[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, QUEEN'S UNIVERSITY]

OCCURRENCE OF STEARIC ACID IN BAYBERRY TALLOW (WAX)

A. F. McKAY

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Although Chevreul (1) reported the presence of stearic acid in bayberry tallow, later workers (2–4) have found no more than a trace. Sauer, Hain, and Boutwell (2) state that myristin and palmitin constitute 95% of the bayberry wax obtained from commercial supply houses. This wax is extracted from the berries of *Myrica cerifera*, a shrub common along the North American seacoast. Smith and Wade (3), using crystallization technique, were able to identify palmitin as a component of bayberry tallow, but concluded that stearic acid was not present. Jamieson, McKinney, and Gertler (4) examined the fat from the bayberries of *Myrica Mexicana* collected in Salvador, C.A. They reported that the fat had an iodine value of 1.2 (Hanus) and a saponification value of 216.7. It contained 1.3% oleic, 58% myristic, 35.6% palmitic, and a trace of stearic acid. Thus, in the use of a reputed sample of bayberry tallow for the preparation of myristic and palmitic acids, the author was surprised to find over 11% stearic acid present.

A sample of bayberry tallow was saponified and the acids liberated on acidification of the alkaline solution were methylated. The resulting mixture of methyl esters was fractionally distilled at a pressure of 30 mm. The methyl ester fractions obtained were further purified by crystallization from acetone. It proved more economical to purify the methyl esters before saponification to the fatty acids than to saponify the impure methyl ester fractions and then attempt to purify the free acids. The loss accompanying the purification by crystallization from acetone was much greater in the case of the fatty acids.

EXPERIMENTAL

Bayberry tallow. The bayberry tallow was supplied by Eimer and Amend, New York. It gave an iodine value of 0.00[1] and melted at 46–49°, soft 43° (capillary method).

Methyl esters of the fatty acids from bayberry tallow. Forty-five grams of KOH was dissolved in 250 cc. of hot 95% ethanol. To this solution, 102 g. of bayberry wax was added and heated at reflux temperature for twenty minutes. This alcoholic solution was diluted with 200 cc. of hot water and acidified with 200 cc. of 25% sulfuric acid. The aqueous layer was siphoned off and the fatty acid layer was washed with hot water (2 × 500 cc.). The fatty acid fraction was then dried by heating rapidly with stirring to 150°, yield 95 g.

The fatty acids were converted to their methyl esters in the usual manner (2) by refluxing with methanol containing 5% sulfuric acid (sp. gr. 1.84). The yield was almost quantitative.

Fractionation of methyl esters. A charge of 81.2 g. of the methyl esters was added to the still-pot and fractionated in a Todd (6) fractional distillation apparatus. The three-foot column (internal diameter 5 mm.) having the improved spiral wire packing was used. The distillation curve and operating conditions are given in Figure 1 and the fractions are described in Table I.

Purification of methyl ester fractions. The methyl myristate (m.p. 17.8°), methyl palmitate (m.p. 27.24°), and methyl stearate (m.p. 34.6°) fractions all melted a degree or two

[1] All iodine values were determined by the Rosemund-Kuhnhenn method (5).

below the corresponding pure esters. These melting points were easily raised by dissolving the methyl esters in acetone and cooling to 4°, when the crystalline methyl esters separated. The methyl myristate fraction (13.8 g.) on crystzllization from 30 cc. of acetone melted at 18.58°[2], yield 8.8 g. The methyl palmitate fraction (31.1 g.), after two crystallizations from

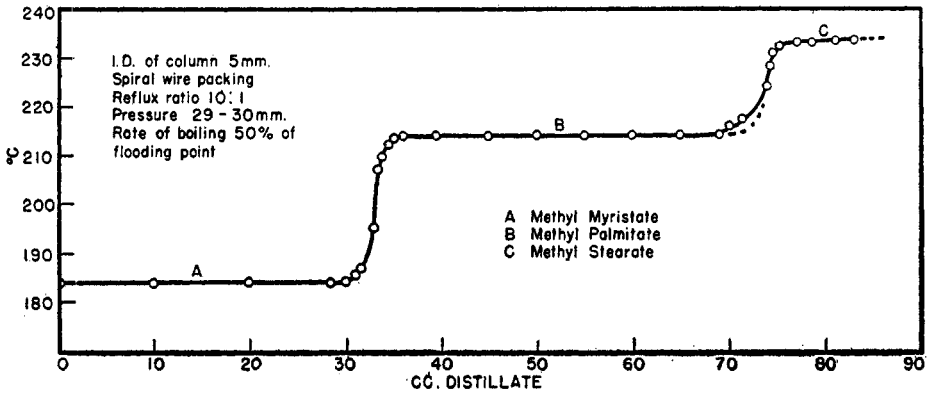

FIG. 1. FRACTIONATION OF METHYLATED FATTY ACIDS FROM BAYBERRY TALLOW

TABLE I

FRACTIONS FROM DISTILLATION OF METHYL ESTERS

NO.	WEIGHT IN GRAMS	PERCENT OF TOTAL	METHYL ESTER	M.P. °C	FINAL M.P. °C
1	24.8	30.6	Methyl myristate	17.8	18.58
2	2.8	3.4			
3	32.0	39.4	Methyl palmitate	27.2	29.60
4	4.2	5.2			
5	9.6	11.8	Methyl stearate	34.6	38.35
6	4.6	5.7	Residue		
Loss	3.2	3.9			

TABLE II

CONSTANTS OBTAINED FOR SATURATED ACIDS

FATTY ACID	M.P. °C	IODINE VALUE	ACID EQUIVALENT	
			found	calc'd
Myristic	54.9	0.0	228.3	228.4
Palmitic	63.0	0.0	256.3	256.4
Stearic	69.8	0.0	284.8	284.5

70-cc. portions of acetone, melted at 29.6° (melting point by capillary method 30–30.5°), yield 20 g. Similarly 11.8 g. of methyl stearate was crystallized three times from 32-cc. portions of acetone to give 5.6 g. of pure methyl stearate melting at 38.35°. (Melting point by capillary method 39–39.5°.)

[2] All melting points, unless otherwise stated, were obtained from melting point curves determined with the bulb of the thermometer and part of the stem immersed in the sample. The accuracy of the thermometer was ±0.05°C.

Myristic, palmitic, and stearic acids. The free acids were obtained from the methyl esters by dissolving them in excess 4% ethanolic KOH and allowing to stand at room temperature for twelve hours. The free acids were then recovered by acidification of the diluted alkaline solution and filtration. The yields were quantitative. The white crystalline products were washed thoroughly with water and crystallized once from acetone to give pure myristic, palmitic, and stearic acids. The constants obtained for these acids are recorded in Table II.

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SUMMARY

The presence of 11% stearic acid in bayberry tallow is reported along with the preparation of pure methyl myristate, methyl palmitate, methyl stearate, and the corresponding acids.

KINGSTON, CANADA

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