Phytochemistry, Vol. 28, No. 2, pp. 661–662, 1989.
Printed in Great Britain.

0031-9422/89 \$3.00+0.00

BICYCLOOCTANOID NEOLIGNANS FROM *OCOTEA COSTULATUM**

WILSON D. DA SILVA, RAIMUNDO BRAZ-FILHO† and OTTO R. GOTTLIEB‡

†Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, 23851 Seropédica, RJ, Brasil ‡Instituto de Química, Universidade de São Paulo, 05508 São Paulo, SP, Brazil

(*Received* 13 *April* 1988)

Key Word Index—*Ocotea costulatum*; Lauraceae; benzodioxan neolignan; bicyclo [3.2.1] octanoid neolignans.

Abstract—An EtOH-extract of wood from *Octoea costulatum* was shown to contain eusiderin and two bicyclo [3.2.1] octanoid neolignans including the new 1-allyl-4-hydroxy-3,5-dimethoxy-7-methyl-6-(3′-methoxy-4′,5′-methylenedioxyphenyl)-8-oxobicyclo [3.2.1] oct-2-ene.

INTRODUCTION

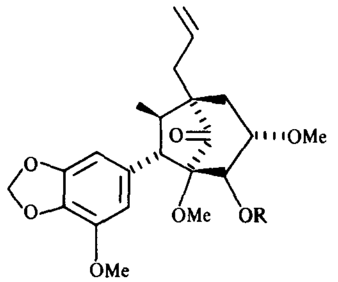
The specimen of *Ocotea costulatum* Mez examined in the present report was collected near Manaus, Amazonas, and identified by Professor Klaus Kubitzki (Hamburg University). Fractionation of an ethanolic extract of its trunk wood gave the benzodioxane neolignan eusiderin, previously isolated from *Aniba*, *Eusideroxylon* and *Licaria* species, i.e. other Lauraceae [2], as well as from Myristicaceae [3] and Schizandraceae [4]; (7*S*,8*R*,1′*R*, 3′*S*,4′*R*,5′*S*)-4′-hydroxy-3,3′,5′-trimethoxy-4,5-methylenedioxy-6′-oxo-Δ-1,3,5,8′-8.1′,7.5′-neolignan (**1a**), previously isolated from an *Aniba* species [5], the novel **2a** and sitosterol.

Comparison of the molecular formulas of **1a**, $C_{22}H_{28}O_7$ and **2a**, $C_{22}H_{26}O_7$, both determined by low resolution mass spectrometry, combined with hydrogen and carbon counts, reveal **1a** to possess two hydrogens more than **2a**. Indeed, in view of the similarity of the IR spectra (both with maxima at 1750, 990 and 910 cm^{-1} for pentanone and terminal vinyl units), **2a** is probably a didehydro-**1a**. The mass spectra of both compounds show prominent peaks at *m/z* 192 assignable to $[C_6H_2.OMe.O_2CH_2.CHCHMe]^{+\cdot}$ and the double bond in **2a** must thus be situated between positions C-2′, C-3′ or C-3′, C-4′. It suffices to compare the ^1H (Table 1) and ^{13}C (Table 2) NMR spectra of **1a** (with two H at sp^3 C-2′) and **2a** (with one H at sp^2 C-2′) to select the former alternative.

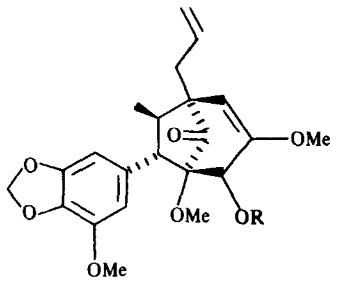
In **1a** the C-2′, C-3′-bond and H-7 are in the endo-configuration. Hence, if **2a** had an analogous overall stereochemistry its Δ-2′;3′ bond should cause magnetic protection on H-7. This is indeed the case, shifts from δ 3.29 (**1a**) to 2.53 (**2a**) and from δ3.40 (**1b**) to 2.56 (**2b**) being observed, respectively, for the compound pair itself and the series of acetates (Table 1). The sterochemistry of the model compound **3** [6] cannot be adopted for the constituent of *Ocotea costulatum*, since here H-7 is exo-oriented as shown by the lower field signal at δ2.93. Furthermore, in both **1** and **2** the high field signal (δ 2.78 $\pm$ 0.07) for the bridgehead methoxyl, as opposed to δ 3.56 in **3**, confirms the *cis*-relationship of Ar-7/OMe-5′.

EXPERIMENTAL

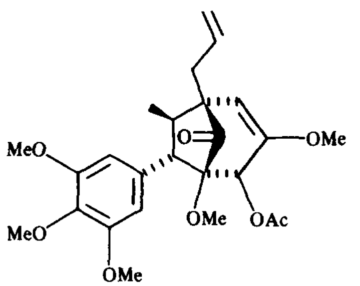
Isolation of the constituents. Dry, powdered wood of *Ocotea costulatum* (9.5 kg) was extracted with EtOH at room temp. The soln was filtered and evapd. The residue (75 g) was washed first with hot C_6H_{14} and next with C_6H_6. The solns were filtered and evapd. The residue of the C_6H_{14} extract (10 g) was submitted to CC (silica gel, 350 g). Elution with C_6H_{14}, C_6H_{14}–EtOAc (19:1) and C_6H_{14}–EtOAc (9:1) gave, respectively, aliphatic material, sitosterol and mixture A, mixture B. Mixture A was crystallized from C_6H_{14} to yield eusiderin (1 g). Mixture B was rechromatographed on a silica gel column. Elution with $CHCl_3$ gave in order C and D. Material C was recrystallized from MeOH to yield **1a** (47 mg) and D gave **2a** (37 mg). The residue of the C_6H_6



1a R = H
1b R = Ac



2a R = H
2b R = Ac



3

---

*Part LXXXVIII in the series 'The Chemistry of Brazilian Lauraceae'. For Part LXXXVII see ref. [1]. This paper is based on the M.Sc. thesis presented by W. D. da S. (present address Departamento de Química, Universidade Federal de Mato Grosso, Cuiabá, MT) to Universidade Federal Rural do Rio de Janeiro, Brazil.

Table 1. ^{1}H NMR spectral comparison of the new neolignans **2a** and **2b** (100 MHz) with the model neolignans **1a** (100 MHz), **1b** (270 MHz) [5] and **3** (270 MHz) [6]*

	1a	**2a**	**1b**	**2b**	**3**
H-2	6.25 *d* (2)	6.32 *d* (2)	6.26 *d* (*bs*)	6.32 *d* (2)	6.57 *s*
H-6	6.36 *d* (2)	6.36 *d* (2)	6.30 *d* (2)	6.35 *d* (2)	
H-7	3.29 *d* (8)	2.52 *d* (8.5)	3.40 *d* (8)	2.56 *d* (8.5)	2.13 *dd* (6,1.5)
H-8	1.95–1.65	2.02 *dq* (8.5,7)	1.89 *dq* (8,7)	1.8–2.2	2.74 *q* (6.5)
3H-9	1.05 *d* (7)	0.97 *d* (7)	1.10 *d* (7)	0.98 *d* (6.5)	1.04 *d* (7)
H-2′	2.0–2.3	4.54 *d* (2)	2.02 *dd* (15.5,6.5)	4.64 *d*(2)	4.96 *d* (1)
H-2′			2.20 *br d* (15.5)		
H-3′	3.50 *dd* (6.5,2)		3.37 *br d* (6.5)		
H-4′	4.49 *dd* (2, < 0.5)	4.68 *br s*	5.75 *dd* (2,1)	6.08 *d* (2)	6.07 *dd* (1.5, 1)
H-7′	2.0–2.3	2.2–2.5	2.14 *dd* (14,8)	2.39 *d* (7)	2.28 *ddt* (14,7.1)
H-7′	2.30 *dd* (14,6.5)		2.34 *dd* (14,6.5)		2.44 *ddt* (14,7.1)
H-8′	5.6–6.0	5.7–6.2	5.8–5.9	5.7–6.2	5.89 *m*
H-9′	5.01 *dd* (16,2)	4.9–5.2	5.00 *dd* (16,2)	5.0–5.2	5.21 *br d* (16.5)
H-9′	5.04 *dd* (10,2)		5.04 *dd* (10,2)		5.20 *br d* (10.5)
OMe-3	3.84 *s*	3.90 *s*	3.86 *s*	3.90 *s*	3.85 *s*
OMe-3′	3.42 *s*	3.66 *s*	3.51 *s*	3.62 *s*	3.61 *s*
OMe-5′	2.82 *s*	2.92 *s*	2.78 *s*	2.78 *s*	3.56 *s*
O_2CH_2 −4,5	5.91 *s*	5.94 *s*	5.93 *s*	5.94 *s*	
OMe-4					3.83 *s*
OMe-5					3.85 *s*
OAc-4			2.12 *s*	2.12 *s*	1.48 *s*

*Chemical shifts in δ; coupling constants (J) in Hz in parentheses; internal standard TMS; solvent $CDCl_3$.

Table 2. ^{13}C NMR spectral comparison of the new neolignan **2a** with the model neolignan **1a** [5] (25.2 MHz, $CDCl_3$, TMS, δ)

C	**1a**	**2a**
1	135.67 *s*	132.66 *s*
2	108.50 *d*	108.99 *d*
3	148.52 *s*	148.59 *s*
4	135.67 *s*	134.07 *s*
5	143.03 *s*	143.04 *s*
6	103.01 *d*	103.34 *d*
7	47.23 *d*	52.70 *d*
8	44.41 *d*	48.67 *d*
9	11.62 *q*	12.30 *q*
1′	50.99*s*	49.01 *s*
2′	36.02 *t*	100.19 *d*
3′	77.78 *d*	154.34 *s*
4′	78.36 *d*	77.98 *d*
5′	85.50 *s*	83.09 *s*
7′	37.49 *t*	35.21 *t*
8′	136.67 *d*	133.56 *d*
9′	117.86 *t*	117.93 *t*
OMe-3	56.61 *q*	56.68 *q*
OMe-3′	57.11 *q*	55.61 *q*
OMe-5′	50.73 *q*	51.24 *q*
O_2CH_2-4,5	101.21 *t*	101.26 *t*

extract (15 g), treated in a similar way gave eusiderin (2 g), **1a** (68 mg) and **2a** (48 mg).

Identifications of eusiderin [3] and of **1a** [5] relied on direct comparison with authentic samples.

rel-7S,8R,1′S,4′R,5′R)-4′-*Hydroxy*-3,3′,5′-*trimethoxy*-4,5-*methylenedioxy*-6′-*oxo*-Δ-1,3,5,2′,8′-8.1′,7.5′-*neolignan* (**2a**), mp 170–172° (MeOH). ν_{max}^{KBr} cm^{-1}: 3360 (OH), 1750 (C=O), 1650, 1635, 1620, 1505 (Ar), 990, 910 ($CH=CH_2$). ^{1}H NMR: Table 1. ^{13}C NMR: Table 2. MS m/z (rel. int.): 402 $[M]^+$ (12), 361 (34), 210 (14), 209 (11), 193 (10), 192 (20), 169 (100).

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.

REFERENCES

1. Andrei, C. C., Braz-Filho, R. and Gottlieb, O. R. (1988) *Phytochemistry* **27**, 3992.
2. Gottlieb, O. R. (1978) *Progr. Chem. Org. Nat. Prod.* **35**, 1.
3. Cavalcante, S. de H., Yoshida, M. and Gottlieb, O. R. (1985) *Phytochemistry* **24**, 1051.
4. Li, L. and Xue, H. (1985) *Planta Med.* 217.
5. Dias, S. M. C., Fernandes, J. B., Maia, J. G. S., Gottlieb, O. R. and Gottlieb, H. E. (1982) *Phytochemistry* **21**, 1737.
6. Gomes, M. C. C. P., Yoshida, M., Gottlieb, O. R., Martinez V., J. C. and Gottlieb, H. E. (1983) *Phytochemistry* **22**, 269.