therefore, of sepiol, was established by its synthesis from 2,3-diethoxy-4-methoxyacetophenone. This was converted via the Willgerodt reaction (Brown, 1975) to the phenylacetic acid **10**, which was condensed with 2,4-dihydroxybenzaldehyde in acetic anhydride and potassium acetate (Donnelly and Kavanagh, 1974) to yield the 3-phenylcoumarin (**11b**). Hydrolysis of this monoacetate gave **11a** which was then ethylated to yield 3-(2,3-diethoxy-4-methoxyphenyl)-7-ethoxycoumarin (**9d**), identical in all respects with the product obtained from sepiol.

The minor phenolic constituent, $C_{17}H_{16}O_5$, of *Gliricidia sepium* does not reduce ammoniacal silver nitrate. It contains two methoxyl groups and forms a diacetate whose NMR spectrum shows the presence of a methylene group at δ 5.03 allylically coupled to a methine proton at δ 6.61. The aromatic region of the spectrum is closely similar to that of sepiol triacetate in all respects. This phenol, therefore, is a 7-hydroxyisoflavene derived from sepiol by methylation of one of the two hydroxyl groups. On catalytic hydrogenation the diacetate yields a diacetoxyisoflavan (oil), in which three aromatic protons appear as ortho-coupled doublets at δ 6.70, 6.95, and 7.06 and two aromatic protons as a 2 H multiplet at δ 6.60–6.63. These chemical shifts agree precisely with those reported (Donnelly et al., 1973) for the protons at positions 5′, 6′, 5, 6, and 8, respectively, in mucronulatol diacetate (**12b**). On this basis the *Gliricidia* phenol is the 2′-*O*-methyl derivative **13** of sepiol.

The phenol, $C_{17}H_{18}O_5$, isolated in a very small amount from the heartwood, is optically active, and contains two methoxyl and two hydroxyl groups. Both the mass spectrum, which has prominent ions at 123, 167, and 180, and the NMR spectrum of the phenol establish that it is a 7-hydroxyisoflavan with two methoxyls and a hydroxyl group located at positions 2′, 3′, and 4′ of the B ring. The melting point and rotation of the phenol and the NMR spectrum of its diacetate differ, however, from those reported (Kurosawa et al., 1968; Donnelly et al., 1973) for mucronulatol **12a**. This new phenol, therefore, is either the isomeric isoflavan **14** or laxifloran **3a**, which as previously noted has been isolated and described only in the form of its dimethyl derivative **3b**. Because of a lack of material, an unequivocal decision between these two possible structures **14** and **3a** for the *Gliricidia* phenol cannot be made at this time.

The third minor constituent of the heartwood, $C_{15}H_{12}O_5$, reduces silver nitrate and gives a flavanone color reaction. On the basis of its physical and spectral properties, it is clearly identical with the known (Shinoda, 1929) 7,3′,4′-trihydroxyflavanone (**15**).

Prior to the isolation of sepiol and 2′-*O*-methylsepiol only one other isoflavene has been detected in plants (Brink et al., 1974). However, since they are highly reactive intermediates, they may be expected to play a central role in the biosynthesis of isoflavans and other types of isoflavanoids, such as the 3-phenylcoumarins (Donnelly and Kavanagh, 1974).

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New Natural Products from Marine Borer Resistant Woods. A Review.

Gary D. Manners* and Leonard Jurd

The examination of the heartwood extractives of three tropical woods (*Dalbergia retusa*, *Tabebuia guayacan*, and *Cordia alliodora*), specifically regarding their established natural resistance to marine borer attack, has resulted in the characterization of several new natural products. These new compounds include several structural types: cinnamylphenols, isoflavones, naphthaquinones, dibenzoxanthene, oxadibenzoxanthone, and geranylhydroquinone. Several of the new compounds or their derivatives have been successfully synthesized.

Long-term marine exposure tests of 115 tropical woods (Southwell and Bultman, 1971) have established several woods to be naturally resistant to attack by a variety of marine boring organisms. While some of these resistant woods have been examined chemically, no attempt has previously been made to determine the constituents responsible for resistance to natural marine borers. Biologically active compounds obtained from these recognized resistant species may serve as models for the development

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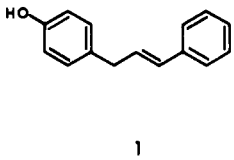
of new types of wood preservatives capable of replacing those presently in use whose toxicity and environmental effects are in question.

The most resistant wood in marine exposure tests proved to be *Dalbergia retusa* (Leguminosae). Previous chemical work on other related *Dalbergia* species (Ollis, 1966; Gregson et al., 1968; Gottlieb et al., 1970; de Oliveira et al., 1971; Seshadri, 1972; Donnelly et al., 1973) indicated that the *Dalbergia* genus contains a unique series of cinnamylphenols, e.g., obtusastyrene (**1**), which co-occur with related neoflavanoids, e.g., 4-phenylcoumarins such as a dalbergin (**2**) and quinones such as 4-methoxy-



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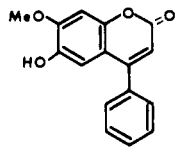

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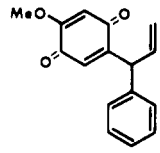
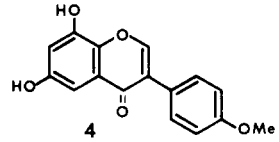


3

dalbergione (**3**). Although microbiocidal data had not been obtained, it was suggested that the observed resistance of *D. sissoo* to terrestrial fungi (Ahluwalia et al., 1957) might be due to the presence of **2**, and it has been reported (Eyton et al., 1966) that the dalbergione **3** is active against some bacteria at concentrations of about 100–200 ppm. Following the development of a simple synthesis of cinnamylphenols of type **1** (Jurd, 1968), by an aqueous acid-catalyzed condensation of phenols with cinnamyl alcohol, obtusastyrene was shown to be a highly effective microbiocide (Jurd et al., 1971; King et al., 1972; Lewis and Jurd, 1972) and algicide (Chan and Jurd, 1973) at concentrations as low as 10–25 ppm.

The demonstrated biocidal properties of cinnamylphenols suggested that these or derived compounds could be responsible for the resistance of *D. retusa* to marine boring organisms. Extraction of the *D. retusa* heartwood yielded two new 7,8,4′ trioxygenated isoflavones (Jurd et al., 1972a), retusin (**4**) and its 8-*O*-methyl derivative, the cinnamyl methoxycatechol (**5**) (Manners et al., 1974), and the highly reactive *p*-quinone methide, obtusaquinone (**6**) (Jurd et al., 1972b).

Marine tests of obtusaquinone-treated pine disks by the U.S. Naval Research Laboratory have shown the compound to be an active marine borer larvicide, causing abnormal shell formation by the larvae and interrupting their metamorphosis (Waite, 1976). Synthetic *p*-quinone methides, e.g., **7**, related to the natural **6** have proven to be just as effective in controlling marine borer attack (Jurd and Bultman, 1976).



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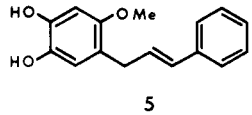

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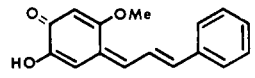

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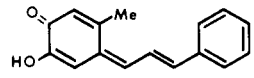
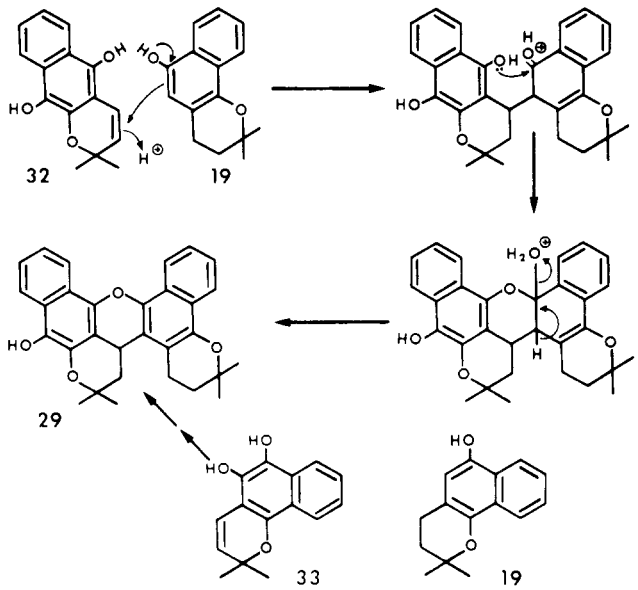


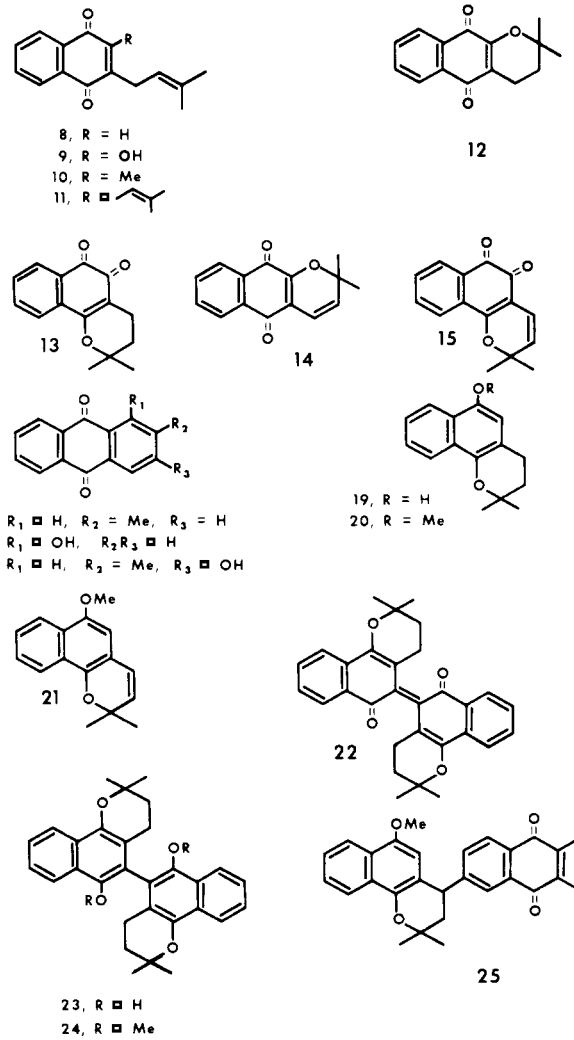
7

Tabebuia guayacan (Bignoniaceae) was one of the more resistant woods tested in the marine environment. Previous chemical work on *Tabebuia avellanedae* (Burnett and Thomson, 1967) and *Tabebuia chrysantha* (Burnett and Thomson, 1968) reported the occurrence of several prenylnaphthaquinone derivatives (**8–10**, **12–14**), three

Scheme I



anthraquinones (**16–18**), three prenylated naphthaquinols (**19–21**), three prenylated naphthaquinol dimers (**22–24**), and a prenylated naphthaquinol–anthraquinone dimer (**25**).



8, R = H
9, R = OH
10, R = Me
11, R =

12

13

14

15

16, R_1 = H, R_2 = Me, R_3 = H
17, R_1 = OH, R_2R_3 = H
18, R_1 = H, R_2 = Me, R_3 = OH

19, R = H
20, R = Me

21

22

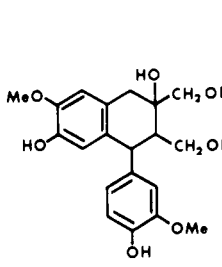
23, R = H
24, R = Me

25

Lapachol (**9**), the only constituent previously reported in *T. guayacan* (Wise et al., 1951), has been reported to be toxic to termites (Thomson, 1971) and to possess

anti-tumor properties worthy of clinical testing (Rao et al., 1968). The examination of the heartwood extractives of *T. guayacan* in relation to its marine borer resistance (Manners et al., 1976) confirmed the occurrence of lapachol and other previously described naphthaquinone derivatives (**12**, **13**, **14**) in the wood. In addition, a new diprenyl naphthaquinone (**11**) was isolated and sythesized in an oxidative, acid-catalyzed diprenylation of naphthalene-1,4-diol (Manners and Jurd, 1976).

The ether and acetone extracts of *T. guayacan* yielded the two lignans, isoolivil (**26**) and olivil (**27**) (Manners, 1974), and the naphthalene-1,4-diol monochromene dimer, tectol (**28**), previously described in teak (*Tectona* sp.) (Sanderman and Dietrichs, 1959). Two new and unique dimeric compounds (guayacanin, **29**, and guayin, **31**) were also isolated and characterized from these extracts (Manners et al., 1975, 1976).



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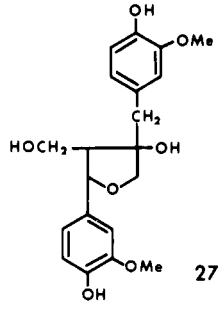
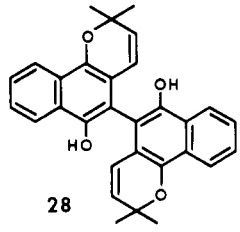


27



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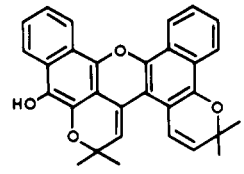
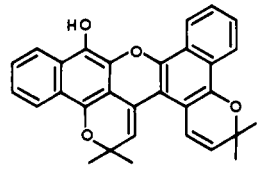
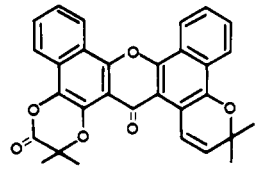


29



30

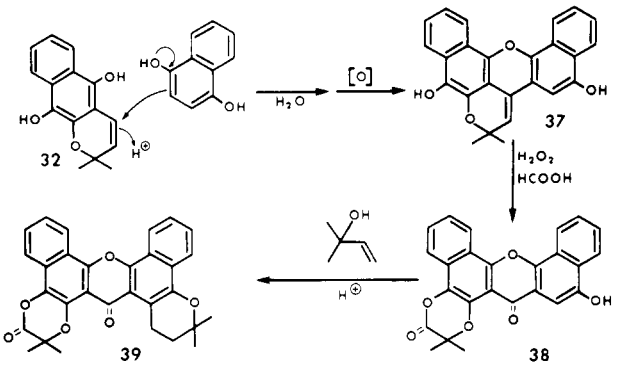


31

Guayacanin ($C_{30}H_{24}O_4$) was found to contain a single phenolic hydroxyl, formed a deep-purple pyrilium salt in ethanol upon addition of HCl, and showed two chromene *gem*-dimethyl groups, two coupled chromene vinyl protons, an uncoupled vinyl proton, eight aromatic protons, and a hydroxyl proton in its NMR spectrum. These data and the observed uptake of 3 mol of hydrogen upon catalytic hydrogenation suggested the dibenzoxanthene structures **29** and **30** for guayacanin.

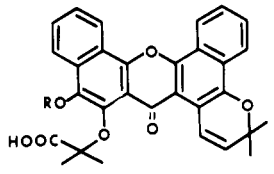
The attempted synthesis of a tetrahydro derivative of **29** and **30** in an acid-catalyzed condensation of nordihydrolapachenole (**19**) with dehydro-α-lapachonediol (**32**) and dehydro-β-lapachonediol (**33**), respectively (Scheme I), yielded **29** from both reactions. This equivocal result required the final determination of structure **29** for the natural guayacanin by x-ray crystallographic methods (Wong et al., 1976).

Scheme II

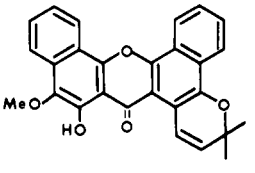


Guayin ($C_{30}H_{22}O_6$), isolated from the ether extract of *T. guayacan* heartwood, is nonphenolic and contains a highly conjugated keto and a lactone carbonyl group. The NMR spectrum of guayin showed a *gem*-dimethyl group, an isolated *gem*-dimethyl group, two coupled chromene protons, and eight aromatic protons.

A six-membered aryl lactone was established in the compound through alkaline methylation of **31** to the aromatic methyl ether, methyl ester. Alkaline hydrolysis of the ester yielded the carboxylic acid **34** which thermally decomposed, with the loss of $C_4H_8O_2$, to a monophenolic aromatic methyl ether (**35**) displaying a characteristic xanthone UV, spectrum with a significant bathochromic shift upon addition of aluminum chloride. These data indicated structure **35** for the monophenolic xanthone and structure **31** for guayin.

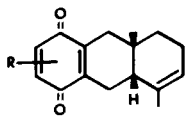


34, R = Me
36, R = H

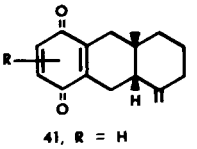


35

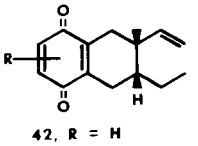
The biogenesis of guayin from guayacanin can be rationalized through the oxidative cleavage of the benzylically substituted chromene ring, followed by lactonization of the oxabutanoic acid **36** to the free phenolic hydroxyl. Using this biogenetic model, dihydroguayin (**39**) was successfully synthesized through nuclear chromanylation of the oxidatively cleaved and lactonized product **38** obtained from the dibenzoxanthene **37**. The latter was formed in an oxidative, aqueous, acid-catalyzed condensation of dehydro-α-lapachonediol (**32**) and naphthalene-1,4-diol (Scheme II).



40, R = H
43, R = OMe



41, R = H
44, R = OMe

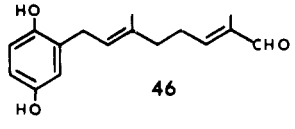


42, R = H
45, R = OMe

Investigation of *Cordia alliodora* heartwood extractive in relation to natural marine resistance has resulted in the

isolation and characterization of seven new geranylhydroquinone compounds (**46**, **48–53**). These new compounds are structurally related to phenolic terpenoids reported to possess antibacterial and/or antifungal properties (Hirai et al., 1967; Isobe and Goto, 1968; Suzuki and Nozoe, 1969, 1971).

Alliodorin ($C_{16}H_{30}O_3$) was the first constituent isolated from the ether extract of *C. alliodora* heartwood (Stevens et al., 1973). The IR and UV spectra of this compound indicated the presence of an α,β-unsaturated aldehyde group which was confirmed by the observed low-field aldehyde proton NMR resonance. The remainder of the NMR spectrum was characteristic of a geranyl-substituted phenol with two vinyl protons, a benzylic methylene, two methylene groups, and two vinyl methyl groups. These data suggested alliodorin to be a geranyl aldehyde (3 or 7 substituted) hydroquinone (**46** or **47**). Assignment of structure **46** for alliodorin was based upon an observed



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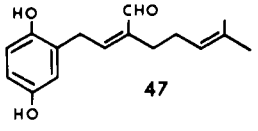

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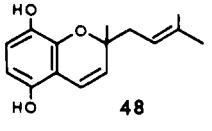
β-vinyl proton in the NMR of the Δ^3-chromene obtained from alliodorin upon cyclization in hot pyridine and consideration of the products obtained in a reverse aldol condensation of the compound. The trans,trans stereochemistry of the geranyl side chain was established through comparison of NMR characteristics with known compounds. The diacetate of alliodorin was successfully synthesized (Stevens and Jurd, 1975) through the selenium oxide oxidation of geranylhydroquinone diacetate.

Six other geranylhydroquinone derived components were isolated from the acetone extract of *C. alliodora* (**48–53**) (Manners and Jurd, 1977). Structural assignment for these compounds was based primarily on NMR spectral comparisons with those of previously described phenolic terpenoiods (Inouye et al., 1968; Manners et al., 1972).



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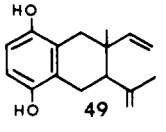

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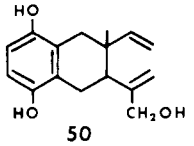
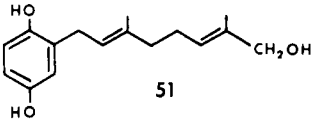


50



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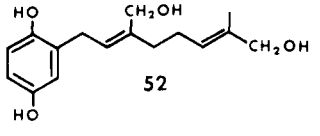

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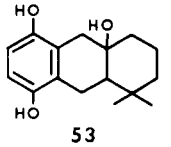
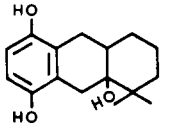


53

Confirmation of structural assignment by synthesis was obtained for three of the compounds (**48 49, 51**). Cordiachromene A (**48**) was synthesized from geranylhydroquinone by oxidative cyclization in boiling pyridine. Cordiaquinol C (**49**) was oxidized with silver oxide to the previously described cordiachrome C (**42**). Alliodorol (**51**) was synthesized from natural alliodorin (**46**) by sodium borohydride reduction in methanol.

Allioquinol C (**50**) and cordallinol (**52**) differ from **49** and **51** only by possessing an allyl alcohol group in place of a vinyl methyl. The distinct allyl alcohol methylene NMR resonances and those of the acetate derivative allowed close structural comparison of **50** and **52** with **49** and **51**, providing strong evidence in support of the **50** and **52** structural designations.

Cordiol A (**53**) was the most unique of the seven new compounds isolated from *C. alliodora*. NMR data for the compound and its di- and triacetate suggested two possible structures (**53** and **54**) which could not be resolved by the usual chemical or spectral methods. Designation of



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structure **53** for cordiol A was finally accomplished by considering the NMR coupling characteristics of the compound's single methine proton in an INDOR (Baker, 1962) experiment. The results of this experiment showed the methine proton to be coupled *only* to benzylic methylene protons and no other alkyl protons, thereby establishing structure **53** for cordiol A. The NMR coupling data also suggested cordiol A to exist with a trans diequatorial cyclohexane/cyclohexene ring junction.

While no biological activity data have yet been obtained for these compounds, they are of interest in connection with proposed biogenetic routes to phenolic terpenoids in *Cordia* species (Moir and Thomson, 1973). The new compounds support the biogenetic proposals and allow their expansion to include the initial formation of a geranyl phenol precursor capable of undergoing allylic methyl oxidations to the allyl alcohols (e.g., **51**, **52**). These alcohols may undergo further oxidations to the corresponding aldehydes (e.g., **46**) or they may undergo simple acid-catalyzed intramolecular cyclizations and rearrangements to yield the cordiaquinols (**49**), allioquinols (**50**), or cordiols (**53**). Subsequent oxidation of these cyclized compounds leads to the cordiachromes (**40–45**) and related compounds.

The examination of the heartwood extractives of the marine borer resistant woods *Dalbergia retusa*, *Tabebuia guayacan*, and *Cordia alliodora* has resulted in the characterization of several new and unique compounds. While the biological activity of many of these compounds has not yet been determined, their structural similarity to naturally occurring constituents with recognized biological activities suggests their possible importance in the protection of these woods in marine use. The varied structural character of these compounds also provides a reference point to the synthesis of potential biologically active chemical analogues as has already been successfully applied in the case of *D. retusa*.

Characterization of these compounds has also yielded important biogenetic information, while providing potentially useful new synthetic routes to complex phenolic compounds.

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Hot-Water Extractives of the Leaves of *Populus heterophylla* L.

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Fresh May leaves of swamp cottonwood (*Populus heterophylla* L.) were extracted with ethanol, and the hot water soluble portion was fractionated by means of ethyl acetate extraction and polyamide chromatography employing step-gradient elution with water and dilutions of ethanol. The results obtained for the leaves of this species from the *Leucoides* section of the *Populus* genus were entirely different from those obtained in the past from leaves of species of all other sections of this genus. Thus, salicin and salicortin were not found, but tremulacin was. *C*-Glycosyl flavones such as vitexin and orientin were found for the first time in the Salicaceae family. A new diterpenoid, heterophyllin, is the major component in the water-soluble extractives of these leaves.

In our continuing investigations on the components of the barks and leaves of *Populus* species, fresh leaves of swamp cottonwood (*P. heterophylla* L.) were gathered from a tree in Quitman County, Miss. in May and were covered immediately with ethanol. The wet leaves were extracted with ethanol by the Waring Blendor technique (Pearl and Darling, 1970), and all ethanol extracts were combined. The hot water soluble portion of the ethanol extractives was extracted fractionally with ethyl acetate, and the ethyl acetate soluble fractions were chromatographed on columns of polyamide and eluted with water, followed by 20% ethanol and 50% ethanol as described previously (Pearl and Darling, 1968, 1970). As in previous studies, all eluate fractions were monitored by thin-layer chromatography, concentrated to small volumes, allowed to stand, filtered if crystals separated, and finally freeze-dried. Weights of all fractions and of separated crystals were noted, and elution curves were obtained.

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RESULTS

Fractional ethyl acetate extraction of the hot water extractives representing 1230 g of original oven-dry leaf solids yielded 2.7% of the first extract (A), 2.7% of the second extract (B), and 1.4% of the third extract (C).

Data for the polyamide chromatograms of the three ethyl acetate fractions are presented in Figures 1–3. The weights noted in these figures are actual weights obtained experimentally from the sample aliquots applied to the polyamide column 50 mm in diameter and 80 cm in length. Major components under the peaks are noted on the figures. Quantitative data for the crystalline components isolated from the three ethyl acetate fractions are given in Table I.

The crystalline products isolated in the polyamide chromatograms of Figures 1, 2, and 3 and noted in Table I were quite different from most of the compounds isolated in previous studies of *Populus* species bark and leaf extractives. The most surprising fact was the absence of