of Roozeboom[15] and the three-dimensional space model constructed. This space model showed several interesting features. In the first place the ternary eutectic point was shifted very close to the palmitic acid axis and occurred at 0.68 mole palmitic, 0.16 mole margaric and 0.16 mole stearic acids, the freezing point being 52.9°. In the second place the convexity of the surface due to the compound between palmitic and stearic acids disappeared rapidly as margaric acid was added to this mixture.

Curve IV shows the freezing points of margaric acid with the equimolecular mixture of stearic and palmitic acids. It will be

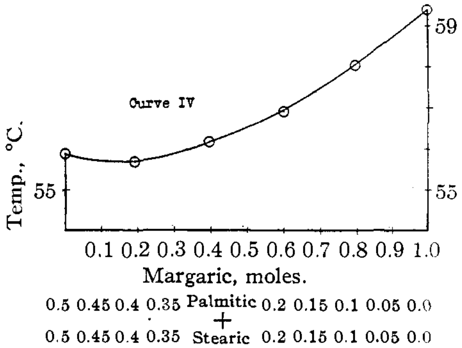

Fig. 2.

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(14) Findlay, "The Phase Rule," Longmans, Green and Co., New York, 1923, p. 148.

(15) Roozeboom, *Z. physik. Chem.*, **15**, 147 (1894).

noted that the drop in freezing point along this curve is not very great, the minimum occurring at 0.15 mole margaric, 0.425 mole stearic and palmitic acids and freezing at 55.75°. While this drop would be readily detected by accurate freezing point determinations, it would pass unnoticed in the ordinary mixed melting point determination.[7b] A mixture of 0.15 mole of margaric acid with 0.425 mole of stearic and 0.425 mole of palmitic was made up and its melting point determined by the ordinary capillary tube method. The observed melting point range was 57.6–60.6°. The relationship between the melting points[16] of the pure acids, compounds and mixtures is shown in Table V.

TABLE V

CAPILLARY MELTING POINTS

		M. p., °C. Softens at	Liquid at
1	Pure palmitic acid	62.2	62.4
2	Pure margaric acid	59.9	60.0
3	Pure stearic acid	69.6	69.8
4	Equimolecular mixture of palmitic and stearic acids	57.5	60.0
5	Remelt temperature of (4) (compound)	58.0	59.0
6	Compound (5) plus margaric acid	56.6	59.6
7	Palmitic (0.425), stearic (0.425), margaric (0.15)	57.6	60.6

The melting points given in the literature for margaric acid[1,2] vary from 54 to 60°. Hence it is easily seen how the equimolecular mixture of palmitic and stearic acids may be mistaken for margaric acid and why mixed melting points are not conclusive evidence for identification. The data in Table V also show how greatly these temperatures obtained by the ordinary capillary tube method differ from the true equilibrium temperatures recorded in Tables I–IV.

Summary

The freezing points for the ternary system of palmitic, margaric and stearic acids have been determined.

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(16) The melting points were determined in an open beaker fitted with a mechanical stirrer. The temperature was raised at the rate of 0.5° per minute.