The Structural Constituents of Carnauba Wax[1]

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Abstract

Type 1 yellow carnauba wax has been separated into its structural constituents. Analyses of these constituents by a variety of conventional techniques has shown the composition to be: hydrocarbon 0.3–1%, aliphatic esters 38–40%, monohydric alcohols 10–12%, ω-hydroxy aliphatic esters 12–14%, p-methoxycinnamic aliphatic diesters 5–7%, p-hydroxycinnamic aliphatic diesters 20–23%, an uncombined triterpene type diol 0.4% and uncombined acids and other unknown constituents 5–7%. Type 4 carnauba wax, the common wax of commerce, was found to be essentially the same as Type 1, with the exception that for Type 4, the cinnamic esters were highly polymerized and none of the uncombined triterpene diol could be isolated.

Introduction

The analysis of carnauba wax in nearly all reported work has been based upon examination of the products of alkaline hydrolysis. The analysts have recognized, in most instances, a loss of about 5%. This usually has been attributed to mechanical losses or in some instances to material described only as an intractable tar or polymeric resin acid.

Work by Vandenburg and Wilder has shown that this loss was brought about by the hydrolytic liberation of p-hydroxy and p-methoxycinnamic acids and/or polymers thereof (1). It was further revealed that these acids appeared to be part of a diester with a molecular weight in excess of 1000 which comprised about 30% of the whole wax.

The structure of this diester as well as that of the other previously unidentified compounds occurring naturally in carnauba wax have been determined.

Experimental Procedures

The thin layer chromatogram (TLC) of Type 1 carnauba wax (Fig. 1) and the various isolated and identified constituents, was developed by a modified procedure of Kaufman and Das (2). Most of the structural types were applied according to their approximate composition in the whole wax and then reapplied for the composite T.

Downing et al. have quantitatively established the chain length distribution of the various carnauba wax hydrolysis products (3). The tabulation of their results has been reproduced in this presentation (Table I) for the purpose of correlation and in an attempt to make this paper essentially complete.

Approximately 3 g of Type 1 carnauba wax (saponification value 81.5, acid value 11.3, ester value 70.2, hydroxyl value 37.0, iodine value 12, mp–85.2 C) was placed on a heated 8 × 2 in. column containing 160 g of 60–200 mesh silica gel. The column was then eluted, while monitoring by TLC, with warm heptane to give the hydrocarbons, 3% ethylene dichloride in heptane to give the aliphatic esters, 15% ethylene dichloride in heptane to give the uncombined alcohols, and 15–20% ethylene dichloride in heptane followed by 20–25% benzene in heptane to give the ω-hydroxy esters. At this point, the quantitative nature of the separation

became increasingly complex. The remaining highly polar materials were then eluted with 2–5% isopropanol in heptane.

The hydrocarbons (mp 48–58 C) were obtained in a yield of 1.08%. Though this yield was higher than the 0.3–0.5% normally expected, the IR curve was quite typical. The vapor phase chromatogram showing C_{27}, C_{29} and C_{31} as being predominant, was consistant with the results of Downing et al. (Table I).

Aliphatic esters (ester value 66.5, mp 83–85.3 C, average mol wt 844) were obtained in a yield of 38.8%. These esters yielded upon hydrolysis 45.3% monocarboxylic acids (acid value 145, average mol wt 390, mp 73–75 C) and 54.7% monohydric alcohols (hydroxyl value 120, average mol wt 470, mp 85–87 C).

Partitioning of the acids and alcohols by the method of Kartnig and Scholtz (4) gave six spots for the acids corresponding to C_{20}, C_{22}, C_{24}, C_{26}, C_{28} and C_{30}, with C_{24} being predominant. The alcohols produced three spots consistant with C_{30}, C_{32} and C_{34}, with C_{32} being predominant.
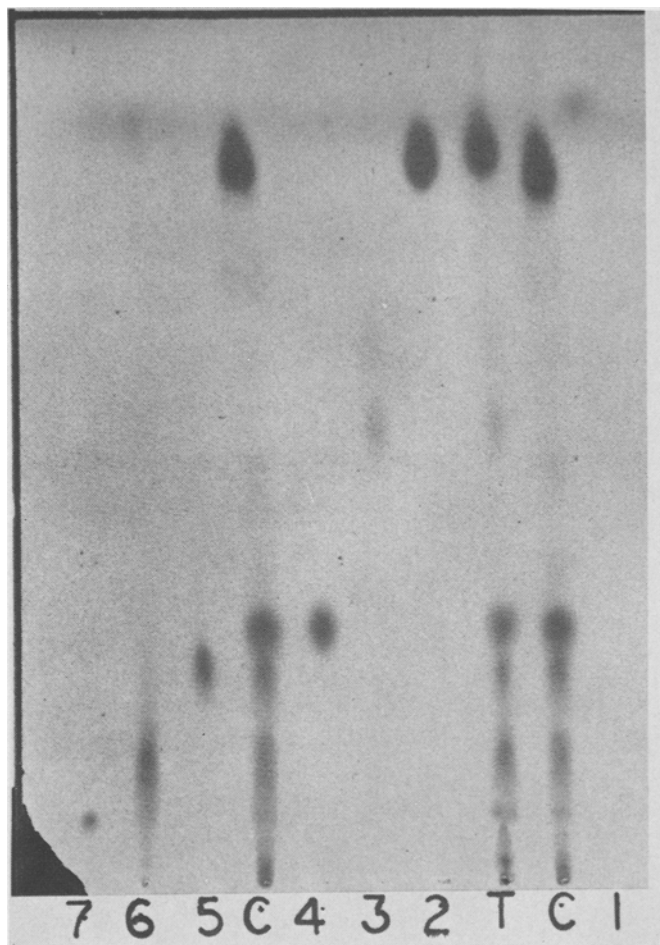

FIG. 1. Plate: Silica Gel G (0.25 mm). Developed: 1:1, 1,1,2-trichloroethane:chloroform at 42 C. Visualized: 5% phosphomolybdic acid in ethanol. (C) Type I yellow carnauba wax 100 μg, (1) hydrocarbons 2μg, (2) aliphatic esters 40 μg, (3) P-methoxycinnamic aliphatic diesters (semisynthetic) 5 μg, (4) uncombined monohydric alcohols 10 μg, (5) ω-hydroxy esters 10 μg, (6) p-hydroxycinnamic aliphatic diesters 20 μg, (7) triterpene type diols 2 μg. (T) Combination of fractions 1–7 in the same proportions shown for each individual component.

TABLE I

Hydrocarbons Derived from Carnauba Wax Fractions (wt %)[a]

Carbon No.	Natural alkanes	Alkanols	Alkane-diols	Alkanoic acids	Hydroxy-alkanoic acids
16	(<17)0.8	....	(<19)1.9	0.7	0.9
17	0.7	....	....	....	....
18	0.8	....	...	1.9	1.5
19	0.8	....	0.5	...	...
20	0.6	....	1.0	9.1	4.4
21	1.2	0.8	1.0	0.3	0.5
22	1.2	0.9	8.4	9.8	6.2
23	5.4	0.5	2.0	1.0	0.8
24	2.0	1.5	19.2	28.4	24.4
25	5.7	Trace	1.0	1.0	1.1
26	1.4	0.9	9.5	13.5	22.2
27	15.3	0.3	1.0	0.4	0.8
28	2.5	3.0	12.4	21.2	30.9
29	25.0	Trace	1.2	0.3	0.3
30	1.3	13.0	12.3	7.6	4.4
31	28.9	Trace	Trace	....	Trace
32	0.6	62.8	17.8	3.1	1.6
33	5.8	Trace	Trace	...	....
34	....	16.3	10.8	1.7	Trace
35 and 36	Absent	Absent	Absent	Absent	Absent

[a] Reproduced from Reference 3.

The uncombined alcohols (mp 84–85.5 C) were obtained in a yield of 10.5% and were chromatographically similar to the monohydric alcohols obtained from the aliphatic esters. These alcohols, however, were noticeably different in the IR, showing increased absorption at 8.9 μ indicative of other than all primary alcohols.

ω-Hydroxy esters were obtained in a yield of 17.0% but had to be further purified by recrystallization from chloroform. This reduced the yield to about 13% (ester value 65, hydroxyl value 64, mp 94–95 C, average mol wt 864). Hydrolysis gave 46.6% acids (acid value 136, mp 94–97 C, average mol wt 413) and 53.4% alcohols (mp 85–86 C, hydroxyl value 131, hydroxyl eq wt 430).

The TLC of the total acids revealed the presence of a small amount of monocarboxylic acid with the bulk of the sample being the more polar ω-hydroxy acids.

The total alcohols were chromatographically separated to give 90% monohydric alcohols which were similar to the previously characterized alcohols from the aliphatic esters. The remaining 10% of the alcohols were a,ω-diols (hydroxyl value 251, mp 98–102 C, average mol wt 450).

The remaining 32.6% of the wax was extremely high in those esters which contained the p-hydroxycinnamic acid. Attempts at rechromatography and solvent crystallizations of this and similar fractions did not produce a sample free enough of acidic materials for reliable indentification, but did give a fraction deemed suitable for characterization in the IR (solid film between NaCl windows) (Fig. 2).

As previously mentioned, the chromatographic separation and identification of carnauba wax constituents became increasingly more complex after the ω-hydroxy esters had been removed and identified. As a consequence, a less direct method was devised. The whole wax was separated into three major fractions by elution through tandem columns of Florite (Floridin Co.) and activated silica (1).

The 40.9% of the whole wax passing through the tandem columns with 10% ethylene dichloride in heptane was characterized as being aliphatic esters in the IR. This yield was in good agreement with the 39.9% combined yield of hydrocarbons and aliphatic esters which had been previously established.

When the silica column was stripped of adsorbed material using 10% isopropanol in heptane, a yield of 31.0% of the whole wax was obtained. This fraction contained essentially all of the uncombined alcohols (10–12% of the whole wax) and ω-hydroxy esters

Para Hydroxycinnamic Aliphatic Diesters

WAVELENGTH IN MICRONS

Fig. 2.

Acetate of Para Hydroxycinnamic Aliphatic Diesters
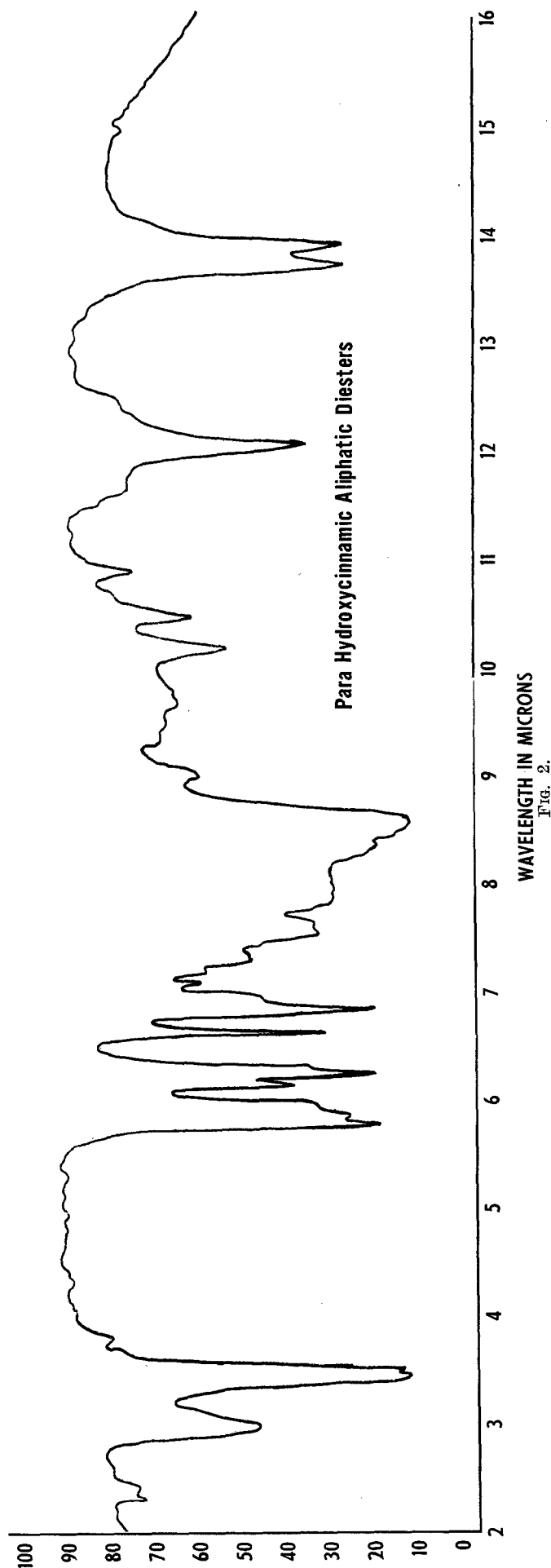—— From Acetylated Carnauba
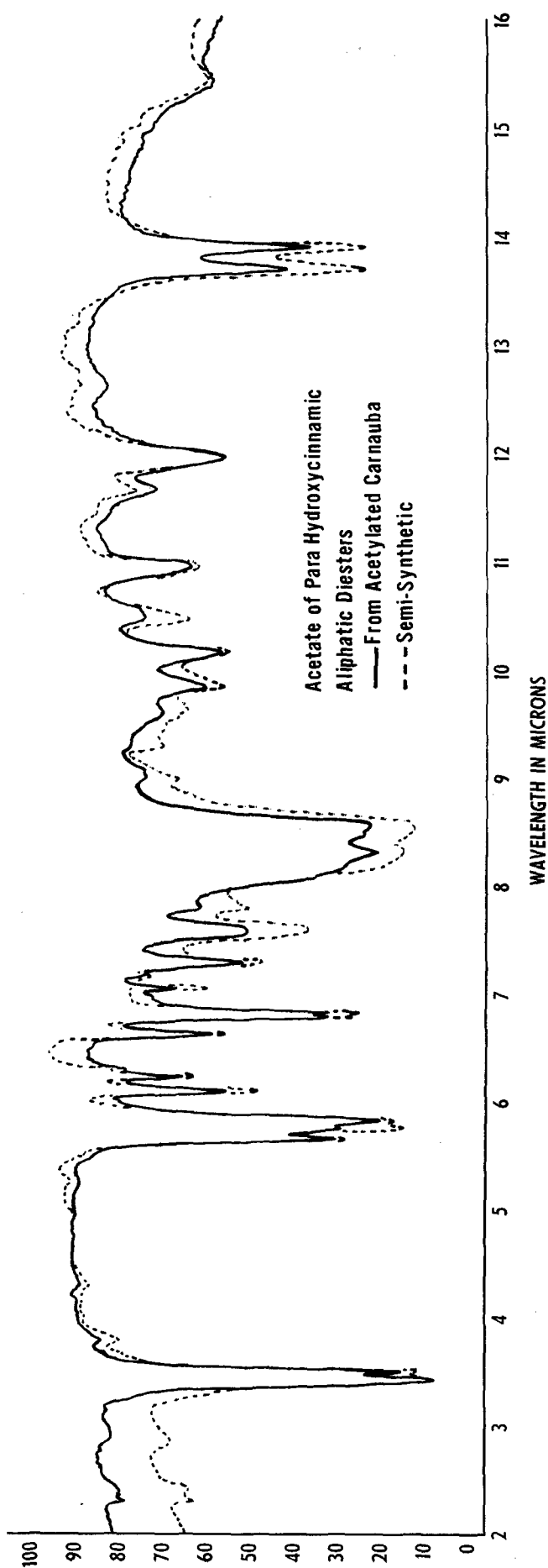– – – Semi-Synthetic

WAVELENGTH IN MICRONS

FIG. 3.

(12–14% of the whole wax) plus unknown aromatic esters (5–7% of the whole wax). The aromatic moiety was found to be *p*-methoxycinnamic acid (1).

The *p*-methoxycinnamic esters were further purified by rechromatographing on activated silica followed by crystallizations from ethyl acetate and chloroform. The chloroform soluble material had an IR spectra which suggested that these aromatic esters might be diesters, obtainable by the reaction of *p*-methoxycinnamic acid with ω-hydroxy esters. This observation was confirmed by the reaction of authentic *p*-methoxycinnamic acid with carnauba ω-hydroxy esters. The IR spectra of the natural and semisynthetic samples compared favorably (1). The semisynthetic esters contained two materials of about the same R_f as materials found in the whole wax (Fig. 1). These two materials were chromatographically separated and identified as the *cis* (upper spot) and *trans* (lower spot) isomers by IR comparison to pure *cis* or *trans* ethyl-*p*-methoxycinnamate (*para* substitution absorption for *cis* isomers, about 11.8 μ; *trans* isomers, about 12.1 μ).

The third major fraction, amounting to 25.6% of the whole wax, was eluted from the Florite column with 10% isopropanol in heptane. This fraction contained all of the *p*-hydroxycinnamic esters. The entire fraction was acetylated and rechromatographed on activated silica using 5–20% ethylene dichloride in heptane.

With the aid of TLC, an acetate fraction was isolated which had an average molecular weight of 1055 (ester value 159, mp 83–87 C).

As may be seen, the IR spectra (solid films between NaCl windows) (Fig. 3) and TLC (Fig. 4) of the sample obtained from the acetylated carnauba fraction, and of the product obtained by the reaction of *p*-acetoxycinnamoyl chloride with the carnauba ω-hydroxy esters, are nearly the same.

Reduction of the Type 1 and Type 4 carnauba waxes with LiAlH₄ gave 95% yields of alcohols in both cases with hydroxyl values of 145 and 146 respectively. This indicated no gross differences in the overall composition of the two waxes. The 5% losses were due to tarry residues from the reduction and polymerization of the cinnamic moieties.

When pulverized Type 1 carnauba wax was leached overnight in ether, and the ether extract recovered and crystallized from heptane containing a small amount of methanol, 0.4% of a white, flaky solid (mp 163–165 C) was obtained. This solid was a triterpene diol identified by Barnes et al. (5) as being 25 β-methyldammar-25-ene-3β, 20-ζ-diol.
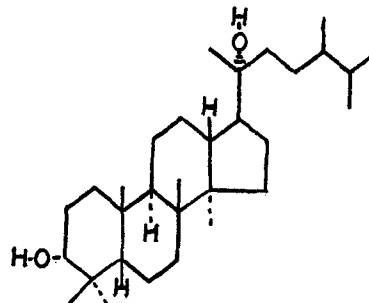
In addition, a small amount of the esters of *p*-methoxycinnamic acid with the monohydric alcohols was obtained chromatographically from the tacky semisolid from which the triterpene diol was crystallized.

Discussion

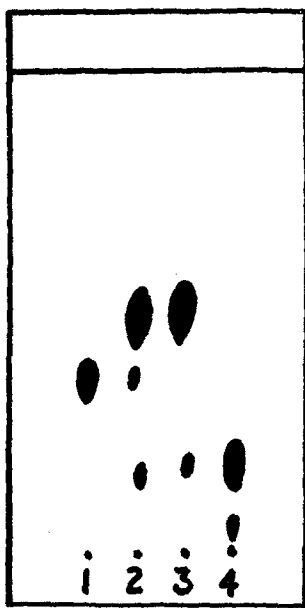The hydrolysis products of carnauba wax have long been investigated and characterized. The major prob-

FIG. 4. Plate: Silica Gel G (1½ × 3 in.) (0.25 mm). Developed: Chloroform at 42 C. Visualized: 0.5% KMnO₄ followed by 20% H₂SO₄. (1) ω-Hydroxy aliphatic esters from carnauba wax, (2) semisynthetic p-acetoxycinnamic ester of the carnauba ω-hydroxy esters, (3) eluted fraction from acetylated carnauba wax, (4) p-hydroxycinnamic aliphatic diester from carnauba wax.

lem has been in the determination of how the hydrolytic pieces were originally combined in the whole wax. Our primary contribution to the solution of this problem has been the isolation and identification of about 30% of previously unidentified cinnamic diesters and secondly the separation and identification of the other major constituents observed by TLC.

The p-substituted cinnamic esters contribute substantially to the hydroxyl and ester values, account for nearly all of the iodine value, and explain the presence of about 5% of acidic resinous materials commonly reported after hydrolysis. It is these cinnamic esters or their polymers, or both, which apparently are responsible for the desirable properties generally attributed to carnauba wax.

It should be brought to mind, however, that cinnamic acids are not unique with carnauba wax. Ferulic acid was isolated by Kurth from Douglas Fir bark wax (6) and IR spectra suggests the presence of similar cinnamic moieties in hospita, caranda, ceroxylin andicola, cork, ouricuri, saw palmetto, Spanish moss and candellia (trace) waxes.

The esters of carnauba wax were found to be of three general types: aliphatic esters, ω-hydroxy aliphatic esters and p-substituted cinnamic aliphatic diesters. These esters proved to be of a predictable sequence with approximate average molecular weights of 840, 860 and 1010–1020 respectively.

Aliphatic Esters

Aliphatic esters (ester eq wt 844) were solely the esterification product of monocarboxylic acids of average chain length C_{26} (theoretical mol wt 396) and monohydric alcohols of average chain length C_{32} (theoretical mol wt 466).

Omega Hydroxy Esters

Omega hydroxy esters (ester eq. wt 864) were of the same average chain length as the aliphatic esters. Two ester types were found to be present. The pre-

dominant ester (90% of the total) was the esterification product of ω-hydroxy acids of average chain length C_{26} (theoretical mol wt 412) with monohydric alcohols of average chain length C_{32}. The remaining 10% was the esterification product of a,ω-diols of average chain length C_{30}, (theoretical mol wt 454) and aliphatic acids of average chain length C_{28} (theoretical mol wt 424). Even though the possibility for polyester formation exists, there was no experimental evidence to support this contention. As expected with an ω-hydroxy monoester, the hydroxyl and ester values were about the same (64 and 65 respectively).

Cinnamic Esters

Cinnamic esters were of two predominant classes. The first was a diester obtainable by the reaction of p-methoxycinnamic acid with the ω-hydroxy esters (average mol wt 1025) and the second was a diester obtainable by the reaction of p-hydroxycinnamic acid with ω-hydroxy esters (average mol wt 1010). The trans esters predominate as shown by IR spectroscopy (strong absorption at 12.1 μ rather than at 11.8 μ). Although the p-hydroxycinnamic diesters were not isolated in a state pure enough for reliable identification, a small amount of the less polar acetate derivative was successfully isolated and characterized.

With the establishment of the structure, and knowing that about 16% of the cinnamic diester hydrolysis products are aromatic, the whole wax had to contain about 30% of these esters to account for the 4.5–5% of cinnamic acids or polymers, or both, found upon hydrolysis (1). Column chromatography and optical density measurements of the aromatic band at 1600 cm⁻¹ were used to estimate the p-methoxycinnamic diester content at about 5–7% of the whole wax with the p-methoxycinnamic acid representing about 20–25% of the total aromatic acids (1). The p-hydroxycinnamic diesters (20–25% of the whole wax) must then account for the remainder.

Little if any of the cinnamic esters appear to be of a monomeric nature in Type 4 carnauba wax (1), a fact which can be easily observed by direct thin layer comparison of Type 4 carnauba with Type 1 carnauba. Similar observations can be obtained from the IR comparison (solid films between NaCl windows) of the two waxes. Type 4 is conspicuously different from Type 1 with noticeable decreases in the p-substitution region (830 cm⁻¹), aromatic regions (1600, 1515 cm⁻¹) and unsaturated regions (980, 1630 cm⁻¹). These decreases were in spite of the fact that about equal amounts of the cinnamic acids or polymers, or both, were isolated from both waxes (1).

The iodine value appears to be deceptive in determining the total unsaturation of the whole wax. This is in all probability due to halogenation of the ring system as well as the aliphatic double bond of cinnamic acid. This phenomena is well known particularly with unsaturated hydrocarbons containing aromatic ring systems as impurities.

Uncombined Alcohols

The uncombined alcohols were found to be chromatographically similar to the monohydric alcohols obtained from the aliphatic esters. Increased IR absorption at 8.9 μ indicated the presence of a small amount of secondary alcohol (OH absorption of 2-hexadecanol 8.8 μ).

The following composition for Type 1 carnauba wax has been proposed and has been found to be reasonably consistent with the experimental data: hydrocarbons,

1%, aliphatic esters 40%, uncombined alcohols 12%, ω-hydroxy esters 13%, p-methoxycinnamic aliphatic diesters 7%, p-hydroxycinnamic aliphatic diesters 21%, triterpene diol 0.5%, ω-hydroxy acids 0.5%, aliphatic acids 4%, aromatic acids 1%. Calculated ester value 66 (found 70), calculated hydroxyl value 36 (found 37), calculated acid value 10 (found 11), calculated nonsaponifiables 54.7% (found 56.4%), calculated hydroxyl value of nonsaponifiables 123 (found 125), calculated aliphatic saponifiables 39.8% (found 39.2%), calculated acid value of saponifiables 142 (found 145), calculated aromatic and/or resins 5.5% (found 4.4% by hydrolysis, 5% after LiAlH$_4$ reduction).

With the exception of being unable to isolate the triterpene diol from Type 4 carnauba wax and finding the cinnamic esters are in a more polymeric state in Type 4, the two waxes appear to be the same. Other features of the TLC and IR are identical. Upon total reduction of both waxes with LiAlH$_4$, alcohol yields of 95% with hydroxyl values of 95–96 were obtained. Likewise, the chemical constants between Type 4 and Type 1 carnauba are very similar. All in all, it has been concluded that Type 4 carnauba wax is merely a more polymeric form of Type 1. This polymerization may well have been brought about by longer exposure of Type 4 to the sun's radiation and other climatic conditions.

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