Phytochemistry, Vol. 27, No. 12, pp. 3992 3993, 1988.
Printed in Great Britain.

0031 9422/88 $3.00 + 0.00

ALLYLPHENOLS FROM *OCOTEA CYMBARUM**

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(*Received* 13 *April* 1988)

Key Word Index—*Ocotea cymbarum*; Lauraceae; 4-hydroxy-2,3,5-trimethoxyallylbenzene; apiolglycol.

Abstract—An ethanol extract of *Ocotea cymbarum* wood was shown to contain apiol, dillapiol, 4-hydroxy-2,3,5-trimethoxyallylbenzene, apiolglycol and lyoniresinol.

The wood of *Ocotea cymbarum* (H.B.K.) Nees has been shown to contain three allylphenol derivatives: eugenol, dehydrodieugenol, mono-*O*-methyldehydrodieugenol and dehydrodieugenol B [2]. In the present study the ethanolic wood extract of another specimen of this species collected in a similar locality near Manaus, Amazonas, was also found to contain allylphenol derivatives but of a much higher oxygenation pattern: apiol (**1a**), dillapiol (**1b**) [3], 4-hydroxy-2,3,5-trimethoxyallylbenzene (**1c**) and apiolglycol (**2**). Compound **1c**, the common putative precursor of **1a** and **1b**, is here described for the first time. Among the apiol, dillapiol, isoapiol and isodillapiol derived glycols only the latter has been isolated previously from *Ostericum citriodorum* (Apiaceae) [4]. Although a known synthetic derivative [5], **2** is thus a new natural product. The extract contained in addition the 4-aryltetralin type lignan lyoniresinol, previously isolated from *Lyonia ovalifolia* (Ericaceae), *Alnus glutinosa* (Betulaceae) and *Ulmus thomasii* (Ulmaceae) [6].

Spectral comparison of **1a** and **1b** (both $ArH.CH_2CH=CH_2(OMe)_2O_2CH_2$ by NMR and MS), **1c** [$ArH.CH_2CH=CH_2.OH(OMe)_3$] and **2** [$ArH.CH_2CH(OH)CH_2OH(OMe_2)O_2CH_2$] led to the indicated structures via the following observations. The aromatic protons of **1c** and **2** can be *ortho*-related only with one oxy-group (^1H–^{13}C NMR δ **1a** 6.25/108.25; **1b**, 6.40/102.56; **1c** 6.42/107.11; **2** 6.30/109.27) as in **1a** and **1b**. As in **1a**, but not as in **1b**, a methoxyl must be vicinal to the sole free aromatic position in **1c** and in **2** (^{13}C NMR δ **1a** 56.80; **1b** 61.08; **1c** 56.39; **2** 56.92). A minimal paramagnetic shift (Δ0.1 ppm) of the ArH singlet occurs upon acetylation of the, hence, *meta*-related free hydroxyl of **1c**. Osmium tetraoxide oxidation [7] of **1a** gives **2**.

*Part LXXXVII in the series 'The Chemistry of Brazilian Lauraceae'. For Part LXXXVI see ref. [1]. This paper is based on the M.Sc. thesis presented by C.C.A. (present address Centro de Ciências Exatas, Universidade Estadual de Londrina, 86052 Londrina, PR).

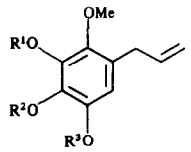
EXPERIMENTAL

Isolation of the constituents. An EtOH extract of *Ocotea cymbarum* was kindly supplied by the Instituto Nacional de Pesquisas da Amazônia, Manaus, there registered as extract no. 407. Part of the extract (56 g) was re-extracted with EtOAc, the soln. evapd. and the residue (16 g) submitted to CC (silica gel). Elution with CH_2Cl_2 gave, in order, a mixture of **1a**, **1b** and **1c** (purified by TLC silica gel, $CHCl_3$–MeOH 49:1), **1c** and sitosterol. Elution with CH_2Cl_2–MeOH 49:1 gave **2** (172 mg) (purified by recryst. from EtOAc. Another part of the extract (95 g) was submitted directly to CC (silica gel, 750 g). Elution with $CHCl_3$ gave in order **1a** (30 g), **1b** (9 g), and **1c** (150 mg) (purified by TLC) and sitosterol (100 mg). Elution with $CHCl_3$–MeOH 19:1 gave lyoniresinol (415 mg) (purified by recryst. from Me_2CO).

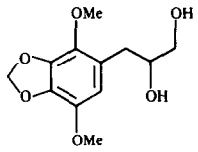
Lyoniresinol, a (8*R*,7′*S*,8′*R*)-8.8′,6.7′-lignan (OH: 4,9,4′,9′; OMe: 3,3′,5,5′; Δ: 1,3,5,1′,3′,5′) [8], mp 195–197° (Me_2CO). Diacetate, mp 144–146°. Dimethyl ether, mp 168–170°.

4-Hydroxy-2,3,5-trimethoxyallylbenzene (**1c**). Oil, UV λ_{max}^{MeOH} nm: 218 (ε 6900), 283 (ε 2050). IR ν_{max}^{film} cm^{-1}: 3450 (OH), 1650, 1600, 1500 (Ar), 990, 915 (CH=CH_2). ^1H NMR (60 MHz, $CDCl_3$) δ: 3.31 (*d*, *J* = 7Hz, 2H-7), 3.80, 3.86, 3.92, (3*s*, 3 OMe), 4.8–5.3 (2H-9), 5.6–6.2 (H-8), 5.57 (*s*, OH), 6.42 (*s*, H-6). ^{13}C NMR (25 MHz, $CDCl_3$) δ: 33.74 (*t*, C-7), 56.31 (*q*, OMe-5), 60.64, 60.98 (2*q*, 2OMe-2,3), 107.11 (*d*, C-6), 115.27 (*t*, C-9), 123.07 (*s*, C-1), 137.49 (*s*, C-4), 137.49 (*d*, C-8), 140.46 (*s*, C-3), 143.46 (*s*, C-2), 145.01 (*s*, C-5). MS *m/z* (rel. int.): 224 (M, 100), 209 (48), 195 (13), 117 (35), 163 (9), 149 (22), 121 (10). Acetate, oil. IR ν_{max}^{film} cm^{-1}: 1775 (OAc), 1655 (CH=CH_2), 1615, 1490 (Ar), 984, 913 (CH=CH_2). ^1H NMR (60 MHz, $CDCl_3$) δ: 2.28 (*s*, OAc), 3.42 (*d*, *J* = 7 Hz, 2 H-7), 3.80, 3.82, 3.90 (3*s*, 3 OMe), 4.9–5.3 (2 H-9), 5.7–6.1 (H-8), 6.55 (H-6).

Apiolglycol (**2**). Mp 100–101°. UV λ_{max}^{MeOH} nm: 216 (ε 6650), 280 (ε 550). IR ν_{max}^{KBr} cm^{-1}: 3260 (OH), 1605, 1500, 1490 (Ar). ^1H NMR (100 MHz, $CDCl_3$) δ: 2.40 (*br s*, OH), 2.73 (*d*, *J* = 7Hz, 2H-7), 3.4–3.6 (2 H-9), 3.84, 3.92 (2*s*, 2 OMe), 5.94 (*s*, CH_2O_2), 6.30 (*s*, H-6). ^{13}C NMR (25 MHz, $CDCl_3 + C_5D_5N$) δ: 34.46 (*t*, C-7), 56.92 (*q*, OMe-5), 59.81 (*q*, OMe-2), 65.92 (*t*, C-9), 72.41 (*d*, C-8), 101.27 (*t*, CH_2O_2), 109.27 (*d*, C-6), 123.98 (*s*, C-1), 135.34 (*s*, C-4), 136.63 (*s*, C-3), 138.37 (*s*, C-2), 138.88 (*s*, C-5). MS *m/z* (rel. int.): 256 (M, 100), 238 (8), 225 (38), 196 (97), 195 (100), 181 (73), 180 (59), 165 (38), 151 (21), 137 (21), 135 (62), 109 (16). Diacetate, mp 110–112°. ^1H NMR (60 MHz, $CDCl_3$): δ 2.08, 2.11 (2*s*, 2 OAc), 2.85 (*d*, *J* = 7 Hz, 2H-7), 3.90, 3.99 (2*s*, 2 OMe), 4.1–4.3 (2H-9), 5.2–5.5 (H-8), 6.01 (*s*, CH_2O_2), 6.38 (*s*, H-6).



1a R^1—R^2 = CH_2, R^3 = Me
1b R^1 = Me, R^2 = R^3 = CH_2
1c R^1 = R^3 = Me, R^2 = H



2

Transformation of **1c** *in* **2**. A soln of OsO_4 (100 mg) in C_5H_5N (1 ml) was added to a soln. of **1c** (90 mg) in C_5H_5N (0.5 ml). After stirring (3 hr, room temp.) a soln of $NaHSO_3$ (120 mg) in C_5H_5N (3 ml) and H_2O (2 ml) was added and the mixture stirred for 30 min before addition of 10% HCl (3 ml). Stirring continued for 30 min and the mixture then extracted with $CHCl_3$. The organic layer was washed, dried and evapd. The residue was purified (TLC, Si gel) to give **2**.

Acknowledgements—The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for fellowships and to Professor Antônio J. R. da Silva, NPPN, Universidade Federal do Rio de Janeiro for NMR and mass spectra.

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Phytochemistry, Vol. 27, No. 12, pp. 3993–3994, 1988.
Printed in Great Britain.

0031–9422/88 $3.00+0.00

4,4′-DIHYDROXYCHALCONE FROM THE HEARTWOOD OF *CHAMAECYPARIS OBTUSA*

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(*Received* 11 *April* 1988)

Key Word Index—*Chamaecyparis obtusa*; Cupressaceae; heartwood; phenolic extractives; 4,4′-dihydroxychalcone.

Abstract—A new chalcone, 4,4′-dihydroxychalcone was isolated from the heartwood of *Chamaecyparis obtusa*. The structure was elucidated by direct comparison with a synthetic sample.

INTRODUCTION

Japanese cypress (*Chamaecyparis obtusa* Endl.), is highly valued for its pink heartwood. The phenolic extractives responsible for this colour are hinokinin, hinokiresinol, hinokione and hinokiol [1–7]. The present authors while reinvestigated the basis of this colour found, in addition to four known compounds (Sawaranin, cryptoresinol, 3-methoxyhinokiresinol and isocryptoresinol) [8–10], one new substance which is now described in this note.

RESULTS AND DISCUSSION

The phenolic part of ethyl acetate-soluble fraction from the methanolic extract of the heartwood of *C. obtusa* was acetylated, and this eventually provided the acetate (**1b**) of the new compound, in a yield of 0.001% based on dried heartwood powder.

Upon preliminary TLC analysis of the original ethyl acetate fraction, compound **1a** appeared as a yellow spot which was positive to 2,4-dinitrophenylhydrazine and