The n-Aliphatic Acids of Carnauba Wax
The Isolation of Tetracosanoic Acid

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THE HISTORY of the chemistry of the acids of carnauba wax has been reviewed in a previous paper (3). These acids are believed to include the even carbon n-aliphatic acids from C_{18} to C_{34} inclusive. Various workers have reported the isolation of carnaubic acid (C_{24}), cerotic acid (C_{26}), heptacosanoic acid (C_{27}), and "the ester anhydride of an hydroxy acid" (C_{21}). In the light of present knowledge, none of these compounds was pure. In 1941 Bowers and Uhl (1) reported the isolation of arachidic acid (C_{20}) which was 97 mol per cent pure.

In the course of a study of carnauba wax conducted in this laboratory, the ethyl esters of the wax acids were fractionally distilled in vacuo. The resulting fractions were re-crystallized to constant melting point and examined. Tetracosanoic acid was obtained from one of these fractions. Other fractions yielded mixtures of n-aliphatic acids ranging from C_{18} to C_{30}.

Altogether the above fractions comprised approximately 32% of the total wax acids. Of the remaining 68%, only 30% were distillable in our apparatus. Examination of these latter fractions and of the residue indicated that they contained esters of acids which were different in nature from the n-aliphatic acids. These substances have not yet been identified. Bowers and Uhl (1) found that less than 50% of the methyl esters of the wax acids were distillable under somewhat similar experimental conditions.

This paper describes the isolation of tetracosanoic acid and of mixtures containing other n-aliphatic acids.

Preparation of Crude Wax Acids

The potassium soaps of the wax acids were obtained as a residue from the exhaustive extraction of saponified carnauba wax (No. 3 Chalky Grade)[3] with ethyl ether (4). The soaps were melted over dilute HCl, stirred for five minutes, and the mixture was permitted to cool until the wax acids formed a solid layer. This layer was removed, re-melted over fresh dilute HCl, stirred as before, and again permitted to cool. Excess HCl was removed by melting the acids over distilled water, stirring for five minutes, and permitting the acids to solidify by cooling. Nine such washings were necessary to remove all of the mineral acid. The resulting crude wax acids (87 g., 43% of the original weight of the wax) had a melting point range of 76-83°C., and a mean molecular weight of 485. To supplement these acids, more were prepared in the same manner from the sodium soaps of No. I Yellow carnauba wax.[4] These soaps had been previously exhaustively extracted in the same manner as the potassium soaps above in order to remove wax alcohols. These acids (80 g.) had a melting point range of 76-78°C. and a mean molecular weight of 474.

Preparation of Ethyl Esters

The two portions of wax acids were combined and refluxed for 168 hours with 1,570 grams of absolute ethyl alcohol and 157 grams of concentrated sulfuric acid. The alcohol was then removed by distillation at 18 mm. pressure. The residual cake of esters was freed from sulfuric acid by melting and stirring it over 500 cc. portions of distilled water in the same manner as described above for the preparation of the crude wax acids. Five washings were required to remove the sulfuric acid.

The ethyl esters contained 3.6% of free fatty acids, calculated as the C_{30} acid, molecular weight 452. It had been found that the esters contained 5.3% of free fatty acids after 96 hours of reflux. Seventy-two hours additional refluxing, therefore, reduced the amount of free fatty acids by only 1.7%. The melting point range of the crude ethyl esters was 72.5-75.5°C.

Distillation of Ethyl Esters

The crude esters (144 g.) were fractionally distilled in the apparatus described previously (4), using a reflux ratio of 8 to 1. The results of the fractionation are shown in Table I.

TABLE I

Fractional Distillation of Ethyl Esters of Wax Acids.

Fraction No.	Gauge Pressure mm.	Boiling Range °C.	Weight g.	Melting Point °C.
1	0.27	135-137	1.1	liquid
2	0.25	137-153	0.8	34.3-34.5
3	0.23	153-157	6.4	39.5-40.0
4	0.26	157-172	2.5	45.0-46.0
5	0.26	172-177	10.5	51.8-52.5
6	0.26	177-189	2.1	54.7-54.9
7	0.27	189-191	6.2	54.7-55.1
8	0.28	191-200	3.8	55.0-56.0
9	0.30	200-207	2.5	57.2-58.0
10	0.30	207-210	3.1	59.2-59.7
11	0.35	208-214	7.4	62.6-63.1
Total			46.4	....
Percentage of Total Distilled			32.2	....

Fractions 3, 5, 7, and 10 were re-crystallized from petroleum ether (b.p. range 30-60° C.) until their melting points remained unchanged (See Table II).

Recovery of Acids from Ethyl Ester Fractions

One gram of each re-crystallized fraction was refluxed for two hours with 25 cc. of 0.5 N alcoholic KOH. The alcohol was boiled off and the residue was dissolved in warm glacial acetic acid. The acetic acid solution was cooled and diluted with distilled water whereupon the fatty acid separated. The solid acid was filtered off by suction, re-crystallized once from acetone at 4°C., and dried. The molecular weight was determined by neutralization equivalent. The melting points of the re-crystallized ethyl esters, and the melting points and mean molecular weights of the

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[4] Obtained through the courtesy of E. E. Dickey.

acids derived from them are shown, together with the values of Piper and co-workers (5), in Table II.

TABLE II

Summary of Re-crystallized Ethyl Esters and Derived Acids.

Fraction No.	Ester M. P.°C.	Acid			
		M. P.°C.	S. P.°C.*	R. M. P.°C.*	Mean Mol. Wt.
3	41.8-41.9	72.0-72.4	72.1	72.3-72.9	319.5
5	53.9-54.1	84.2-84.5	82.1	84.1-84.3	365.9
7	56.0-56.5	....	77.6	78.4-78.6	377.7
10	62.1-62.4	83.4-83.8	83.5	83.8-84.0	417.2

Published Values of Piper (5)

C content of acid	(*a*)			Theoretical Mol. Wt.
18	31.05	69.6	69.2	284.5
20	40.36	75.35	74.9	312.5
22	47.80	79.95	79.6	340.6
24	54.20	84.15	83.8	368.6
26	59.60	87.7	87.2	396.7
28	64.22	90.9	90.4	424.7

* S. P.—Solidification Point; R. M. P.—Re-melting Point.

Analysis of Fractions

Analysis of the fractions, using the melting point and solidification point data of Piper and co-workers (5) and of Schuette and co-workers (6), indicates that only Fraction 5 fits the pattern of constants. Considering only the melting point and molecular weight of the acid, this fraction contains more than 99% ethyl tetracosanoate. However, from interpolation of the solidification point of the acid and the melting point of the ethyl ester on their appropriate curves for binary mixtures, it is apparent that approximately 5% of this fraction consists of ethyl docosanoate. Thus the re-crystallized Fraction 5 contains ethyl tetracosanoate of a purity exceeding 95%, and the acid derived from it is the purest tetracosanoic acid as yet isolated from carnauba wax.

The remaining three fractions of Table II do not fit the pattern of constants either for pure compounds or for binary mixtures. On the basis of Chibnall's data (2) Fraction 3 is a ternary mixture consisting of approximately equal amounts of the ethyl esters of eicosanoic acid (C_{20}) and docosanoic acid (C_{22}) together with a small amount of octadecanoic acid (C_{18}). Similarly, Fraction 7 consists of a 2:2:1 mixture of the ethyl esters of tetracosanoic (C_{24}), hexacosanoic (C_{26}), and octacosanoic (C_{28}) acids.

This range of homologs is in agreement with Bowers and Uhl (1), who reported the presence of all even carbon n-aliphatic acids from C_{18} to C_{30}. Chibnall (2) had suggested that the acids ranged from C_{26} to C_{34}.

Discussion

"Carnaubic acid," reported by Stürcke (7) has long been presumed to be a constituent of carnauba wax. This acid (m.p. 72.5°C.) could not have been the C_{24} acid as he believed, but it may have been a mixture of the C_{18}, C_{20}, and C_{22} acids (cf. Fraction 3). Similarly, "cerotic acid," also reported by Stürcke (7), has long been presumed to be the chief acid of the wax. This acid (m.p. 79°C.) could not have been the C_{26} acid as he believed, but it may have been the C_{24} acid mixed with 20 to 40% of the C_{26} acid. In Table I above the C_{24} acid (cf. Fraction 5) was found to be the most abundant acid of the n-aliphatic series. Stürcke was correct, therefore, in believing that a C_{24} acid did occur in the wax although he did not actually isolate it as he had thought. He was also correct in believing that one member of the n-aliphatic acid series was predominant in the wax, but he was incorrect in believing that it was the C_{26} acid. Instead one acid fits both conditions: tetracosanoic acid is the most abundant of the n-aliphatic acids of carnauba wax.

Although the n-aliphatic acids are now generally agreed to range from C_{18} to C_{30} and perhaps higher, yet the nature of fully 50% of the acids in the wax is still unknown. The only clue which we have is the lactone or hydroxy acid (m.p. 103.5°C.) which Stürcke (7) reported more than 60 years ago. In view of the profound effect which they must exert in defining the chemical and physical properties of the wax, these unknown compounds merit investigation. With the development of research tools possessing greater powers of resolution than heretofore possible, such as the fractionating high vacuum still, the problem of their nature may soon be capable of solution.

Summary

1. The ethyl esters of the acids of carnauba wax were fractionally distilled at 0.3 mm.

2. Approximately 32% of the wax acids are n-aliphatic acids. Evidence was found which indicated the presence of all the even carbon acids from C_{18} to C_{30}.

3. The remaining 68% of the acids are unidentified, but the greater part of them are different in nature from n-aliphatic acids.

4. Tetracosanoic acid, the most abundant of its n-aliphatic acids, has been isolated from the wax for the first time in a degree of purity exceeding 95%.

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