Aromatic Acids of Carnauba Wax

L. E. VANDENBURG and E. A. WILDER, S. C. Johnson & Son, Inc., Racine, Wisconsin

Abstract

Cinnamic acid with *para*-hydroxy and *para*-methoxy substitution has been isolated from carnauba wax in a yield of about 5%. The *para*-hydroxycinnamic acid accounts for approximately 75% of the total aromatic acids.

These hitherto unreported aromatic acids occur predominantly as part of a polymerizable diester of approximate average molecular weight 1025. Certain properties of carnauba wax are believed to be due to the presence of about 30% of these diesters. Except for trace amounts, no significant quantities of these aromatic acids could be isolated in the free state from the whole wax.

Introduction

INFRARED SPECTRA of carnauba wax consistently show absorption peaks at 1600, 1515, and 830 cm^{-1} indicative of aromatic or substituted aromatic rings. The intensities of the absorption bands indicate that the aromatic component is more than a minor constituent. Yet, in none of the extensive analytical investigations published (1–3) on the constituents of carnauba wax has any particular recognition been given to this fact. An obscure publication by Williamson (4), however, does mention the fact that these bands "indicate that this wax contains aromatic groups which are *para* substituted."

These aromatic acids now have been isolated from the total carnauba wax saponifiables and identified as *para*-hydroxy and *para*-methoxycinnamic acids with the *para*-hydroxycinnamic being the dominant component. Further, a portion of the aromatic acids has been found to exist as the polymer with polymerization occurring through the aliphatic double bond. It has been noted that yellow carnauba wax, taken from the young, unopened leaves of the carnauba palm, contains a high ratio of cinnamic monomer to polymer (resin), whereas the older, dark-colored wax, taken from the outer, fully opened leaves, contains a high ratio of the cinnamic polymer to monomer. Speculation at this time suggests that prolonged exposure of the wax to the sun's radiation, and other climatic conditions, causes polymerization of the aliphatic double bonds of the cinnamic acids.

The analysis of carnauba wax in nearly all reported work has been based on 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 a polymerized resin acid.

The identification of these aromatic moieties appeared important in attempting to explain certain unusual characteristics of the wax as well as ascertaining the nature of the compounds responsible for the infrared absorption in the area assigned to aromatic structures.

We were aware from our own analysis of the products of hydrolyzed carnauba wax that nonsaponifiable material recovered by extraction with a water immiscible solvent gave no evidence of aromatic absorption in the infrared. The same is true of the acids recovered by solvent extraction of the acidified alkaline liquor. It seemed reasonable, therefore, to conclude that the aromatic moiety was either water soluble or was, under some conditions, subject to polymerization to a tar or resin. Our study of the isolation and identification of the aromatic moiety proceeded upon this inference.

Experimental

Two hundred and fifty grams (250) of yellow carnauba wax (Type 1) was saponified 8 hr with moderate agitation in 2,500 ml of refluxing 0.2 N isopropanolic KOH. Upon completion of the saponification, most of the isopropanol was evaporated leaving a thick, mud-like slurry in the reaction flask. Residual isopropanol was azeotropically removed by codistillation with a commercial grade heptane. It was found necessary to remove all isopropanol to obtain a quantitative separation of total nonsaponifiables from the total saponifiables.

Repeated washing of the slurry with hot heptane, followed by filtration and evaporation of solvent yielded 141 g (56.4%) of white solid (mp 85–87C, hydroxyl value 125, hydroxyl eq wt 450) having absorption (3350, 1060 cm^{-1}) in the infrared characteristic of aliphatic alcohols.

Hot water was added to the total heptane insoluble material and acidified to pH 3. The mixture was held at 90–95C with moderate agitation for 15 min, then allowed to stand until the waxy material separated and rose to the surface. The dark brown aqueous layer was siphoned off and the waxy material twice washed with hot water. All washings were combined for later use.

Ninety-eight grams (39.2%) of a hard, brown solid (mp 74–88C, saponification value 145, ester value 53, saponification eq wt 385) was obtained from the filtered hot heptane solution of acidified, waxy saponifiables. Aliphatic acid absorption (1710, 1300 cm^{-1}), aliphatic ester absorption (1735, 1170 cm^{-1}), and no aromatic absorption was noted in the infrared.

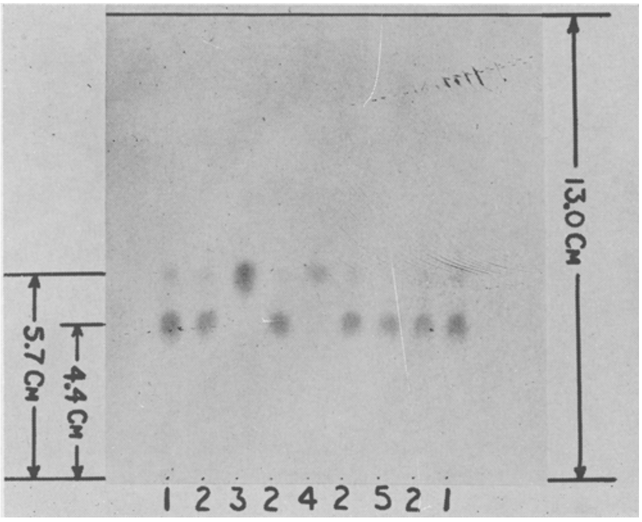


FIG. 1. Plate: 20 × 20 cm coated to a thickness of 250μ with Silica Gel G acidified with 1% H_2SO_4. Developing system: 1:1 heptane-ethyl acetate. Visualizing system: 20% H_2SO_4 in ethanol.

1) Crude carnauba aromatic acids. 2) Recrystallized carnauba acids. 3) *p*-methoxycinnamic acid from carnauba. 4) Authentic *p*-methoxycinnamic acid. 5) Authentic *p*-hydroxycinnamic acid.

Apparently, esterification of carboxylic acid with known *omega* hydroxy acids (1,2) occurred during the 110C vacuum drying.

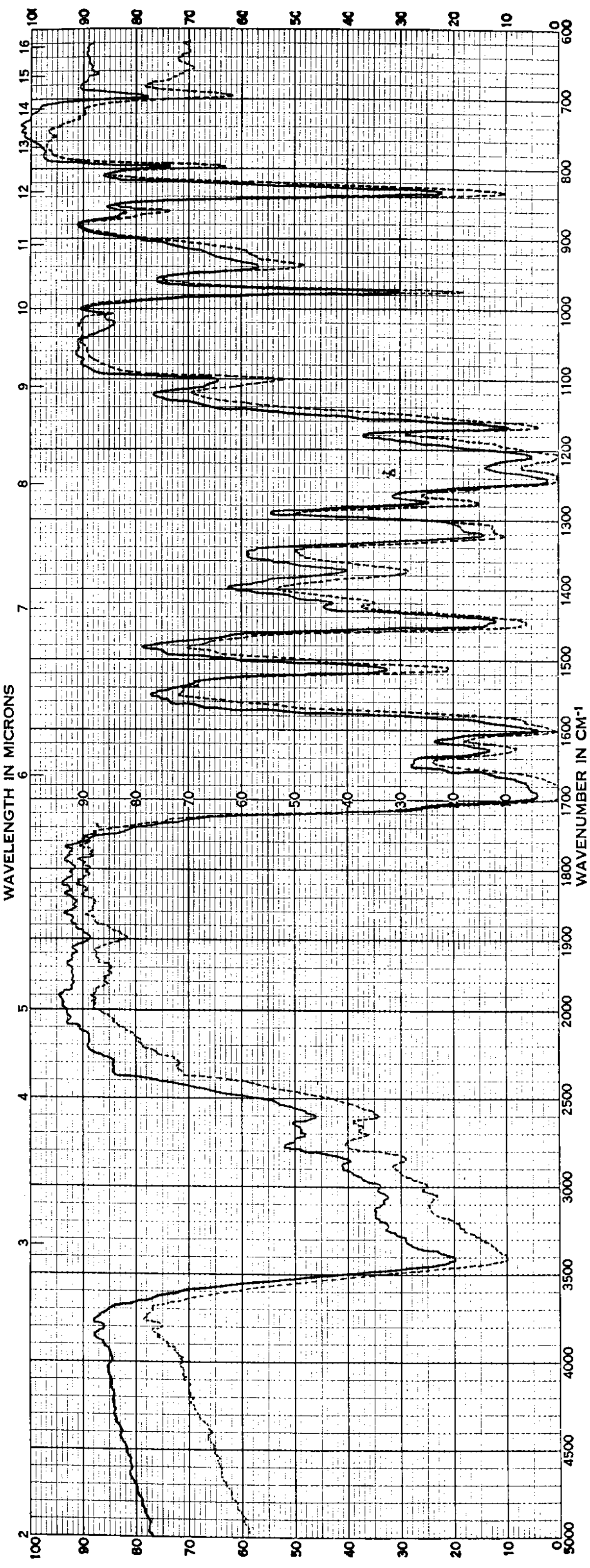


FIG. 2. Infrared spectra of authentic *p*-hydroxycinnamic acid (dotted line) and *p*-hydroxycinnamic acid from carnauba wax (solid line).

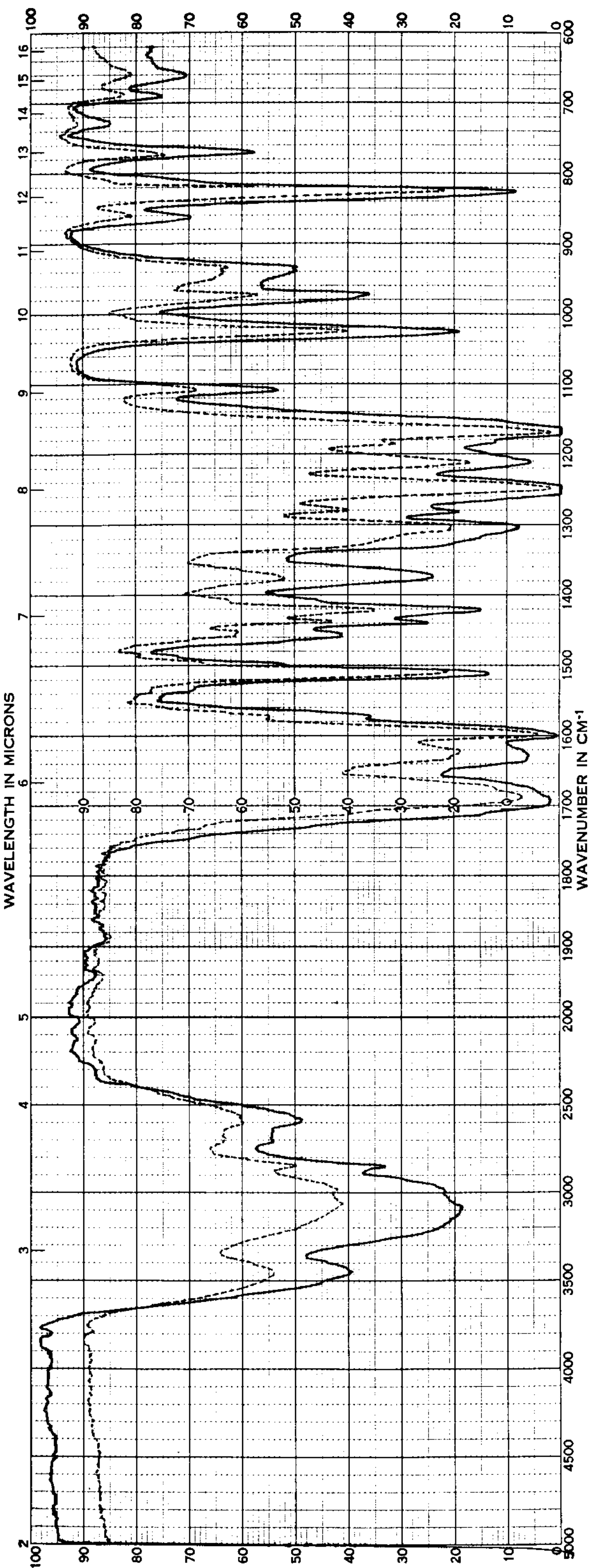


FIG. 3. Infrared spectra of authentic *p*-methoxycinnamic acid (dotted line) and *p*-methoxycinnamic acid from carnauba wax (solid line).

The combined water washes were made alkaline, evaporated to about 500 ml, cooled, acidified, and extracted with ether. Evaporation yielded 11 g (4.4%) of a hard, brown, resinous-appearing solid characterized in the infrared by absorptions of hydroxyl (3450 cm^{-1}), acid (1685, 1170 cm^{-1}), unsaturation (1630, 980 cm^{-1}), aromatic (1600, 1515 cm^{-1}) and *para* substitution (830 cm^{-1}). A thin-layer chromatogram (Fig. 1) showed two spots. Decolorization of an aqueous solution of the sodium salt followed by several recrystallizations of the reacidified material from aqueous solution gave 0.9 g (20%) of a white solid having a melting point of 203–205C, an acid value of 334 and an acid eq wt of 168. The literature values found for *p*-hydroxycinnamic acid include a melting point of 207–210C and a calculated acid eq wt of 164. This recrystallized solid had the same two spots of the original material and were found to be chromatographically identical to *p*-hydroxy and *p*-methoxycinnamic acids (Fig. 1). Comparison of the infrared absorption (KBr) of the recrystallized, recovered acid and that of *p*-hydroxycinnamic acid (Fig. 2) showed identical patterns except for weak absorption in the recovered material at 1020 cm^{-1} due to the contaminating influence of *p*-methoxycinnamic acid.

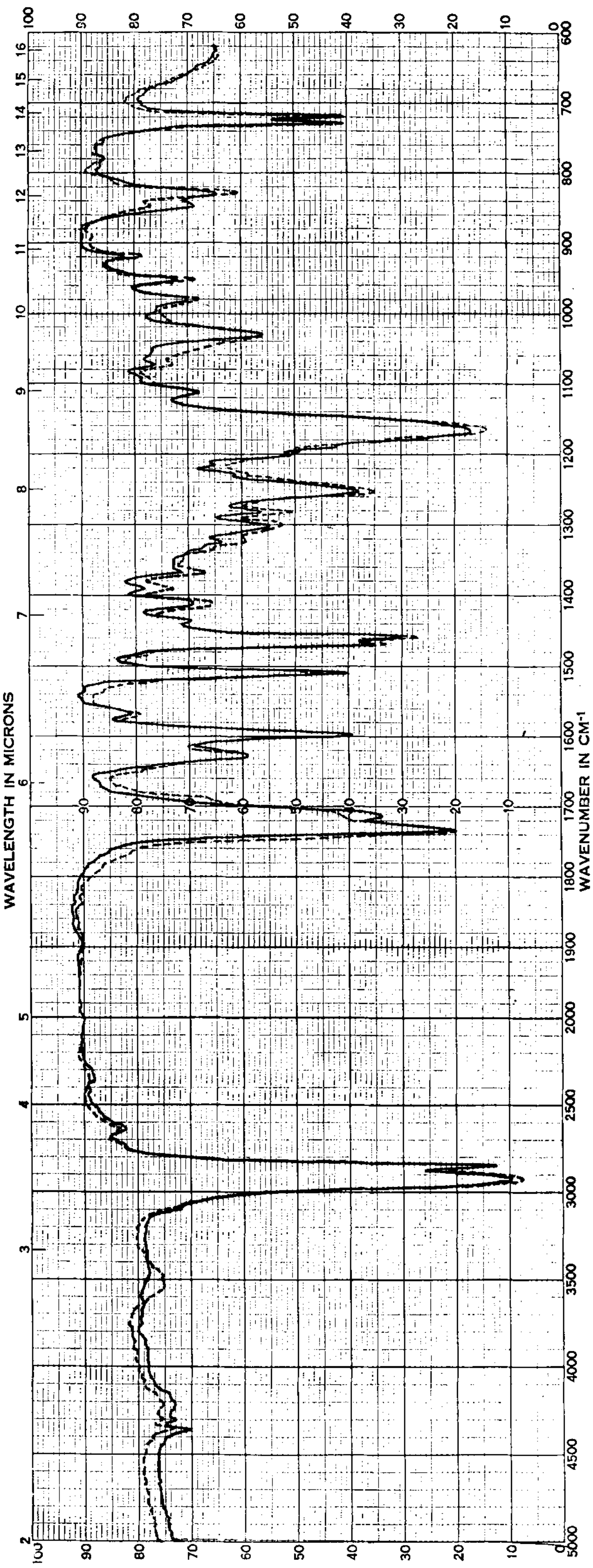


FIG. 4. Infrared spectra of semi-synthetic *p*-methoxycinnamic diester (solid line) and carnauba wax derived aromatic ester concentrate (dotted line).

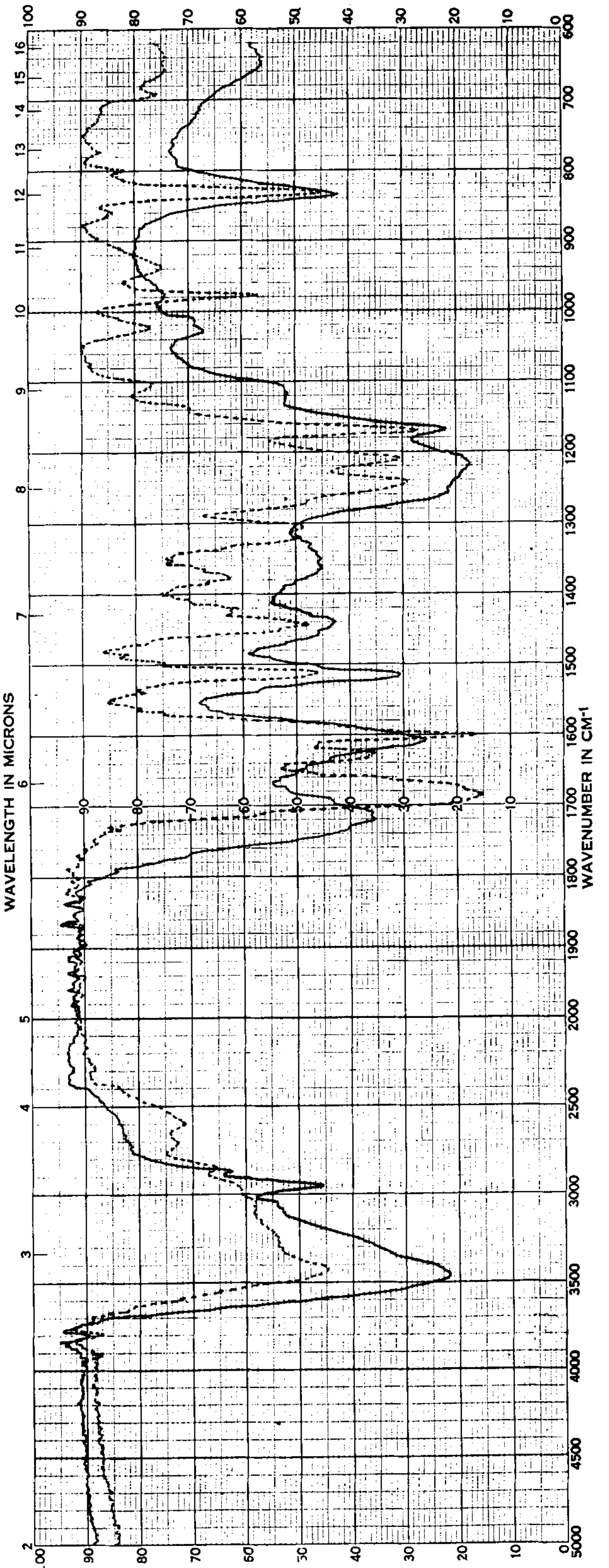


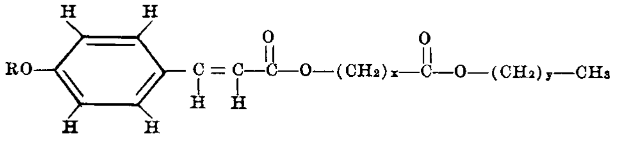
FIG. 5. Infrared spectra of a mixture of monomeric *p*-methoxy and *p*-hydroxycinnamic acids from carnauba (dotted line) and carnauba wax polymer (solid line).

Material identifiable as pure *p*-methoxycinnamic acid was isolated by the following chromatographic elution. Forty-four and one half grams of yellow carnauba dissolved in 500 ml of hot solvent (90%

heptane, 10% ethylene dichloride) was placed on a column (3.8 × 46 cm) of 20/60 Florite, 400 g, and eluted with 2500 ml of the same solvent mixture. The total eluate was then run into a similar column of activated silica and the column washed with an additional 500 ml of solvent mixture. The waxy material that was recovered showed absorption in the infrared consistent with that of aliphatic esters.

The silica gel column was stripped of adsorbed residue with 2000 ml of 10% isopropanol in heptane. The eluate, 13.8 g (31.0%) was characterized by aliphatic ester, hydroxyl, and aromatic ester absorption in the infrared. The aromatic esters appeared to be solely the *p*-methoxy derivative as evidenced by the lack of a 1585 cm^{-1} shoulder on the 1600 cm^{-1} aromatic band, which was found to be characteristic of the esters of *p*-hydroxycinnamic acid but not the *p*-methoxy counterpart. Rough calculation from the yield and optical density measurements of the 1600 cm^{-1} band indicated that this fraction contained approximately 20–25% of the total aromatic acids found in whole, yellow carnauba wax. Hydrolysis of the isopropanol eluate and recovery of the aromatic acids in a manner previously described gave small white needles (mp 173–175C, clearing pt. 183C; lit. for *p*-methoxycinnamic acid, mp 170–173.8C, clearing pt. 185C) which were chromatographically homogeneous and of the same R_f as *p*-methoxycinnamic acid (Fig. 1). The infrared curves of the authentic and isolated *p*-methoxycinnamic acids were identical (Fig. 3).

Though it is beyond the limited scope of this paper to present in detail all of the pertinent data, it has been reasonably well established that these substituted cinnamic acids occur predominantly in diesters (5). These diesters account for about 30% of carnauba wax and are of the generalized form:



$R = CH_3$ (about 20–25%) and H (about 75–80%)
X plus Y = average of about 58

Fig. 4 compares the infrared curve of a highly concentrated aromatic ester from carnauba wax with a semi-synthetically prepared *p*-methoxycinnamic diester (mp 90.2–90.8C, ester value 109, average mol wt 1025). The natural material contained a small amount of impurity, probably hydroxylated, as indicated by thin-layer chromatography and infrared. The semisynthetic ester, chromatographically containing two materials identifiable as the *cis* and *trans* isomers and of the same R_f as materials found in the carnauba concentrate, was prepared by reacting *p*-methoxycinnamic acid with chromatographically homogenous, carnauba derived, *omega* hydroxy esters (mp 94–95C, ester value 65, hydroxyl value 64, average mol wt 865).

Only trace amounts of the aromatic acids could be recovered in the free state by washing carnauba wax-heptane solutions with 5% aqueous bicarbonate. The pleasant fragrance of *p*-methoxycinnamic acid and its esters in all probability account for the reported isolation of material with a "coumarin-like" odor by von Pieverling (6) as early as 1876.

Similar treatment of 250 g of Type 4 carnauba (from fully expanded leaves) failed to yield any of the aromatic monomer. All of the aromatic moieties were isolated as a hard, dark brown resinous material in a yield of about 4.5%. Decreased absorption of unsaturation bands (1625, 980 cm^{-1} in KBr), accompanied by the anticipated shift in carbonyl absorption (1685 to 1720 cm^{-1}) (Fig. 5), is very strong evidence that polymerization of the cinnamic acids at the aliphatic double bond is responsible for the formation of resinous material. The fact that no monomer could be isolated, coupled with the fact that unsaturation bands at 1625 and 980 cm^{-1} are greatly diminished in the infrared curves of Type 4 carnauba suggests that most, if not all, of the cinnamic esters are in a polymeric state before hydrolysis. Products which were similar to the natural resin in the infrared were prepared by polymerization of a mixture of *p*-methoxy and *p*-hydroxycinnamic acids in acidified hot water (18 hr at 90C) and by carefully melting the two acids together in a sealed glass tube.

Analysis of Type 3 carnauba wax (from partially opened leaves) showed the ratio of cinnamic monomer to polymer to be intermediate between the high monomeric form in the Type 1 wax and the apparent total polymeric form in the Type 4 wax.

Discussion

These findings indicate a definite change in the molecular structure of carnauba wax upon aging. It is believed that the cinnamic esters are mainly responsible for the unusual properties attributed to carnauba wax, and exposure of this wax to the sun's radiation, and other climatic conditions, causes increased polymerization of these esters with the increased age of the leaves upon which the wax is found.

ACKNOWLEDGMENTS

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