An Historical Review of the Chemistry of Carnauba Wax

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An article of export from Brazil since 1845, carnauba wax today plays a significant role in the economy of that country. During 1941 the total exports were 11,766 metric tons (19) of which the United States took over 75 per cent. Carnauba wax ranks in sixth place among the exports of Brazil, and constitutes 20 to 30 per cent of the exports of the State of Ceará.

The wax is an exudate from the pores of the leaf and from the petiole of the carnauba palm tree, known botanically as *Copernicia cerifera.* It is obtained by a series of processes consisting of cutting the leaves from the tree, drying them, and beating them until the wax falls off as a fine powder. Depending upon the size and age of the leaf, several commercial grades of wax are thus procured.

From the older pendent leaf comes the "pahla" or straw wax which constitutes 70 per cent of the output. This powder, when melted in the absence of water, yields the "gordurosa" or waxy wax. When heated over water, it yields the "arenosa" or chalky wax. The "pahla" wax is darker in color and contains more foreign matter than the wax beaten from the smaller upright leaf. This latter grade, the "ohlo" or eye wax, is prepared in the same manner as the "gordurosa" type above, but is much lighter in color, and much more desirable from a commercial standpoint.

Carnauba wax finds a variety of industrial uses, including shoe, floor, and furniture polishes, phonograph records, electrical insulation, waterproofing compounds, sound film, carbon paper, artificial fruit, paints, and sealing material for dry cells.

In spite of the industrial importance of carnauba wax, there have been relatively few attempts to explore its fundamental nature. It is the purpose of this paper to review these attempts and to summarize the modern knowledge of the wax.

The first recorded experiments on this subject were made by Brande (3) in 1811. While his work is of little more than historical importance, he was the first to attempt distillation of the wax, a technique which was not used again for over a century. Upon destructive distillation the wax yielded an "acid liquor," volatile oil, and a "butyraceous oil," leaving a residue of charcoal and lime.

The first to claim the isolation of definite compounds from the wax was Maskelyne (11,12), who in 1869 reported melissyl alcohol and ceryl alcohol. Since his methods have served as a pattern for all subsequent work, they deserve a brief description.

The wax was saponified with alcoholic KOH, and the lead soaps of the wax acids were formed by adding lead acetate. The resulting mixture was dried, powdered, and extracted with ethyl alcohol. Thus, the wax was divided into two portions. One soluble in alcohol, contained the wax alcohols and other unsaponifiables. The other, insoluble in alcohol, contained the lead soaps from which the wax acids could be recovered.

Investigation of the alcohol soluble portion was carried out by recrystallization from ether. Two alcohols (m. p.'s 88° and 78°) were found. The former was characterized by elementary analyses of the alcohol, its halogen derivatives, its derived acid (m. p. 91°), and salts of this acid. On the basis of these data, Maskelyne concluded that the original compound was melissyl alcohol $C_{30}H_{61}OH$. The latter alcohol, on the basis of its elementary analysis, was characterized as ceryl alcohol, $C_{23}H_{47}OH$. Another substance (m. p. 105°) was also obtained during the fractionation. It was not identified, but the elementary analysis indicated the formula $C_{39}H_{82}O_3$. Maskelyne also showed that melissyl alcohol occurred free in the raw wax.

Fractional crystallization of the acid portion yielded several unidentified fractions ranging in melting point from 40° to 90.5°.

In 1868, Bérard (1) reported the isolation of cerotic acid (m. p. 77°), an unidentified mixture of acids (m. p. 75°), and an unidentified alcohol (m. p. 88°). Cerotic acid was characterized on the basis of its elementary analysis.

In 1876, von Pieverling (13) reported the isolation of melissyl alcohol and ceryl alcohol. By extraction of the wax with ethyl alcohol at 20-25° prior to saponification, a coumarin-like substance was obtained. After saponification, both the lead and barium soaps were prepared. Apparently, either soap worked equally well in the subsequent extraction with absolute ethyl ether. Fractional crystallization of the ether soluble portion yielded melissyl alcohol (m. p. 85°) which was characterized as $C_{30}H_{61}OH$ from its elementary analysis and the analyses of its iodide, chloride, amine, hydrosulfide, derived acid (m. p. 88.5°) and the lead and silver salts of this acid. Ceryl alcohol (m. p. 80°) was characterized as $C_{27}H_{55}OH$ on the basis of its elementary analysis.

The most ambitious study of carnauba wax as yet reported was that made by Stürcke (20) in 1884. He reported the following substances in the wax: (1) ceryl alcohol, (2) melissyl alcohol, (3) a di-hydroxy alcohol, (4) carnaubic acid, (5) cerotic acid, (6) the lactone of an hydroxy acid, and (7) an hydrocarbon.

To facilitate extraction after saponification (with NaOH), Stürcke washed the saponified wax with cold sodium chloride solution to remove the excess alkali before drying and extraction. As a result, after 160 hours of extraction with petroleum ether in a "Gantter'schen" apparatus, 55.4 per cent of the total wax mass was extracted. By fractional extraction, using extraction periods from 15 minutes to 10 hours, Stürcke obtained a total of 20 fractions which ranged in melting point from 81° to 99°. Reworking of these by combination and recrystallization reduced the twenty fractions to three.

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The first fraction yielded a compound (m. p. 59-59.5°) which was analyzed but not identified, and was believed to be heptacosane, $C_{27}H_{56}$. This fraction also yielded an alcohol (m. p. 76°). On the basis of its elementary analysis and the melting point of its derived acid (78.1°), it was characterized as ceryl alcohol, $C_{27}H_{55}OH$. This fraction comprised less than 2 per cent of the total weight of the wax.

The second fraction yielded an alcohol (m. p. 85.5°) which crystallized from petroleum ether in white, glistening plates. On the basis of its elementary analysis, and the analyses of its derived acid (m. p. 90-91°) and the lead and silver salts of the acid, the alcohol was characterized as melissyl alcohol, $C_{30}H_{61}OH$. It comprised 45 per cent of the total weight of the wax.

The third fraction yielded a finely crystalline powder (m. p. 103.5°) which elementary analysis indicated was $C_{24}H_{50}O_2$ or $C_{25}H_{52}O_2$. Oxidation of the compound yielded an acid (m. p. 102.5°). On the basis of the elementary analysis of the lead salt of this acid, and the amount of hydrogen evolved in the formation of the acid, Stürcke concluded that the original compound was $C_{23}H_{46}(CH_2OH)_2$. It comprised approximately 1 per cent of the total weight of the wax.

The wax acids were also subjected to fractional extraction followed by combining of fractions and exhaustive recrystallization. Three fractions were finally obtained.

The first fraction (m. p. 72.5°), on the basis of its elementary analysis and the analysis of its lead salt, was characterized as carnaubic acid, $C_{24}H_{48}O_2$.

The second fraction (m. p. 78.8°) was the principal acidic constituent of the wax. On the basis of its elementary analysis and the analysis of its lead salt, Stürcke characterized it as cerotic acid, $C_{27}H_{54}O_2$.

The acid nature of the third fraction (m. p. 103.5°) was "doubted until boiling of it with alcoholic KOH yielded a jelly." Elementary analysis of the regenerated acid indicated the formula $C_{21}H_{40}O_2$. Oxidation of this acid yielded another acid (m. p. 90°) and evolved 2 moles of hydrogen. Analysis of the lead salt of this latter acid indicated that it was $C_{19}H_{38}$-$(COOH)_2$. On the basis of this information and on its behaviour with alkalies and magnesium acetate, Stürcke concluded that the original compound was "the ester anhydride of an hydroxy acid," $C_{19}H_{38}$-$(COOH)(CH_2OH)$.

In 1919, Heiduschka and Garies (8) reported the isolation of melissyl and ceryl alcohols from the wax. Their treatment was the same as Stürcke's except that extraction of the saponified wax was carried out in a Soxhlet type extractor with petroleum ether. Fractional crystallization of the ether soluble portion yielded two alcohols (m. p.'s 76° and 87.5°). On the basis of its elementary analysis, the lower melting compound was characterized as ceryl alcohol, $C_{27}H_{55}OH$. On oxidation, the higher melting alcohol yielded an acid (m. p. 90°) with a mean molecular weight of 454.4 (theoretical for C_{30} saturated acid is 452.8). On the basis of this information and the elementary analyses of the alcohol, several of its esters, its derived acid and the lead salt of this acid, the authors characterized it as melissyl alcohol, $C_{30}H_{61}OH$.

In 1926, Gottfried and Ulzer (7) reported the isolation of melissyl alcohol, ceryl alcohol, and heptacosane from carnauba wax. Like von Pieverling, these workers made a preliminary extraction of the raw wax with ethyl alcohol at 20-25°, and, like him, they thus removed the plant pigments. Comparing the three different methods of using the lead soaps, the barium soaps, and the washed potassium soaps, according to Stürcke (20), for the extraction after saponification of the wax, they showed that the last method was far superior to the others. Thus, they were able to extract 46 per cent of the total wax mass in 14 hours with trichloroethylene in a Soxhlet extractor.

To isolate the various substances in the trichloroethylene extract, these workers used the method which Krafft (10) had used to separate hexadecanol and octadecanol. The wax alcohols were converted to their acetates and fractionally distilled at 10 mm. Three fractions were finally obtained after combining and redistilling the ten original fractions.

The first fraction yielded a substance (m. p. 59-59.5°) which was unchanged by refluxing with alcoholic KOH. On the basis of its melting point and elementary analysis, this compound was characterized as heptacosane, $C_{27}H_{56}$.

The second fraction yielded a substance (m. p. 64.5°) which on saponification yielded silvery glistening needles (m. p. 79°). On the basis of the melting point and elementary analyses of these two compounds, the latter was characterized as ceryl alcohol, $C_{26}H_{53}OH$.

The third fraction (m. p. 74°) was unchanged by recrystallization from a 1:5 mixture of trichloroethylene and ethyl alcohol, but on saponification, yielded a compound (m. p. 88°). On the basis of the melting points and elementary analyses of these two compounds, the latter was characterized as melissyl alcohol, $C_{30}H_{61}OH$. To confirm the unsatisfactory method of characterization on the basis of elementary analysis, Gottfried and Ulzer determined the saponification number of the third fraction. The average of several determinations corresponded to the theoretical value for the acetate of $C_{30}H_{61}OH$.

In a study of the n-fatty acids, Francis, Piper, and Malkin (5) prepared supposedly pure cerotic acid (m. p. 78°) from carnauba wax by a method similar to that used by previous workers. The acid was converted into its ethyl ester and fractionally distilled at 3 mm., yielding two fractions. One of these fractions was further separated into two fractions. Analysis of these on the basis of the melting points and long crystal spacings (15,17) of the free acids and ethyl esters showed that the supposed cerotic acid contained n-fatty acids ranging from C_{24} to C_{30}.

The wax alcohols (m. p. 86-87°) were converted to their acetates and fractionally distilled at 2.5 mm. Analyses of the resulting fractions, on the basis of the melting points and long crystal spacings of the derived acids and their ethyl esters, showed that the distillate contained alcohols ranging from C_{32} to C_{36}.

The whole problem of the identification of the high molecular weight alcohols and acids was extremely simplified by the work of Piper, Chibnall, and Williams (14), and Francis and Piper (6), who published the melting points and long crystal spacings of the even carbon acids and their ethyl esters, and the alcohols and their acetates from C_{26} to C_{36}. Moreover, they constructed cooling curves for binary mixtures of these compounds and data on ternary mixtures so that the composition of unknown simple mixtures could be estimated. On the basis of these data, Chibnall *et al.* (4) interpreted the melissyl alcohol of Heiduschka and Garies (8) as a mixture containing approximately 20 per cent C_{30}, 40 per cent C_{32}, and 40 per cent C_{34} alcohols, and the ceryl alcohol of Gottfried and Ulzer (7) as a mixture containing approximately 40 per cent C_{26}, 40 per cent C_{28}, and 20 per cent C_{30} alcohols. They likewise interpreted melissic acid (m. p. 90°, ethyl ester, m. p. 73°) as containing C_{30}, C_{32}, and C_{34} acids, and the cerotic acid of Stürcke (20) as containing C_{26} and C_{28} acids.

The most recent published work on the constituents of carnauba wax is that of Bowers and Uhl (2) who investigated the wax acids. Following saponification of the wax and extraction of the unsaponifiable portion, the acids were converted to the methyl esters and fractionally distilled at 0.01 to 0.04 mm. By recrystallization of the acids obtained from the ester fractions, a total of nine acid fractions was obtained. On the basis of the mean molecular weights and setting points of these fractions, using the method of Schuette and Vogel (18), Bowers and Uhl obtained evidence for the presence of all the even carbon n-fatty acids from C_{18} to C_{30}. The purest fraction (setting point 73.4°) contained 97 mol. per cent of the C_{20} acid.

A summary of the findings of all these workers is listed in Table I below:

TABLE I

Compounds Isolated From Carnauba Wax

Alcohols

Alcohol M.P.°C.	Derived Acid M.P.°C.	Composition	Worker
78	....	$C_{23}H_{47}OH$	Maskelyne (11, 12)
80	....	$C_{27}H_{55}OH$	von Pieverling (13)
76	78.1	$C_{27}H_{55}OH$	Stürcke (20)
76	....	$C_{27}H_{55}OH$	Heiduschka and Garies (8)
79	....	$C_{26}H_{53}OH$	Gottfried and Ulzer (7)
88	....	unidentified	Bérard (1)
88	91	$C_{30}H_{61}OH$	Maskelyne (11, 12)
85	88.5	$C_{30}H_{61}OH$	von Pieverling (13)
85.5	90-91	$C_{30}H_{61}OH$	Stürcke (20)
87.5	90	$C_{30}H_{61}OH$	Heiduschka and Garies (8)
88	....	$C_{30}H_{61}OH$	Gottfried and Ulzer (7)
87-88	92-93	C_{32} to C_{36}	Francis *et al.* (5)

Acids

Acid M.P.°C.	Composition	Worker
72.5	$C_{24}H_{48}O_2$	Stürcke (20)
73.4 (setting point)	$C_{20}H_{40}O_2$	Bowers and Uhl (2)
77	cerotic	Bérard (1)
79	$C_{27}H_{54}O_2$	Stürcke (20)
77-81	C_{24} to C_{30}	Francis *et al.* (5)

Miscellaneous Compounds

M.P.°C.	Composition	Worker
105	$C_{39}H_{82}O_3$	Maskelyne (12)
103.5	$C_{23}H_{46}(CH_2OH)_2$	Stürcke (20)
103.5	$C_{19}H_{38}(COOH)(CH_2OH)$	Stürcke (20)
59-59.5	hydrocarbon	Stürcke (20)
59-59.5	$C_{27}H_{56}$	Gottfried and Ulzer (7)

It is obvious that much disagreement exists among the above workers. This is not surprising considering their methods of isolation and criteria of purity. Except for the last three groups of workers, all the others depended entirely on fractional crystallization to achieve their separations. Work in this laboratory (9) has shown that this method is entirely inadequate to separate the high molecular weight alcohols.

Also, characterization of these compounds on the basis of their elementary analysis and melting point is subject to criticism. The very small differences in carbon and hydrogen content between the higher homologs—on the average 0.2 per cent for carbon and 0.01 per cent for hydrogen—renders the carbon, hydrogen analysis of little value for purposes of identification. Furthermore, these compounds readily form mixtures which fortuitously resemble pure compounds in melting point and in molecular weight. Because of these conditions the method of Chibnall and coworkers (4,14), mentioned earlier, is far more useful. In the case of a high molecular weight alcohol, the criteria they require for identification include (1) the melting point of the alcohol, (2) the melting point of its acetate, (3) the melting point of the acid derived from the alcohol, (4) the melting point of its ethyl ester, and (5) the long crystal spacings of these compounds, although in later papers they have not required the acetate constants. In the case of the high molecular weight acids, the criteria are the same except that there is no necessity for the melting point and spacings of the corresponding alcohol. From these physical constants it is possible to identify a high molecular alcohol or acid, or to estimate its composition if the unknown is a simple mixture of alcohols or of acids.

Pollard, Chibnall and Piper (16) state that because of the extremely large effect of melting point depression which is exerted on one acid by another, a mixture of high molecular weight alcohols, when oxidized, will yield a mixture of acids with a melting point only 2° to 3° above that of the original alcohol mixture. On the other hand, if the alcohol is pure, or nearly so, the melting point of the derived acid will be 6° to 8° above that of the alcohol. Inspection of Table I indicates that only the melissyl alcohols of Stürcke (20) and of Francis, Piper and Malkin (5) approach this specification. Among the acids, none approach the melting points of the acids (6) which they were alleged to be except the arachidic acid of Bowers and Uhl (2).

It is apparent, therefore, that none of the alcohols and only one of the acids which have been isolated from the wax were very pure compounds. Furthermore, except for heptacosane, the identity of which has been established by Gottfried and Ulzer (7), all the other compounds which were not normal aliphatic alcohols and acids, and which were isolated by Maskelyne (12) and Stürcke (20) are still unconfirmed.

The present knowledge of the constituents of carnauba wax, therefore, can be summarized as follows:

1. The wax is believed to consist for the most part of the esters of high molecular weight n-aliphatic primary alcohols and n-aliphatic acids. Some of the alcohols, and some of the acids also, occur in a free state in the raw wax. Other types of compounds, including hydrocarbons, pigments, and inorganic salts are present.

2. The alcohols allegedly isolated are ceryl alcohol (C_{26}) and melissyl alcohol (C_{30}). Other even carbon alcohols, ranging from C_{32} to C_{36}, have been inferred to be present. There may also be a di-hydroxy alcohol (C_{25}).

3. The acids are generally believed to include the even carbon members from C_{24} to C_{34}, and probably as low as C_{18}. Carnaubic acid (C_{24}), cerotic acid

(probably C_{26}), and "the ester anhydride of an hydroxy acid" (C_{21}) have allegedly been isolated. Arachidic acid (C_{20}) has been isolated in a purity of 97 mol. per cent.

4. In the light of present knowledge, only two compounds have been isolated in any reasonable degree of purity from carnauba wax. These compounds are heptacosane and arachidic acid.

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Foaming Properties of Soap Solutions

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Although a number of investigations on the foaming properties of soap solutions have been made (7), the results are difficult to produce and as Lascaray (6) points out are, in many cases, apparently contradictory. Few quantitative data on the stability of foams from soap and detergent solutions are available in the literature. This paper reports reproducible quantitative data obtained by two methods on the stability of foams from solutions of various soaps and detergents and on the effects of added substances, pH, and soap or detergent concentration on foam stability. Soaps and detergents are often appraised by the volume and stability of the suds produced, and the data may prove valuable in the development of new detergents and in the understanding of mechanisms of foam formation and decay.

The first of the two methods used involves measuring the rate of drainage of liquid from a foam produced in an arbitrary manner. This simple, rapid method, requiring little special apparatus, has been frequently used as a measure of foam stability (1,3,4, 13). The second method involves measuring the lifetime of a definite area of foam monolayer (single layer of bubbles). The latter is "foam time" method developed by Schutz (16) and McBain and Ross (reported by Ross, 14) and modified by ourselves for use with soap foams.

Experimental Methods

Foam drainage method. The foam drainage apparatus (Fig. 1) is made of Pyrex glass from a 2-liter flask, a 100-ml. graduated cylinder, and a 30-mm. sintered-glass Büchner funnel (Corning medium pore size). Preliminary experiments showed that the rate of drainage of solution from a soap foam varies with the method of producing the foam. For example, foams formed rapidly are drier and lose solution more rapidly than those formed more slowly. In order to obtain comparative results on different solutions, it is therefore necessary to adopt a standard procedure of producing the foam and measuring its rate of drainage. The following method was adopted for this investigation:

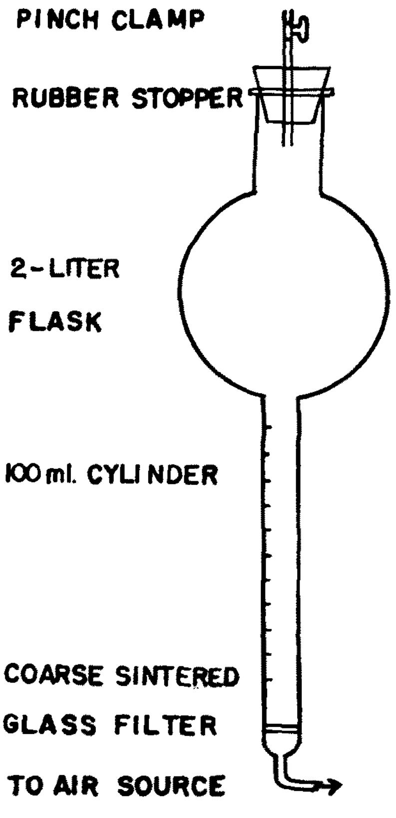

FIG. 1. Foam drainage apparatus.

All experiments were performed with the apparatus immersed in a water bath at a constant temperature of 25° C. The apparatus was filled with solution to the 70-ml. mark. Foam was produced by blowing air through the solution for exactly two minutes under a constant pressure of 6.0 cm. of mercury. This air had been passed through glass wool, soda lime,