Phytochemistry, 1979, Vol. 18, pp. 1495–1500. © Pergamon Press Ltd. Printed in England. 0031-9422/79/0901-1495 $02.00/0

PHENOLIC AND TERPENOID HEARTWOOD CONSTITUENTS OF *LIBOCEDRUS YATEENSIS**

HOLGER ERDTMAN† and JURAJ HARMATHA‡

†Department of Organic Chemistry, Institute of Technology, S-100 44 Stockholm, Sweden; ‡ Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Science, 16610 Prague, Czechoslovakia

(*Received* 30 *January* 1979)

Key Word Index—*Libocedrus yateensis*; Cupressaceae; terpenoid aromatic acids; (−)-cryptomerione; 1,4-bis-(*p*-hydroxyphenyl)-butadiene; yateresinol; yatein; hinokiresinol.

Abstract—The heartwood of *Libocedrus yateensis* has been found to contain cumic acid and several related hydroxy-acids so far not reported from any conifer, a sesquiterpene (−)-cryptomerione and (*E*,*E*)-1,4-bis-(*p*-hydroxyphenyl)-buta-1,3-diene, both known from Taxodiaceae. Further constituents were 'conioids'; hinokiresinol and a related ketone, probably dehydroagatharesinol, a lignan, 'yatein', and a novel diphenylbutane derivative, yateresinol. Structural relations between conioids, lignans and diphenylbutanes are discussed.

INTRODUCTION

The conifer families Taxodiaceae and Cupressaceae, forming according to Pulle [1] (cf. Florin [2]) the order Cupressales, pose many difficult taxonomic problems. An example is Endlicher's disjunct genus *Libocedrus* (Cupressaceae). Pilger (1926) divided *Librocedrus* into two subgenera, the northern hemispheric *Heyderia* (K. Koch) Pilg. (now *Calocedrus* Kurz), embracing three species, and the southern *Eulibocedrus* Pilg. From the latter, Florin (1930) segregated the Chilean *Libocedrus uvifera* (D. Don) Pilg. (now *Pilgerodendron uviferum* (D. Don) Florin) and in 1954 [3], *Libocedrus chilensis* (D. Don) Endl. (now *Austrocedrus chilensis* (D. Don) Florin et Boutelje).

Li (1953) [4] recognized four genera, *Heyderia* (placed in Endlicher's tribe *Thujopsis*), *Pilgerodendron*, *Papuacedrus* (3 species, New Guinea) and *Libocedrus* (including the above *Austrocedrus*). The three latter form with *Diselma*, *Widdringtonia*, *Neocallitropsis* and *Octoclinis* the tribe *Libocedreae* Li of Saxton's subfamily Callitroideae. Florin considered that the three New Caledonian and the two New Zealand *Libocedrus* species might be subdivided into two sections. All these genera are small or monotypic and this is one of the reasons why they are difficult to classify.

We have tried to find chemical characteristics which might become useful in future taxonomic deliberations and have therefore studied the heartwood constituents [5] of the *Widdringtonia* species, *Pilgerodendron*, *Diselma*, and *Austrocedrus*, of Libocedreae, and *Fitzroya* [6] and a few *Callitris* [5] species of the tribe Actinostrobeae Endl. Tropolones, so common in the northern genera of Cupressaceae, were only found in *Austrocedrus*. There is one report [7] on the occurrence of tropolones in *Papuacedrus* (*P. torricellensis*) and one on their absence in *Libocedrus bidwillii* (N. Zealand) [8].

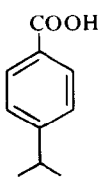
An opportunity arose in 1960 to include one of the New Caledonian *Libocedrus* species when, together with M. Luc Chevalier, Nouméa, an expedition was made to Rivière Bleue, a tributary of the Yaté river, where an unusually tall (6 m high) specimen of *L. yateensis* Guillaumin was sacrificed. Voucher specimens were deposited in Musée Néo-Calédonien, Nouméa, and a wood sample also in the collections of the Forest Products Research Laboratory, Princes Risborough, Aylesbury, Bucks., England.

RESULTS

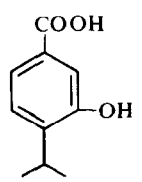
The wood of *Libocedrus yateensis* is dense [9] and its heartwood turns red on storing.

Extraction 1. The heartwood furnished a dark methanol extract (18.5%), part of which consisted of amorphous products, insoluble in ether. The ether-soluble fraction

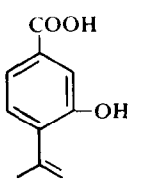
* Part 58 in the series "The Chemistry of the Order Cupressales". For Part 57 see ref [19]; for Part 56 see (1969) *Acta Chem. Scand.* **23**, 2024.



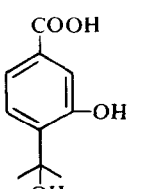
1



2



3



4

(13.5%) was a dark oil from which acid (1.9%), phenolic (3%) and neutral fractions (7.5%) were obtained by standard methods. *Extraction* 2. Extraction with hot water gave an extract from which an ether-soluble fraction (A, 2%) was obtained.

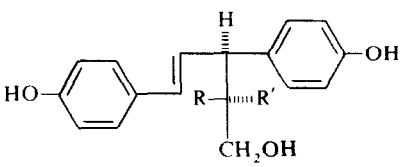
From the acid fraction of extraction 1, four compounds were isolated: 4-isopropylbenzoic acid (**1**), 3-hydroxy-4-isopropylbenzoic acid (**2**), 3-hydroxy-4-isopropenylbenzoic acid (**3**) and 3-hydroxy-4-(α-hydroxyisopropyl)-benzoic acid (**4**).

A small fraction containing less strongly acidic components furnished a minute amount of a crystalline phenolic ketone (DNP). It was not obtained quite pure (TLC), but the mass spectral investigation strongly indicated that the main constituent was 'dehydroagatharesinol' (**5b**).

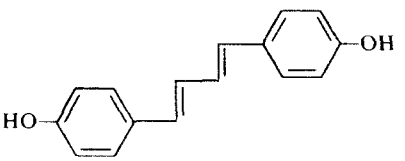
From the phenol fraction, a sparingly soluble, high melting compound $C_{16}H_{14}O_2$ was isolated. UV and IR spectra showed it to be a highly conjugated phenol. It was identified as (*E,E*)-1,4-bis-(*p*-hydroxyphenyl)-buta-1,3-diene (**6**).

of material precluded further investigation of these products. None of the acidic fractions gave any positive tests for the presence of tropolones.

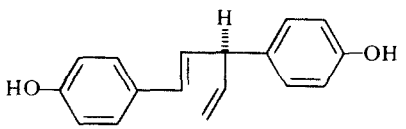
The neutral fraction from extraction 1 was likewise very complex, containing many compounds of terpenoid nature as well as at least one aromatic substance. Chromatography furnished an oily ketone, $C_{15}H_{22}O$ (0.85%), which turned out to be identical with (−)-cryptomerione (**9**) isolated from *Cryptomeria japonica*, Taxodiaceae, by Nagahama [11] and synthesized by Hodgson *et al.* [12] and others. According to TLC, the non-ketonic fraction contained many compounds. The most prominent of them was a liquid sesquiterpene alcohol, $C_{15}H_{22}O$. A more polar compound called yatein, $C_{22}H_{24}O_7$, $[\alpha]_D^{20}$ −28.4° ($CHCl_3$), was isolated from the non-ketonic fraction. It could not be obtained crystalline but gave a crystalline tribromo derivative and, on reduction with $LiAlH_4$, a crystalline diol. Analytical data and spectral properties indicated that yatein was a lignan lactone possessing one methylenedioxy group attached to one of the aromatic nuclei and



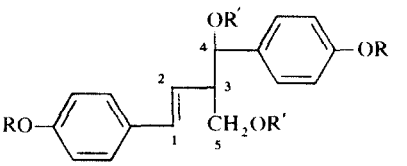
5a R = H, R' = OH
5b R + R' = O



6



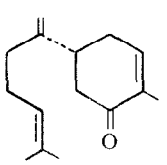
7



8a R = Me; R' = H
8b R = Me; R' = Ac
8c R = R' = H

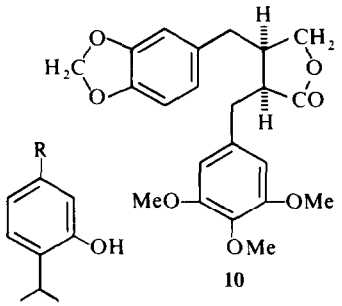
Another compound isolated from this fraction was, according to TLC, hinokiresinol (**7**) [10]. It was obtained crystalline although not quite pure. From this product pure hinokiresinol dimethyl ether was prepared. Hinokiresinol was the major constituent isolated from the phenol fraction. TLC indicated the presence of several minor products none of which could be isolated in a quantity sufficient for a closer examination.

The ether-soluble fraction A from extraction 2 was methylated and the product subjected to column chromatography. Small amounts of several crystalline compounds, $C_{22}H_{24}O_6$, $C_{22}H_{26}O_6$ and $C_{22}H_{26}O_8$, all apparently of lignan type (IR, NMR), were isolated. Another compound was a dimethyl ether $C_{17}H_{16}O_2(OMe)_2$. The corresponding phenol called yateresinol (**8c**) is an isomer of agatharesinol (**5a**). A detailed ^1H NMR analysis, however, showed the dimethyl ether to be a derivative of 1,4-diphenylbutane possessing the structure **8a**. This conclusion was corroborated by the similar analysis of its product of acetylation (**8b**) and the mass spectral fragmentation. The acetate was more easily soluble and gave a better NMR spectrum. The paucity three methoxyl groups to the other. The orientation of the benzyl groups followed from a comparison of the mass spectra of the diols obtained by reduction of yatein with $LiAlH_4$ and with $LiAlD_4$. This method [13] is very useful for the structural elucidation of this type of lignan lactones.

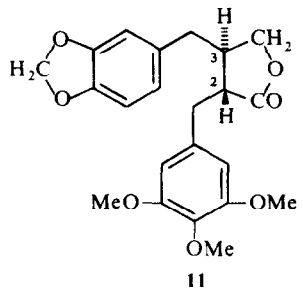


9

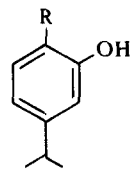
It was noted that, during their studies on the lignan glucoside podorhizol, Kuhn and v. Wartburg [14] had obtained (2*S*, 3*R*)-*cis*-dihydroanhydropodorhizol **10**, mp 89–93°, $[\alpha]_D$ +71.2° ($CHCl_3$), which is an isomer of yatein. Its structure was firmly established. The Swiss authors kindly sent us a generous sample of this compound. When treated with alkali, it was isomerized (in position 2) to yatein (**11**).



10



11



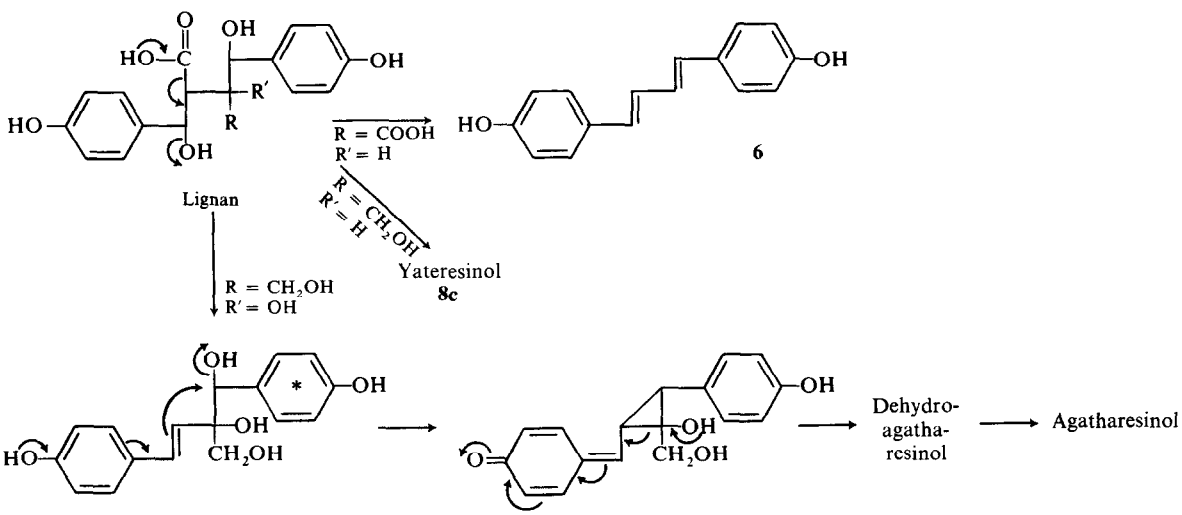
12 13

Yatein was isolated by us in 1969. Only recently [15] we became aware of the fact that this compound ('compound 1') had been isolated from *Bursera schlechtendalii* (Burseraceae) and assigned structure **11** (with reversed configuration at C-2 and C-3) [16]. Nishibe *et al.* [17] prepared 'compound 1' (**11**) by alkaline isomerization of compound **10**. This will be further discussed in a forthcoming paper [13].

DISCUSSION

Non-cyclized lignan lactones are common conifer constituents and yatein has only limited taxonomic interest. Phenols of the C_{17} type, such as hinokiresinol as well as yateresinol and the diphenylbutadiene (**6**), seem to be more important. At the sixth Annual Meeting of the Phytochemical Society of North America, Austin, Texas, 6–8 August, 1966, H. L. Hergert lectured on 'A Chemotaxonomic Comparison of Bald Cypress, Redwood and *Cryptomeria*'. In the stencilled abstract he stated: "A chromatographic comparison of the woods of these species and those of the related trees, *Metasequoia*, California giant redwood and Pond cypress indicated that sugiresinol, hydroxysugiresinol and 1,4-bis-(*p*-hydroxyphenyl)-butadiene are common to all." These important observations have not been published. When in 1969 we wrote to Dr. Hergert about the isolation of the butadiene derivative from *L. yateensis*, he kindly sent us a sample for comparison. The priority of the discovery of this novel conifer constituent goes to Hergert. The isolation of this phenol from *Libocedrus yateensis* is the first from outside Taxodiaceae.

It is rather surprising that it has escaped observation for so long. It crystallizes readily and gives a sparingly soluble acetate. The isolation of the C_{17} phenols is mostly cumbersome—especially from aged wood. They are easily oxidized to amorphous products and frequently co-occur. The very acid-sensitive [18] sugi- and hydroxy-sugiresinols may actually be artefacts, slowly formed in the wood from agatharesinol and sequirin, respectively. The formation of sugiresinol during large scale extractions of the wood of *Athrotaxis selaginoides* has been reported [19]. Kai [20] referred to the C_{17} phenols as "a sort of nor-lignans" whilst Hatham and Whiting [21] called them "non-lignans". There is presently a tendency to classify many natural products of widely different structural types as lignans, simply because they—like lignans and lignins [22]—are believed to be formed from C_6–C_3 precursors by oxidative coupling. To our minds this is inappropriate and we propose the generic name conioids for hinokiresinol and its allies.



* Or quinone methide structure.

Scheme 1.

Nevertheless, one can imagine a common denominator.* Structural relations between lignans, yateresinol and the diphenylbutadiene on one side and all known conioids on the other can be visualized as schematically indicated—for agatharesinol—in Scheme 1. (For earlier biogenetic hypotheses see refs. [23] and [24].)

True lignans possessing monohydroxylated phenyl groups are still rare [25]. In this connexion it is of interest that the lignan pinoresinol gave (*E,E*)-1,4-bis-(4-hydroxy-3-methoxyphenyl)-buta-1,3-diene when subjected to a 'sulfate cook' (NaOH, NaSH) [26]. The yield was poor, however. Conioids occur in several of the Taxodiaceae, in one *Chamaecyparis* and in one *Agathis* species but are so far not known to occur in conjunction with tropolones.

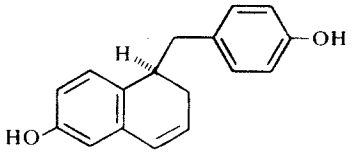
When seriously searched for, carvacrol has almost always been found to co-occur with tropolones. Conversely, lack of tropolones in species of otherwise tropoloniferous genera such as *Chamaecyparis* and *Juniperus* seems to run parallel with lack of carvacrol [5]. In *Libocedrus yateensis* we found conioids but neither carvacrol nor tropolones.

The aromatic acids **1**–**4** have not previously been found in any conifers. Their structural relations to the conifer tropolones and to the rare acids of thujic–chamic acid type are obvious. Most interesting is the location of the phenolic hydroxyl group of the acids **2**–**4** in *o*-position to the isopropyl group as in thymol (**12**, R = Me) but opposed to carvacrol (**13**, R = Me). As far as we are aware, thymol has only been claimed to occur—together with carvacrol—in the tropoloniferous 'Arisan hinoki' (*Chamaecyparis taiwanensis* Mas. et Suzuki), Formosa. It was probably only observed as a spot on a TLC plate [27].

It should, however, be mentioned that *o*-isopropylphenol (**12**, R = H) and *m*-isopropylphenol (**13**, R = H) have been repeatedly detected in tropoloniferous woods [5, 28–30]. Their possible relations to thymol and carvacrol are, however, as difficult to judge as those to hydroxythymoquinone and its derivatives found in *Tetraclinis*, *Calocedrus decurrens* and—in a single case—*Juniperus* [5].

In conclusion, *Libocedrus yateensis* and the likewise non-tropoloniferous *L. bidwillii* differ greatly from *Austrocedrus* and probably also from *Papuacedrus*, which share tropolones with the northern Cupressales. If the latter genera are of northern parentage, their active or passive migrations during the course of evolution might become easier to follow when more is known about the geographic conditions in bygone ages.

* M. J. Begley *et al.* (1978) *J. Chem. Soc. Perkin Trans.* 1, 750 (cf. (1978) *Tetrahedron Letters*, 5145) have recently elucidated the structure of sequirin D:



They assume that it is formed via an initial C6–Cβ coupling between *m*-hydroxycinnamic acid and *p*-hydroxycinnamyl alcohol (A). A coupling C1–Cβ of *p*-hydroxycinnamic acid and A followed by a dienone–phenol rearrangement at the former site would, however, appear more likely and would place sequirin D nearer the *Sequoia* conioids.

EXPERIMENTAL

Extraction 1. The ground heartwood (1.6 kg) was extracted (Soxhlet) with MeOH and the extract (296 g) adsorbed on Celite. The dried product was extracted with peroxide-free Et_2O and the extract (220 g) consecutively shaken with satd $NaHCO_3$, 10% Na_2CO_3 and 5% NaOH solns. Acidification with dil. H_2SO_4 and extraction with Et_2O gave fractions A, B and C, respectively. Neutrals = D.

Fraction A (12 g) was partly soluble in $CHCl_3$ (75 ml). Dissolved product = A_1 (9.5 g). Undissolved: A_2 (2.5 g). A_1 was triturated with CS_2. The soln contained 4-isopropylbenzoic acid (cumic acid) (**1**). The less soluble material was boiled with H_2O (600 ml), leaving cumic acid undissolved (total yield 3 g). The soln gave an acid $C_{10}H_{12}O_3$ (5.5 g), mp 142–143°, identical with synthetic 3-hydroxy-4-isopropylbenzoic acid [31] (**2**). Fraction A_2 was chromatographed (SiO_2: $CHCl_3$–MeOH–HOAc, 100:3:1) to give an acid $C_{10}H_{12}O_4$ (2 g), mp (on fast heating) 184–186° (from CH_3CN) and an acid $C_{10}H_{10}O_3$ (0.5 g), mp 116–118° (after sublimation). (Found: C, 66.6; H, 5.6. $C_{10}H_{10}O_3$ requires: C, 66.6; H, 5.6%).

According to UV, IR and ^1H NMR, the former compound was 3-hydroxy-4-α-hydroxyisopropylbenzoic acid (**4**) and the latter 3-hydroxy-4-isopropenylbenzoic acid (**3**). In accordance with this conclusion, both acids were found to give 3-hydroxy-4-isopropylbenzoic acid (**2**) on catalytic hydrogenation (Pd/C, EtOH–HOAc, 1:1). For acid **4**, Widman gave a lower mp (173°), perhaps due to slow heating [32]. We have observed that slow decomposition (dehydration?) of the acid commences already at 150°.

Fraction B still contained acids **1** and **2** (6 g) which were removed with $NaHCO_3$ leaving a residue which was boiled with H_2O (600 ml). From the soluble material, a few mg of a crystalline ketone were obtained, mp 227–231°. Tentatively structure **5b** may be inferred from a comparison of its MS with those of a series of conioids [33]. As in the case of agatharesinol (**5a**), prominent fragments containing one aromatic nucleus were observed at *m/e* 136 (61%), 131 (61%), 121 (100%) and 107 (94%). The most abundant ion in the upper half of the spectrum occurs at *m/e* 225 (53%). It corresponds to a di-(hydroxyphenyl)-propenyl species. The ion *m/e* 225 is probably formed by loss of CO from an ion *m/e* 253 (40%) which in turn arises from the molecular ion *M/e* 284 (7%) by loss of $^{\cdot}CH_2OH$.

Fraction C weighed 48 g. Part of it (25 g) was dissolved in the smallest possible amount of hot MeOH. On cooling, crystals (2.1 g) separated which were recrystallized from HOAc. Mp 295–296°. IR (KBr) cm^{-1}: 3400, 1600, 1505, 1250, 980, 850, 800; no '*cis* band' [34] at 700. Mmp with (*E,E*)-1,4-bis-(4-hydroxyphenyl)-buta-1,3-diene (**6**): no depression. Identical IR spectra. The compound gave a sparingly soluble diacetate, leaves, mp 224–226° (from Ac_2O). (Found: C, 74.4; H, 5.7. $C_{20}H_{18}O_4$ requires: C, 74.5; H, 5.6%; M, 322). IR (KBr) cm^{-1}: 1760, 1500, 1180, 994, 905 and 860. MS *M/e* 322, *m/e* 280, 238 (100%), 165, 152, 144, 131, 115, and 107.

The dimethyl ether (Me_2SO_4, NaOH) melted at 228–230° (after sublimation *in vacuo*). Lit. [35] 225°. On oxidation (Me_2CO, $KMnO_4$) it gave anisic acid in a 55% yield.

After removing the butadiene derivative, the MeOH soln was adsorbed on cotton wool, dried and extracted with hot H_2O (3 × 500 ml) which dissolved 8 g and then with MeOH (15 g, amorphous). The aq. soln contained a complex mixture of phenolic compounds, including acid **3**. TLC indicated the presence of *ca* 11 phenolic components. Evapn and acetylation of the MeOH extract gave a ppt. consisting of 1,4-bis-(4-acetoxyphenyl)-buta-1,3-diene (0.3 g) and an oil which was chromatographed (petrol–$CHCl_3$, 1:1–0:1) to afford

a viscous fraction which was a pure compound according to TLC and chromatographically identical with hinokiresinol diacetate. It was hydrolysed (NaOH–EtOH) and then methylated to give hinokiresinol dimethyl ether, mp 57–62° (after sublimation). Lit. [10] mp 62–64°; mmp 62–64°.

Fraction D (neutrals, 119 g). Part of this fraction (39 g) was chromatographed (SiO_2, petrol–Et_2O, 1:0–0:1). TLC indicated the presence of at least 11 components. One fraction (8 g), largely consisting of a ketonic product, was rechromatographed and furnished a TLC homogeneous fraction characterized by $n_D^{24} = 1.5050$ and $[\alpha]_D$ −37.5° (*c* 1.2, $CHCl_3$). (More conveniently the same compound was isolated from the crude neutral fraction by extraction with Girard reagent D.) The substance was identical with Nagahama's sesquiterpene (−)-cryptomerione [11] ($n_D^{20} = 1.5050$ and $[\alpha]_D$ −38° ($CHCl_3$)). (Identical IR and ^1H NMR spectra.) With 2,4-dinitrophenylhydrazine in DMSO [36], it gave a hydrazone, mp 167–169°, identical (^1H NMR) with an authentic sample of (−)-cryptomerione-2,4-dinitrophenylhydrazone kindly provided by Prof. Nagahama. When the reaction was carried out in the presence of sulfuric acid, a product was obtained which, after chromatography (SiO_2, C_6H_6) and crystallization from C_6H_6, melted at 227–228°. (Found: C, 63.2; H, 6.6; N, 14.0. $C_{21}H_{26}N_4O_4$ requires: C, 63.3; H, 6.6; N, 14.1%). This compound is obviously a 2,4-dinitrophenylhydrazone of a product formed by acid rearrangement of (−)-cryptomerione.

Column chromatography (SiO_2; CH_2Cl_2–Et_2O, 20:1) of the non-ketonic material, obtained by removal of (−)-cryptomerione from fraction D with Girard reagent D, gave small amounts of several TLC homogeneous fractions, one of which (*M/e* 218) was a compound $C_{15}H_{22}O$ (high resolution MS), $n_D^{21} = 1.5080$, $[\alpha]_D$ +41.9° (*c* 0.105, $CHCl_3$), MS: *m/e* 200, 185, 157, 143, 117, 91, 77, and 65. IR indicated the presence of a hydroxyl and an exomethylene group.

From the more polar fractions, a non-crystalline compound, yatein (**11**), $C_{22}H_{24}O_7$, M = 400 (high resolution MS) was obtained; $[\alpha]_D^{20}$ −28.4° (*c* 0.32, $CHCl_3$). Fragmentation: *m/e* 264, 251, 219, 182, 181 (100%, $C_{10}H_{13}O_3$), 135 ($C_8H_7O_2$), 131 and 77. IR ($CHCl_3$) cm^{-1}: 1764 and 1244 (γ-lactone), 1591, 1506, and 1490 (aromatic ring), and 2775 (methylenedioxy group). UV (EtOH) nm: 214, 258, 288 (log ε 4.31, 2.87, 3.56).

From these spectral data and from the composition of the MS fragments [13], it follows that the molecule contains one methylenedioxybenzyl group A (*m/e* 135) and one trimethoxybenzyl group B (*m/e* 181) bound to a five-membered lactone (rest of the molecule $C_4H_4O_2$). The ^1H NMR spectrum (Varian HA—100 MHz) confirmed the presence of both benzyl groups: δ 2.54 *m*, 2H and 2.90 *bd*, 2H (2 —CH_2— of A and B, respectively); 3.83 *s*, 9H (3 —OMe); 5.92 *s*, 2H (—O—CH_2—O—); 6.36 *s*, 2H (H-2 and H-6 of B); 6.46 *m*, 2H (H-2 and H-6 of A) and 6.69 *d*, 1H (H-5 of A). The signal at δ 2.54 *m*, 2H (of —C—CH—C— type) and the signals at 3.8 *m*, 1H and 4.14, 1H (of —CH—O— type) arise from the 4 protons of the lactone ring.

Reduction of yatein with $LiAlH_4$ in dry Et_2O and chromatographic purification (SiO_2; CH_2Cl_2–Et_2O, 20:1) of the product afforded a diol, mp 132–133° (C_6H_6), $[\alpha]_D^{20}$ −30.8° (*c* 0.32, $CHCl_3$). (Found: C, 65.3; H, 6.7. $C_{22}H_{28}O_7$ requires: C, 65.3; H, 7.0%). IR ($CHCl_3$) cm^{-1}: 3400, 3625 (hydroxyl), 2780 (methylenedioxy), 1332, 2845 (methoxyl), 1494, 1507, 1594 (aromatic). MS: *M/e* 404, *m/e* 250, 225, 182, 181, 135.

Bromination of yatein with $KBrO_3$, KBr and H_2SO_4 was carried out following the method of ref. [37] and furnished a tribromo derivative which, after chromatographic purification (SiO_2; C_6H_6–EtOAc, 100:1) and crystallization from C_6H_6, melted at 183–184°. $[\alpha]_D$ −3.9° (*c* 0.3, $CHCl_3$), MS: *M/e* 634, *m/e* 337, 213. (Found: C, 41.7; H, 3.3; Br, 37.8. $C_{22}H_{21}O_7Br_3$ requires: C, 41.5; H, 3.3; Br, 37.6%; M, 637).

Isomerization of cis-*dihydroanhydropodorhizol* (**10**) *to yatein.* The lactone (25 mg) was dissolved in 3% methanolic KOH (5 ml) and the soln kept at room temp. for 70 hr. After acidification with HOAc (1 ml) and refluxing for 1 hr, the solvent was removed *in vacuo*. The residue was dissolved in H_2O (10 ml) and M H_2SO_4 (3 ml) was added. The mixture was extracted with Et_2O, washed with $NaHCO_3$, dried and the solvent evapd. The residue was purified by chromatography (SiO_2, $CHCl_3$). The pure product (single spot on TLC) was non-crystalline, $[\alpha]_D$ −25.5° (*c* 0.35, $CHCl_3$) and identical (^1H NMR) with yatein. When treated in the same way, yatein was recovered unchanged (IR, ^1H NMR).

Extraction 2. To powdered heartwood (600 g), hot H_2O was added (4 l., 70°, stirring). After 5 hr at 70° the aq. phase was collected. This procedure was repeated ×3. The combined filtrates were concd to 1.5 l. by vacuum distillation. This soln was exhaustively extracted with peroxide-free Et_2O. The Et_2O extract was dried and the Et_2O removed by distillation, leaving a red-brown gum (A, 13 g, 2.2%). Further extraction with MeOH and then Me_2CO furnished extracts B (77 g, 13%) and C (5 g, 0.8%).

The gum A was methylated (MeI, K_2CO_3, Me_2CO) and the product subjected to chromatography (SiO_2; C_6H_6–Me_2CO, 20:1–10:1). The following compounds were obtained in order of increasing polarity:

(1) A compound, mp 172–178°. M 384 (MS) ($C_{22}H_{24}O_6$), *m/e* 269 ($C_{17}H_{17}O_3$), 151 ($C_9H_{11}O_2$).

(2) Yateresinol dimethyl ether (**8a**), mp 156–158° (from Me_2CO). (Found: C, 72.2; H, 6.9. $C_{19}H_{22}O_4$ requires: C, 72.6; H, 7.0%). IR ($CHCl_3$) cm^{-1}: 1515, 1610 (arom.), 1252 (arom. —O). MS: No mol. peak, *m/e* 296: M − H_2O, 266 ($C_{18}H_{18}O_2$): M − (H_2O + CH_2O), 235 ($C_{17}H_{15}O$): 266 − OMe, 160 ($C_{11}H_{12}O$): MeO–C_6H_4–CH=CH—CH=CH_2, 137 ($C_8H_9O_2$): MeO –C_6H_4–C$^+$HOH. ^1H NMR See Table 1.

(3) A compound $C_{22}H_{26}O_6$, mp 170–172°. (Found: C, 68.2; H, 6.7; M, 386 (MS). $C_{22}H_{26}O_6$ requires: C, 68.4; H, 6.8%; M, 386). IR ($CHCl_3$) cm^{-1}: 3605, 3395 (hydroxyl), 1518, 1593, 1610 (arom.), 1255 (arom. —O). ^1H NMR: 4 OMe (arom.).

(4) A compound $C_{22}H_{26}O_8$, mp 173–174.5°. (Found: C, 63.0; H, 6.2; M, 418 (MS). $C_{22}H_{26}O_8$ requires: C, 63.2; H, 6.3%; M, 418). IR ($CHCl_3$) cm^{-1}: 3540, 3450 (hydroxyl), 1609, 1593, 1520 (arom.), 1786 (γ-lactone). ^1H NMR: 4 OMe (arom.).

Table 1. ^1H NMR data of yateresinol dimethyl ether (**8a**) and its diacetate (**8b**) (Measured on TESLA 60 MHz, in $CDCl_3$–TMS)

	8a	**8b**
1H (H-1)	6.47 *d*	6.40 *d*
1H (H-2)	5.97 *dd*	5.89 *dd*
1H (H-3)	2.62 *m*(*br*)	2.92 *m*(*br*)
1H (H-4)	4.79 *d*	5.88 *d*
2H (H-5)	3.64 *d*	4.03* *o*
6H (2 × OMe)	3.77 *s*	3.77 *s*
6H (2 × OAc)	—	2.00 *s*
4H (H-arom.)	6.82 + 7.27†	—
4H (H-arom.)	6.85 + 7.27†	—
8H (2 × H-arom.)	—	6.82 + 7.24†

J (Hz) **8a**: 1,2 = 16; 2,1 = 16; 2,3 = 9; 4,3 = 6.5; 5,3 = 6; **8b**: 1,2 = 16; 2,1 = 16; 2,3 = 8.5; 1,3 < 1 (≠0); 4,3 = 6.9; 5,5 = 11.1; 5,3 = 6.3, 6.0.

* AB part of ABX spectrum (3.89 + 4.11).

† AA'BB' system.

Acknowledgements—We thank Mr. L. Chevalier for guiding us in the Yaté district, Dr. A. v. Wartburg and Professor S. Nagahama for providing authentic specimens, Professor C. Enzell for one of the earlier MS, Drs. M. Budĕšínský and L. Dolejš for valuable discussions and Ingenjörsvetenskapsakademien for a grant (to J.H.).

REFERENCES

1. Pulle, A. (1950) *Compendium van de Terminologie, Nomenclatuur en Systematiek der Zaadplanten*. A. Oosthoek's, Utrecht.
2. Florin, R. (1955) in *A Century of Progress in the Natural Sciences* 1853–1953, p. 368. California Academy of Sciences, San Francisco.
3. Florin, R. and Boutelje, J. B. (1954) *Acta Hort. Berg.* **17**, No. 2, 7.
4. Li, H.-L. (1953) *J. Arnold Arbor. Harv. Univ.* **34**, 17.
5. Erdtman, H. and Norin, T. (1966) *Fortschr. Chem. Org. Naturst.* **24**, 206.
6. Erdtman, H. and Tsuno, K. (1969) *Acta Chem. Scand.* **23**, 2021.
7. Zavarin, E., Smith, R. M. and Anderson, A. B. (1959) *J. Org. Chem.* 1318.
8. Corbett, R. E. and Wright, D. E. (1953) *Chem. Ind.* **47**, 1258.
9. Sarlin, P. (1954) *Bois et Forêts de la Nouvelle-Calédonie*, p. 91. Centre Technique Forestier Tropical, Nogent-sur-Marne (Seine), France.
10. Hirose, Y., Oishi, N., Nagaki, H. and Nakatsuka, T. (1965) *Tetrahedron Letters*, 3665.
11. Nagahama, S. (1964) *Bull. Chem. Soc. Jpn.* **37**, 1029.
12. Hodgson, G. L., MacSweney, D. F. and Money, T. (1973) *J. Chem. Soc. Chem. Commun.* 231 and refs. cited therein.
13. Harmatha, J., Budĕšínský, M. and Dolejš, L. (1979) *Collect. Czech. Chem. Commun.* to be published.
14. Kuhn, M. and v. Wartburg, A. (1967) *Helv. Chim. Acta* **50**, 1546.
15. Tomioka, K., Mizuguchi, H. and Koga, K. (1978) *Tetrahedron Letters* 4687.
16. McDoniel, P. B. and Cole, J. R. (1972) *J. Pharm. Sci.* **62**, 1992.
17. Nishibe, S., Hisada, S. and Inagaki, I. (1974) *Yakugaku Zasshi* **94**, 522.
18. Reifer, R. and Anderson, A. B. (1967) *Phytochemistry* **6**, 1557.
19. Daniels, P., Erdtman, H., Nishimura, K., Norin, T., Kierkegaard, P. and Pilotti, A.-M. (1972) *J. Chem. Soc. Chem. Commun.* 246.
20. Kai, Y. (1965) *Mokuzai Gakkaishi* **11**, 23.
21. Hatham, N. A. R. and Whiting, D. A. (1967) *Tetrahedron Letters*, 781.
22. Erdtman, H. (1933) *Biochem. Z.* **258**, 177; (1933) *J. Liebigs Ann. Chem.* **503**, 288; (1935) *Svensk Kem. Tid.* **47**, 225; (1971) *Lignins* (Sarkanen, K. V. and Ludwig, C. H., eds.) p. 2. Wiley-Interscience, New York.
23. Enzell, C. R. and Thomas, B. R. (1966) *Tetrahedron Letters* 2395.
24. Beracierta, A. P. and Whiting, D. A. (1978) *J. Chem. Soc. Perkin Trans.* I, 1257.
25. Hayashi, T. and Thomson, R. H. (1975) *Phytochemistry* **14** 1085; Rao, M. M. and Lavie, D. (1974) *Tetrahedron* **30**, 3309.
26. Gierer, J. and Smedman, L.-A. (1971) *Acta Chem. Scand.* **25**, 1461.
27. Lin, Y.-T., Wang, K.-T. and Lin, Y.-S. (1962) *J. Chin. Chem. Soc.* **9**, 68 ((1963) *Chem. Abstr.* 9412).
28. Yoshikoshi, A. Y. (1960) *J. Chem. Soc. Jpn.* **81**, 981.
29. Yanegawa, T., Hirose, Y. and Nakatsuka, T. (1967) *J. Jpn. Wood Res. Soc.* **13**, 160.
30. Tomita, B. and Hirose, Y. (1969) *J. Jpn. Wood Res. Soc.* **15**, 337.
31. Heymann, B. and Königs, W. (1886) *Ber. Dtsch. Chem. Ges.* **19**, 3307.
32. Widman, O. (1884) *Ber. Dtsch. Chem. Ges.* **17**, 722.
33. Enzell, C. R., Thomas, B. R. and Wahlberg, I. (1967) *Tetrahedron Letters* 2211.
34. Lunde, K. and Zechmeister, L. (1954) *Acta Chem. Scand.* **8**, 1421.
35. Winternitz, F. and Mousseron, M. (1948) *Bull. Soc. Chim. Fr.* **15**, 567.
36. Parrik, J. and Rasburn, J. W. (1965) *Can. J. Chem.* **43**, 3453.
37. Kofod, H. and Jörgensen, C. (1955) *Acta Chem. Scand.* **9**, 1327.