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CONSTITUENTS OF *TABEBUIA GUAYACAN*
THE STRUCTURE OF GUAYACANIN

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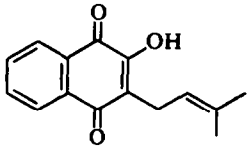
Abstract—The heartwood of *T. guayacan* has yielded tectol and a new, novel dibenz-xanthene derivative (guayacanin). The structure of guayacanin suggests its biogenetic derivation through the condensation of prenylnaphthalene quinols. The tetrahydro derivative of the xanthene was synthesized by an analogous acid catalyzed reaction of prenylnaphthalene quinol derivatives of lapachol and 1,4 naphthalene diol.

Long term marine exposure tests[1] have indicated the heartwood of the Central American tree, *Tabebuia guayacan* Hemsl., to be resistant to attack by marine boring organisms. At the invitation of the U.S. Naval Research Laboratory, an examination of the heartwood extractives of this tree has been undertaken in an effort to determine the identity of the natural protective constituent(s). With the exception of an early report indicating the presence of lapachol (**1**),[2] the constituents of *T. guayacan* have not previously been investigated. However, related *Tabebuia* species (*T. chrysantha* and *T. avellanedae*) have been examined by Thomson[3,4] and others,[5,6] leading to the identification of lapachol (**1**), several lapachol related naphthaquinones, and anthraquinones in this genus. The presence of deoxylapachol (**2**) has also been noted in an unidentified *Tabebuia* species.[7] Lapachol and several of these known naphthaquinone derivatives have been detected in the present investigation of *Tabebuia guayacan.* In addition, tectol (**3**), a colorless dimer previously obtained from teak wood (*Tectona* sp.),[8] and a new dimeric compound (*guayacanin*) have now been isolated and structurally identified.

Ether and acetone extracts of the wood gave a colorless dimer, $C_{30}H_{26}O_4$ (m.p. 212°), and a slightly yellow compound, $C_{30}H_{24}O_4$ (m.p. 225–226°). The colorless dimer contains two phenolic OH groups and forms diacetyl, dimethyl, and tetrahydro derivatives, whose m.ps closely correspond with those reported for tectol diacetate, di-O-methyl-tectol and tetrahydrotectol. Although the NMR spectrum of tectol(**3**) does not appear to have been reported, the NMR spectrum of the *T. guayacan* product (Experimental) is in complete accord with the tectol structure **3**.



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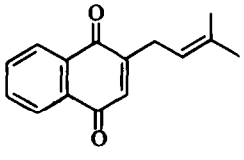

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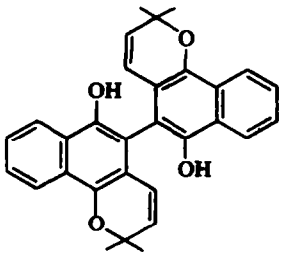
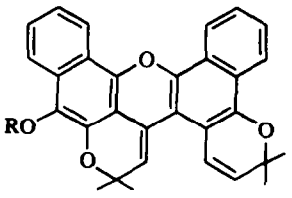


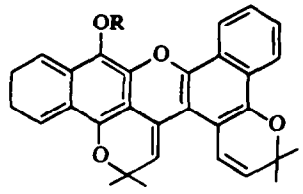
3

The yellow compound, $C_{30}H_{24}O_4$, for which we propose the name *guayacanin*, forms a monoacetate (m.p. 248–249°) and a monomethyl ether (m.p. 205°) and, therefore, contains a single phenolic OH group. Guayacanin yields immediately a characteristic deep purple pyrylium salt (λ_{max} 550 nm) on addition of HCl to its solution in ethanol (λ_{max} 405 nm). The 100 MHz NMR spectrum of guayacanin in $CDCl_3$ shows two chromene *gem* dimethyl groups as 6H singlets at δ1·56 and δ1·58, an aromatic OH as a broad singlet at δ5·60 and two vicinal vinylic (chromene) protons as doublets (J = 10 Hz) at δ5·73 and δ7·05. A non-coupled vinylic proton signal is at δ5·80 and eight aromatic protons are in three multiplet resonances at δ7·42–7·70 (4H), δ8·00–8·35 (2H) and δ8·36–8·65 (2H). These data are consistent with three possible structures, viz. **4a**, **5a**, or **6**, each containing a chromene ring and a benzylically substituted chromene ring. Guayacanin can be further formulated as **4a** or **5a** rather than **6**, on the basis of its catalytic hydrogenation. Compound **6** would be expected to consume three moles of hydrogen with benzylic ether hydrogenolysis to form tetrahydrotectol. Compounds **4a** or **5a**, on the other hand, should take up only two moles of hydrogen to form tetrahydroguayacanin **7a** or **8a**. Guayacanin, in fact, takes up only 2 moles of hydrogen to form the tetrahydro derivative. In accord with structure **7a** or **8a**, tetrahydroguayacanin in acid media undergoes facile oxidation to a compound which in turn forms a deep purple pyrilium salt with acids. This color reaction is characteristic of the conversion of xanthenes of xanthylium salts,[9,10] and this compound must therefore be isomeric with the parent phenol of **9** or **10**, and have a xanthene rather than a chromene double bond.

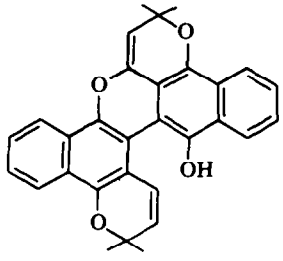
Inspection of the guayacanin structure (**4a** or **5a**) indicates the benzylically substituted chromene ring should be much more readily protonated (with formation of the stable tertiary carbonium ion) than the second, unsubstituted chromene ring. This observation was used to prepare a crystalline dihydro derivative, **9** or **10**, of guayacanin by selective reduction via an acid-catalyzed hydride ion transfer reaction between O-



4a: R = H
b: R = Ac
c: R = Me



5a: R = H
b: R = Ac
c: R = Me



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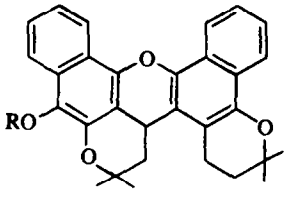
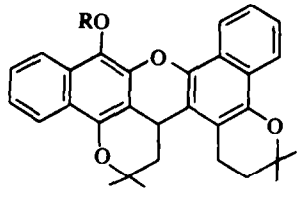
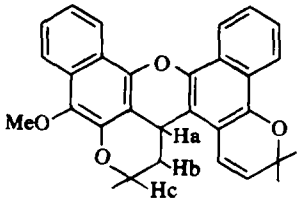


7a: R = H
b: R = Ac
c: R = Me



8a: R = H
b: R = Ac
c: R = Me



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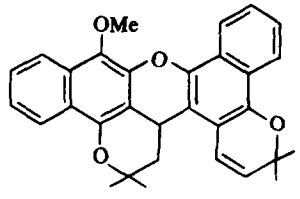

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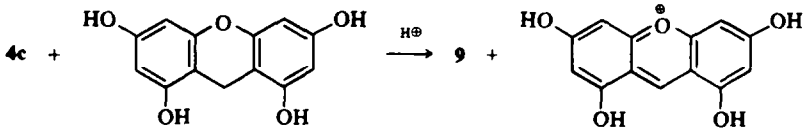
methylguayacanin and 1,3,6,8-tetrahydroxy xanthene: e.g.,



The coupling of the benzylic H_a proton with geminally coupled allylic protons, shown in Fig. 1, confirms structure **9** or **10** for this dihydro derivative, and, therefore, structure **4a** or **5a** for guayacanin.

Synthesis of tetrahydroguayacanin

The inability to specifically formulate guayacanin as either **4a** or **5a** on the basis of its chemical and spectral properties, prompted an attempt to synthesize the two tetrahydro-structures **7a** and **8a**, one of which should then be identical with the hydrogenated natural product. Consideration of the two possible guayacanin structures suggests the molecule is biosynthetically derived by a condensation of the chromenes derived from the oxidative cyclization of the quinols corresponding to lapachol (**1**) and deoxylapachol (**2**). On this basis, a biogenetic type synthesis of tetrahydroguayacanin was devised which would involve an acid catalyzed condensation of dehydro-α or β-lapachone diol (**11a** and **12a**), from lapachol,[11] with nordihydrolapachenole (**13**) (Scheme 1).

As models for this synthetic approach, it was shown that **11a** and **12a** condensed readily with naphthalene-1,4 diol in aqueous formic acid to give, after acetylation, the analogous crystalline diacetates **14** and **15**.

Extension of these model condensations to the synthesis of tetrahydroguayacanin required a convenient source of nordihydrolapachenole **13**. This had been previously prepared in low yield (6%) by the Friedel-

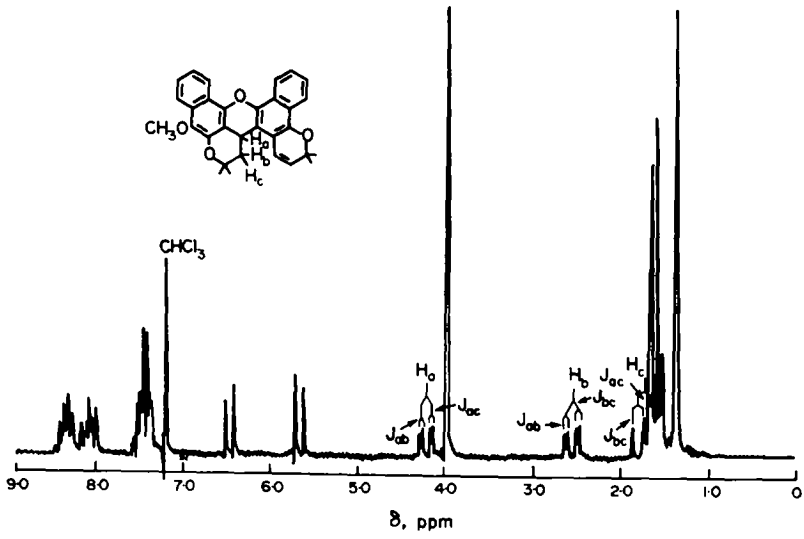
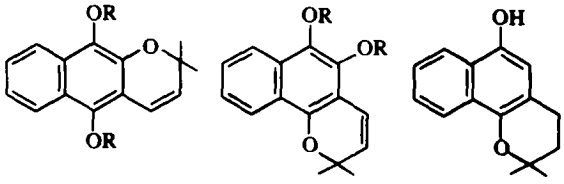


Fig. 1. The 100 MHz NMR spectrum of O-methyl dihydroguayacanin in $CDCl_3$.



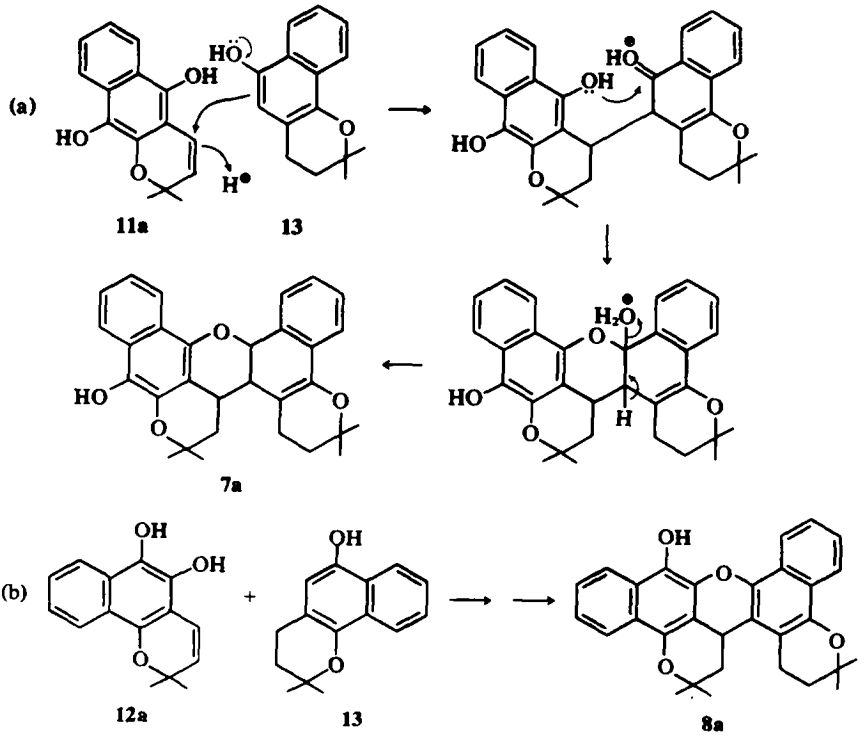
11a: R = H
b: R = Ac

12a: R = H
b: R = Ac

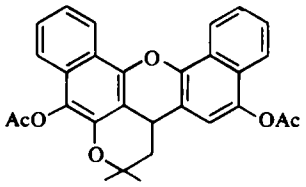
13

Crafts reaction of 1-bromo-3-methylbut-2-ene with naphthalene-1,4-diol[4] and by the reductive cyclization of synthetic deoxylapachol[4] (14·7% overall yield). Better yields (19%) of **13** were now obtained in a one-step reaction involving a condensation (under N_2) of naphthalene-1,4-diol with 3-methylbut-2-ene-3-ol in aqueous formic acid containing ascorbic acid. Nordihydrolapachenole **13** readily condensed with **11a** in aqueous formic acid (under N_2) to yield a colorless crystalline compound (43% yield) which was identical in all respects with tetrahydroguayacanin from the natural source. The analogous reaction of **12a** with **13** gave a colorless crystalline compound (8% yield) which, surprisingly, also proved to be identical with the naturally derived tetrahydroguayacanin.

Thus, although tetrahydroguayacanin has been successfully synthesized, it is clear that a rearrangement of a condensed intermediate of dehydro α- or β-lapachone



Scheme 1.



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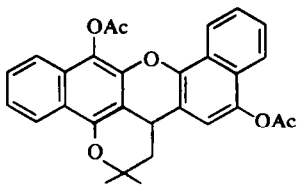


15

diol, as observed by Ettlinger[12] for α- and β-lapachone in aqueous acids, occurs in either the condensation of **13** with **11a** or of **13** with **12a** and, therefore, that the synthesis does not unambiguously establish guayacanin as **4a** or **5a**.†

The structure of guayacanin was unequivocally established as **4a** by X-ray crystallographic analysis. The X-ray molecular structure determination‡ is illustrated in the ORTEP[13] drawing shown in Fig. 2. There are four possible conformations of the molecule defined by the orientation of the two *gem* dimethyl groups of the chromene rings.

The H(5)–H(6) interaction leads to considerable stress in the molecule which results in a twist about the C(14)–C(15)–C(16) bond, so that the C(16) is forced considerably below the molecular plane as viewed in Fig. 2. C(11) is displaced 0·33 Å above the plane formed by C(1), C(12), C(13), C(14) and C(26). Both of these displacements increase the H(5)–H(6) distance, thus reducing the interaction between these two H atoms.

The easy synthesis of nondihydrolapachenole, and tetrahydroguayacanin in aqueous media provides strong support for the hypothesis that 1,4 naphthaquinone (or

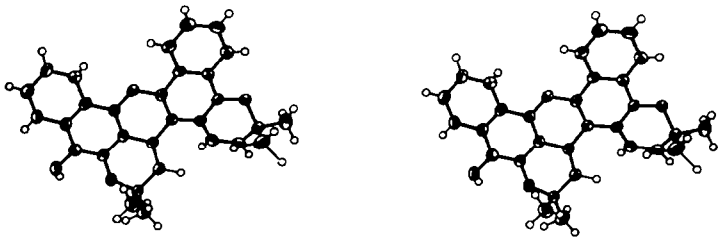
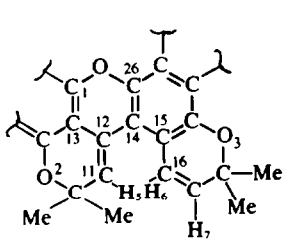


Fig. 2. The ORTEP X-ray crystallographic drawing of guayacanin.

The observed conformer appears to be dictated primarily by the steric interference between the two H atoms H(5) and H(6), shown in partial structure **4a**.§ Inspection of molecular models shows that the distance between these two H atoms is a maximum when the axial Me groups are on the same side of the molecular plane. It is not apparent from models why the conformation illustrated in Fig. 2 is more stable than that with the two axial Me groups oriented away from the viewer. In the two alternative conformations, where the two axial Me groups are placed on opposite sides of the plane, the H(5)–H(6) distance is very small and, therefore, these conformations should be unstable.



4a (partial)

quinol) is an intermediate in the biosynthesis of naphthaquinone derivatives in higher plants.[14] Furthermore, we have observed that prenyl naphthalene diols (**11a**, **12a**, **13**) undergo condensation even more readily than the unsubstituted naphthalene-1,4-diol itself, suggesting that these prenylated diols may be the intermediate biogenetic precursors of natural, dimeric prenylated naphthaquinone derivatives.

EXPERIMENTAL

All m.ps are uncorrected. NMR spectra were determined on a modified Varian HA-100 instrument in $CDCl_3$ with a TMS internal standard. Mass spectral analysis were determined on a CEC 110 high resolution mass spectrophotometer. IR data were obtained on a Perkin Elmer model 237B grating IR spectrophotometer. UV spectra were obtained on a Cary model 15 recording specterphotometer.

Extraction. Hammermilled *Tabebuia guayacan* Hemsl. heartwood (5 kg) was successively hot solvent extracted with petroleum ether 30–60°, ethyl ether, acetone and methanol. Constituents from the ethyl ether and acetone extracts will be primarily considered in this investigation.

Ethyl ether extract

The hot ether extraction yielded 90 g of ether solubles and 35 g of insoluble residue upon cooling. The insoluble residue contained some lapachol. The ether solubles were concentrated to dryness, warmed with chloroform, and filtered.

Guayacanin (**4a**). The chloroform filtrate was cooled and the solid product was recrystallized from acetone-methanol to yield **4a** as yellow cubic crystals, m.p. 225–226° (2·01 g; 0·04%). (Found: C, 79·7; H, 5·43. Calc. for $C_{30}H_{24}O_4$: C, 80·3; H, 5·39%); UV spectrum λ_{max}^{EtOH} nm (log ε), 405 (3·95), 385 (3·95), ~365 (3·86), ~295 (4·31), ~270 (4·67), 257 (4·76), ~251 (4·73), 238 (4·72), 218 (3·82). IR spectrum (Nujol): 3380 cm^{-1}, m; 1655 cm^{-1}, s; 1624 cm^{-1}, w; 1453 cm^{-1}, s; 1449 cm^{-1}, s; 1410 cm^{-1}, s; 1360 cm^{-1}, m;

†In the text we have reported the reaction of naphthalene-1,4-diol with **11a** and **12a** to produce acetates **14** and **15** respectively. In one instance, however, this same reaction produced the opposite acetates (naphthalene-1,4-diol with **11a** and **14a** yielded **15** and **14** respectively). In this reaction, it is clear, that the same rearrangement observed in the synthesis of tetrahydroguayacanin (reaction of **12a** with **13** has occurred. We have not, as yet, been able to duplicate this exceptional reaction.

‡Detailed X-ray data will be published elsewhere.

§The numbering system is that used in the X-ray investigation.

1345 cm^{-1}, m; 1302 cm^{-1}, m; 1260 cm^{-1}, m; 1240 cm^{-1}, m; 1135 cm^{-1}, m; 1125 cm^{-1}, m; 1085 cm^{-1}, s; 1010 cm^{-1}, s; 910 cm^{-1}, m; 765 cm^{-1}, s. NMR spectrum: 6H, s, δ1·56; 6H, s, δ1·58; 1H, s, δ5·60; 1H, d, J = 10 Hz, δ5·73; 1H, d, J = 10 Hz, δ7·05; 1H, s, δ5·80; 4H, m, δ7·42–7·70; 2H, m, δ8·05–8·35; 2H, m, δ8·36–8·65.

Guayacanin acetate (**4b**). Acetylation of **4a** (Ac_2O/pyr) produced **4b** as colorless needles (MeOH), m.p. 248–249°. (Found: C, 78·3; H, 5·42. Calc. for $C_{32}H_{26}O_5$: C, 78·35; H, 5·34%), NMR spectrum: 6H, s, δ1·54; 6H, s, δ1·59; 3H, s, δ2·48; 1H, d, J = 10 Hz, δ5·73; 1H, s, δ5·83; 1H, d, J = 10 Hz, δ7·02; 5H, m, δ7·40–7·85; 1H, m, δ8·18–8·30; 2H, m, δ8·37–8·60.

O-Methyl guayacanin (**4c**). Methylation of **4a** (dimethyl sulfate/acetone) yielded **4c**, light yellow needles (MeOH), m.p. 205°. (Found: C, 80·3; H, 5·66. Calc. for $C_{31}H_{26}O_4$: C, 80·5; H, 5·67%); NMR spectrum: 12H, s, δ1·58; 3H, s, δ4·05; 1H, d, J = 10 Hz, δ5·71; 1H, s, δ5·82; 1H, d, J = 10 Hz, δ7·03; 4H, m, δ7·43–7·70; 2H, m, δ8·00–8·30; 2H, m, δ8·33–8·60.

Tetrahydroguayacanin **7a**. Guayacanin **4a** (0·1 gm) was catalytically reduced in EtOAc, 5% Pd on C, 47 psi, 28 hr, with a two mole uptake of H_2. The hydrogenated soln was filtered, concentrated and recrystallized (acetone/methanol) to yield **7a** as white plates, m.p. 249–250° (0·08 g). (Found: C, 79·5; H, 6·17. Calc. for $C_{30}H_{28}O_4$: C, 79·63; H, 6·24%); IR spectrum (Nujol): 3555 cm^{-1}, m; 1606 cm^{-1}, m; 1585 cm^{-1}, s; 1495 cm^{-1}, s; 1410 cm^{-1}, s; 1385 cm^{-1}, s; 1265 cm^{-1}, m; 1255 cm^{-1}, m; 1190 cm^{-1}, s; 1160 cm^{-1}, s; 1120 cm^{-1}, m; 1110 cm^{-1}, s; 1060 cm^{-1}, s; 980 cm^{-1}, m; 770 cm^{-1}, m; 760 cm^{-1}, NMR spectrum: 6H, s, δ1·37; 3H, s, δ1·53; 3H, s, δ1·68; 4H, m, δ1·60–2·03; 2H, m, δ2·58–3·04; 1H, dd, J = 12 Hz, 3 Hz, δ4·20; 1H, s, δ5·52; 4H, m, δ7·36–7·60; 2H, m, δ8·00–8·26; 2H, m, δ8·28–8·56.

Tetrahydroguayacanin acetate (**7b**). **7a** was acetylated (Ac_2O/pyr) to yield **7b** as colorless needles (MeOH), m.p. 244–245°. (Found: C, 77·6; H, 6·04. Calc. for $C_{32}H_{30}O_5$: C, 77·71, H, 6·11%); NMR spectrum: 3H, s, δ1·35; 3H, s, δ1·37; 3H, s, δ1·54; 3H, s, δ1·65; 3H, m, δ1·72–2·05; 3H, s, δ2·47; 3H, m, δ2·60–3·05; 1H, dd, J = 11·5 Hz, 3 Hz, δ4·21; 5H, m, δ7·39–7·80; 1H, m, δ8·13–8·30; 2H, m, δ8·20–8·53.

O-Methyl-tetrahydroguayacanin (**7c**). **7a** was methylated (dimethyl sulfate/acetone) to yield **7c** as fine pale yellow needles (MeOH), m.p. 225–226°. (Found: C, 79·8; H, 6·47. Calc. for $C_{31}H_{30}O_4$: C, 79·8; H, 6·48%); NMR spectrum: 3H, s, δ1·38; 3H, s, δ1·43; 3H, s, δ1·55; 3H, s, δ1·71; 3H, m, δ1·60–2·01; 3H, m, δ2·60–3·03; 3H, s, δ4·02; 1H, dd, J = 11·5 Hz, 3 Hz, δ4·22; 4H, m, δ7·40–7·65; 2H, m, δ8·00–8·26, 2H, m, δ8·33–8·54.

O-Methyl-dihydroguayacanin (**9**). **4a** (50 mg) in 80% aqueous formic acid (15 ml), was treated with 10% HCl aq (1 ml) and 1,3,6,8-tetrahydroxyxanthene (150 mg), and warmed until solid began to precipitate. Water was added and the mixture was extracted with ether. The ether soln was washed with water and sat. $NaHCO_3$ aq, dried and concentrated with MeOH to yield pink needles, m.p. 223–224°. (Found: C, 80·1; H, 6·23. Calc. for $C_{31}H_{28}O_4$: C, 80·15; H, 6·08%); NMR spectrum: (Fig. 1): 6H, s, δ1·40; 3H, s, δ1·62; 3H, s, δ1·68; 1H, t, J = 13Hz, δ2·75; 1H, dd, J = 13 Hz, 3 Hz, δ2·56; 3H, s, δ3·99; 1H, dd, J = 13 Hz, 3 Hz, δ4·20; 1H, d, J = 10 Hz, δ5·67; 1H, d, J = 10 Hz, δ6·47; 4H, m, δ7·32–7·60; 2H, m, δ7·98–8·22; 2H, m, δ8·24–8·48.

Acetone extract

A portion of this extract was concentrated to dryness, and chloroform was added. The mixture was boiled, and filtered through celite. The soluble portion was evaporated to dryness, and MeOH was added. Tectol (**3**) crystallizes from the cooled MeOH soln as white granular crystals, m.p. 212° (d). (Found: C, 80·1; H, 5·79. Calc. for $C_{30}H_{26}O_4$: C, 79·98; H, 5·82%); NMR spectrum: 12H, s, δ1·51; 2H, br, s, δ5·06; 2H, d, J = 10 Hz, δ5·55; 2H, d, J = 10 Hz, δ5·96; 4H, m, δ7·48–7·64; 4H, m, δ8·15–8·22. Acetylation (Ac_2O/pyr) gave *tectol diacetate* as white needles (MeOH), m.p. 205–205°. Methylation (dimethylsulfate/acetone) gave *tectol dimethyl ether* as needles (MeOH), m.p. 216–217°. Observed physical and spectral properties, with the exception of NMR, of **3** and its derivatives are in close agreement with recorded values.[4]

Synthesis

Dehydro-α and β-lapachone diacetates (**11b** and **12b**). The diacetates **11b** and **12b** were synthesized from **1** (40 g) according to Hooker.[11] The synthesis yielded *dehydro-α-lapachone diacetate* **11b** (19·9 g) as white needle clusters (MeOH), m.p. 131–132°. (Found: C, 70·0; H, 5·56. Calc. for $C_{19}H_{18}O_5$: C, 69·92, H, 5·65%); NMR spectrum: 6H, s, δ1·42; 3H, s, δ2·36; 3H, s, δ2·38; 1H, d, J = 10 Hz, δ5·82; 1H, d, J = 10 Hz, δ6·46; 2H, m, δ7·20–7·45; 2H, m, δ7·53–7·78. The reaction also yielded *dehydro-β-lapachone diacetate* **12b** (9·8 g) as colorless balls (MeOH), m.p. 129°. (Found: C, 70·0; H, 5·60. Calc. for $C_{19}H_{18}O_5$: C, 69·92; H, 5·65%); NMR spectrum: 6H, s, δ1·48; 3H, s, δ2·30; 3H, s, δ2·37; 1H, d, J = 10 Hz δ5·68; 1H, d, J = 10 Hz, δ6·33; 2H, m, δ7·30–7·52, 2H, m, δ7·53–7·72.

Nordihydrolapachenole (**13**). 2-Methyl-3-butene-2-ol was slowly added dropwise to a warm (85°) soln of naphthalene-1,4-diol (20 g) in 70% aq. formic acid (500 ml) containing ascorbic acid (5 g) (N_2). After 30 min, water was added, the mixture was cooled and the solid product was collected. A soln of this product in ether was diluted with MeOH and concentrated to yield a crystalline dichroman. The MeOH filtrate from the dichroman was evaporated to an oil. A soln of the oil in hexane gave, upon concentration and cooling, **13** as colorless needles, m.p. 126–128° (5·0 g; 18·8%) (M.S. observed M^+: 228·1164. Calc. for $C_{15}H_{16}O_2$: 228·1150). NMR spectrum: 6H, s, δ1·27; 2H, t, J = 5 Hz; 2H, t, J = 5 Hz; 1H, br, s, δ5·03; 1H, br, s, δ6·47; 2H, m, δ7·30–7·52; 2H, m, δ7·43–8·828.

Diacetate (**14**). A soln of **11b** (1·0 g) in a minimal amount of MeOH was treated with 10% NaOHaq (10 ml), containing sodium dithionite (3·0 g), warmed on a steam bath for 2 min, acidified with dil HCl aq and cooled. The solid product (**15a**) collected by gravity filtration (suction filtration accelerates oxidation) was washed with 5% aqueous ascorbic acid and used immediately without further purification. It was added to a soln of naphthalene-1,4-diol (0·80 g) in warm 80% aqueous formic acid (30 ml) and heated (stirring) for 2 hr. Excess of water was added and the mixture was extracted with ether. Evaporation of the dried ether extract gave a residual solid which was acetylated by warming with Ac_2O/pyridine. Addition of water, extraction with ether, drying and concentration with MeOH yielded colorless granular crystals **14**, m.p. 276–277°; (Found: C, 74·0; H, 4·93. Calc. for $C_{29}H_{22}O_6$: C, 74·67; H, 4·75%); NMR spectrum: 6H, s, δ1·55; 6H, s, δ2·47; 1H, s, δ5·79; 1H, s, δ7·42; 6H, m, δ7·40–7·85; 2H, m, δ8·30–8·60.

Diacetate (**15**). **12b** was deacetylated as for **11b**, the solid product (**12a**) was immediately added to a soln of naphthalene-1,4-diol in 80% aqueous formic acid, heated for 2 hr, water added, extracted with ether, and acetylated. **15** was crystallized (acetone/methanol) as yellow needles, m.p. 249–250°. (Found: C, 74·6; H, 4·88. Calc. for $C_{29}H_{22}O_6$: C, 74·67; H, 4·75); NMR spectrum: 6H, s, δ1·63; 3H, s, δ2·47; 3H, s, δ2·62; 1H, s, δ5·81; 1H, s, δ7·45; 6H, m, δ7·46–7·90; 2H, m, δ8·10–8·35.

Tetrahydroguayacanin (**12a**). **11a** (2 gm) was immediately added to **13** (2 g) in 80% aq. formic acid containing ascorbic acid (5 g) (N_2), reacted for 2 hr, the mixture poured into water, cooled overnight and the solid filtered off and washed with water. The solid was dissolved in acetone, concentrated and crystallized (MeOH) as colorless granular crystals m.p. 251–253° (1·7 g; 43%). (Found: C, 79·48; H, 6·2. Calc. for $C_{30}H_{28}O_4$: C, 79·62: H, 6·24%). The physical and spectral properties (m.m.p., NMR, IR, UV) were identical to the tetrahydroguayacanin obtained in the catalytic reduction of guayacanin.

Attempted synthesis of **8a**. **12a** was reacted with **13** exactly as in the previously described reaction (**11a** and **13**). The reaction was worked up to yield granular crystals (acetone/methanol) m.p. 251–253° (8% yield). (Found: C, 79·5; H, 6·27. Calc. for $C_{30}H_{28}O_4$: C, 79·62; H, 6·24%). The physical and spectral properties were identical to synthetic and natural **7a**. This product was therefore designated **7a** rather than **8a**.

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