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NEOLIGNANS FROM *URBANODENDRON VERRUCOSUM**

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Key Word Index—*Urbanodendron verrucosum*: Lauraceae; neolignans; porosin-dihydrofutoenone rearrangement.

Abstract—Branch wood of the shrub *Urbanodendron verrucosum* from the Atlantic forest of southern Brazil contains the benzofuranoid neolignans licarin-A, licarin-D, porosin and the novel porosin-B, as well as the tetrahydrofurane neolignans austrobailignan-7, calopiptin and the novel verrucosin. The acid-catalysed rearrangement of the porosins yields the corresponding dihydrofutoenones.

INTRODUCTION

The monotypical genus *Urbanodendron* (Lauraceae) is represented by the shrub *U. verrucosum* (Nees) Mez which occurs in the Atlantic forest region of Rio de Janeiro State. The branch wood contains the benzofurane neolignans licarin-A (**1a**)[2] and licarin-D (**1b**)[3], the tetrahydrobenzofurane neolignans porosin (**2a**)[4] and porosin-B (**2b**), as well as the tetrahydrofurane neolignans austrobailignan-7 (**3a**)[5], calopiptin (**3b**)[6, 7] and verrucosin (**3c**).

For reasons stated in a previous paper of this series[8] nomenclature and numbering of neolignans follow the rules outlined in a recent review[9].

RESULTS AND DISCUSSION

The novel compounds **2b** and **3c** are substitutional variants of known co-specific isolates and the elucidation of their structures relied on trivial spectral comparisons. Both the previously known porosin (**2a**) and the new porosin-B (**2b**) not only give comparable ^{1}H NMR spectra (Table 1), but also identical ORD curves. Thus not only do they possess the same relative configurations but also the same absolute ones. The porosins were submitted to treatment with acid (in methanol), in order to provide additional evidence for the *cis*-relationship between the Ar-7 and the Me-8 (^{1}H NMR δ 0.5) groups[4]. It was hoped that acid-catalysed opening and closure of the benzylic C–O bond might induce the formation of porosins in which an Ar-7/Me-8 *trans*-relationship would be characterized by ^{1}H NMR methyl signals at lower field (*ca* δ 1.1[2]). Indeed, ^{1}H NMR evidence showed the reaction products to include *ca* 1 : 1 mixtures of **2a** + **2c** and **2b** + **2d** respectively. The separation of the epimers from these mixtures proved difficult and was not completed. Furthermore, the reaction gave methanol addition products of the porosins in a yield of 35% in addition to the spiro-derivatives **4a** and **4b**.

Compound **4b** has been obtained previously by the catalytic hydrogenation of futoenone (**4c**), a neolignan from *Piper futokadzura* Sieb. et Zucc.[10]. All reported data for dihydrofutoenone are identical with the data obtained for the acid rearrangement product of porosin-B. With respect to the ^{1}H NMR data, excepting only the signals due to different aromatic substitution, this fact applies also to **4a**, the rearrangement product of porosin. Both rearrangement products therefore have identical configurations.

A topic which merits discussion concerns the location of the double bond in **4a**, **4b**. Although this could, *a priori*, also be placed between C-5′ and C-6′, such an alternative can be dismissed. Indeed, compounds **2a**, **2b**, **4a** and **4b** must have identical chromophores, since their UV spectra are so similar [λ_{max} nm: 259 ± 1, 288 ± 2 inf. (ϵ 15 800, 4000)]. An α,β-unsaturated ketone with an α-ether substituent would give a UV maximum at *ca* 268 nm with a substantially smaller extinction coefficient[4].

The porosin (**2a**, **2b**)–dihydrofutoenone (**4a**, **4b**) rearrangement is mechanistically analogous to the known burchellin (**5**)–guianin (**6**)–futoenone (**4c**) interconversions[11, 12].

The structure of verrucosin (**3c**) was established by comparison with the synthetic racemate[13] (superimposable ^{1}H NMR data) and by preparation of a dimethyl ether (**3d**) (identical in all respects, including $[\alpha]_D$, to veraguensin[14]).

EXPERIMENTAL

Isolation of constituents. Plant material, identified by Professor Klaus Kubitzki, Hamburg University, was collected at Tijuca Forest, Rio de Janeiro. Dried and powdered branch wood (1.5 kg) was percolated with C_6H_6. The extract (15 g) was submitted to CC (300 g Si gel). The following fractions were eluted with the indicated solvents: A–D

*Part LXVII in the series "The Chemistry of Brazilian Lauraceae. For Part LXVI see ref. [1]. Based in part on the M.Sc. Thesis presented by A. de F. D., on leave of absence from Universidade Federal da Paraíba, to Universidade de São Paulo (1980).

Table 1. ^{1}H NMR spectral data of neolignans*

	2a[4]		2b	4a		4b[10]
H-2	6.76 *d* (2)					
H-5	6.83 *dd* (8, 2)		6.5–6.8	6.6–6.9	*m*	6.6–6.9
H-6	6.93 *d* (8)					
H-7	5.89	*d* (5)	5.74	×		×
H-8	2.6	*m*	2.4–2.7			
3H-9	0.52	*d* (7)	0.50	0.75	*d* (6)	0.73
H-3′	5.59	*s*	5.44	5.63	*s*	5.63
H-5′	4.02	*dd* (12, 5)	3.92	3.68	*m*	3.69
H-6′	2.22	*dd* (12, 5)	2.26	2.27		2.27
H-6′	1.92	*t* (12)	1.85	2.14		2.14
H-7′	2.69 *dd* (14, 7)		2.4–2.6	×		×
H-7′	2.36 *dd* (14, 7)					
H-8′	5.9–6.1	*m*	5.6–6.2	4.93	*m*	4.95
2H-9′	5.3–5.4	*m*	5.1–5.3	×		×
MeO-5′	3.62	*s*	3.53	3.58	*s*	3.58
2MeOAr	3.90 *s*	—	—	3.90	*s*	—
CH_2O_2Ar	—	—	5.87 *s*	—	*s*	5.95

*Chemical shifts in δ from internal TMS for $CDCl_3$ solutions at 220 MHz (**2a**) and 60 MHz (all other compounds); coupling constants (Hz) in brackets. ×δ 1.7–2.5, *m* 8H.

(C_6H_6), E (C_6H_6–CH_2Cl_2, 19 : 1), F (C_6H_6–CH_2Cl_2, 9 : 1), G (C_6H_6–CH_2Cl_2, 1 : 1), H (CH_2Cl_2–MeOH, 99 : 1), I (CH_2Cl_2–MeOH, 19 : 1). A (0.2 g) consisted of aliphatic esters. B (1 g) was a mixture of terpenes. C (0.6 g) was re-crystallized from MeOH to **1a** (100 mg). The mother liquor was re-chromatographed on a Si gel column. Elution with C_6H_6 gave terpenes, **1b** (50 mg) and **3a** (50 mg). D (2 g) was re-chromatographed on a Si gel column. Elution with C_6H_6–CH_2Cl_2 mixtures of gradually increasing polarity gave **3a** (130 mg) and **3b** (300 mg). E (0.5 g) was a mixture of **3a**, **3b** and **3c**. F (0.2 G) was purified by prep. TLC (Si gel) to **3c** (50 mg). G (0.2 g) was a mixture of **3c** and **2b**. H (1 g) was crystallized from MeOH–H_2O to **2b** (750mg). I (1 g) was purified by prep.-TLC (Si gel, Et_2O) to **2a** (800 mg).

Identification of known compounds. The known compounds were identified either by direct comparison with authentic samples (**1a**, **1b**, **2a**) or by comparison of mp, $[\alpha]_D$ and spectral data with published data (**3a**, **3b**).

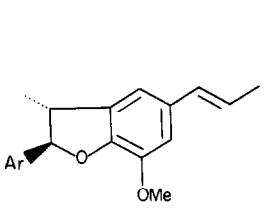
Rel-(7R, 8S, 1′R, 5′R)-$\Delta^{8'}$-*5′-methoxy*-3, *4-methylenedioxy*-1′, 4′, 5′, 6′-*tetrahydron*-*4′-oxo*-7.O.2′, 8.1′-*neolignan* (porosin-B, **2b**). Mp 114–116° (MeOH–H_2O) (Found: 342.1448; $C_{20}H_{22}O_5$ requires 342.1467). UV λ_{max}^{MeOH} nm: 260, 290 inf. (ϵ 14 000, 5100). IR ν_{max}^{KBr} cm^{-1}: 1660, 1630, 1500, 1450. ORD (*c* 1 mg/10 ml MeOH): $[\theta]_{335}$ +6800, $[\theta]_{315}$ 0, $[\theta]_{280}^{tr}$ −41 000, $[\theta]_{262}$ 0, $[\theta]_{252}^{pk}$ +85 500. MS *m/z* (rel. int.): 343 $[M+1]^+$ (10), 342 $[M]^+$ (50), 312 (69), 284 (26), 269 (22), 256 (21), 241 (20), 215 (33), 175 (100), 173 (25), 162 (78), 161 (23), 150 (20), 149 (68), 135 (100), 115 (53), 103 (70), 91 (90).

(7R, 8S, 7′S, 8′S)-4, *4′-Dihydroxy*-3, *3′-dimethoxy*-7.O.7′, 8.8′-*neolignan* (verrucosin, **3c**). Oil (Found: 344.1585; $C_{20}H_{24}O_5$ requires: 344.1624). UV λ_{max}^{MeOH} nm: 280 (ϵ 17 100). IR ν_{max}^{film} cm^{-1}: 3350, 1600, 1500. ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.7–7.1 (*m*, 6 ArH), 4.28 (*d*, *J* = 8.5 Hz, H-7), 5.01, (*d*, *J* = 8 Hz, H-7′), 1.5–2.5 (*m*, H-8, H-8′), 0.63 (*d*, *J* = 6.5 Hz, 3H-9), 1.05 (*d*, *J* = 6 Hz, 3H-9′), 3.81 and 3.87 (2*s*, 2 MeO). $[\alpha]_D^{22}$ + 38° ($CHCl_3$; *c* 0.25). *Dimethyl ether* (**3d**) (**3c**, CH_2N_2, Et_2O), mp and lit.[6, 14] mp 128–129°, $[\alpha]_D^{22}$ and lit.[6, 14] $[\alpha]_D$ +35° ($CHCl_3$; *c* 0.19).

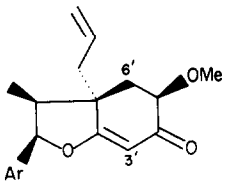
Porosin–dihydrofutoenone rearrangement. Porosin (**2a**, 100 mg) and TsOH (40 mg) were maintained in MeOH (15 ml) at 50° (8 hr). The solvent was evaporated under vacuum and the residue separated by prep. TLC (*Si gel*, Et_2O) into a mixture of **2a** + **2c** (30 mg), an addition product of **2a** and MeOH (25 mg) and **4a** (35 mg). Porosin-B (**2b**) treated in the same way gave **2b** + **2d**, an addition product of **2b** and MeOH and **4b** in similar proportions.

Rel-(7S, 8R, 1′S, 5′R, 8′S)-2′, 8′-*epoxy*-3, 4, 5′-*trimethoxy*-1′, 4′, 5′, 6′-*tetrahydro*-*4′-oxo*-7.9′, 8.1′-*neolignan* (**4a**). Mp 162–164°. UV λ_{max}^{MeOH} nm: 259, 285 inf. (ϵ 15 800, 4000). IR ν_{max}^{KBr} cm^{-1}: 1660, 1640, 1510. ORD (*c* 1 mg/10 ml MeOH): $[\theta]_{328}^{tr}$ −20 000, $[\theta]_{307}$ 0, $[\theta]_{275}^{pk}$ +67 300.

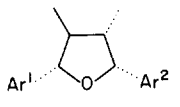
Rel-(7S, 8R, 1′S, 5′R, 8′S)-2′, 8′-*epoxy*-*5′-methoxy*-3, *4-methylenedioxy*-1′, 4′, 5′, 6′-*tetrahydro*-*4′-oxo*-7.9′, 8.1′-*neolignan* (**4b**). Mp and lit. [10] mp 171–173°. UV λ_{max}^{MeOH} nm: 259, 288 inf. (ϵ 15 800, 4000). IR ν_{max}^{KBr} cm^{-1}: 1660, 1640, 1490. ORD (*c* 1 mg/10 ml MeOH): $[\theta]_{327}^{tr}$ −20 500, $[\theta]_{308}$ 0, $[\theta]_{275}^{pk}$ +70 000.



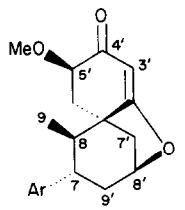
1a Ar = Guaiacyl
1b Ar = Veratryl



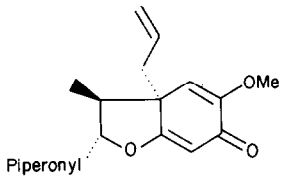
2a Ar = β-Veratryl
2b Ar = β-Piperonyl
2c Ar = α-Veratryl
2d Ar = α-Piperonyl



3a Ar^1 = Piperonyl, Ar^2 = Guaiacyl
3b Ar^1 = Piperonyl, Ar^2 = Veratryl
3c $Ar^1 = Ar^2$ = Guaiacyl
3d $Ar^1 = Ar^2$ = Veratryl



4a Ar = Veratryl
4b Ar = Piperonyl
4c Ar = Piperonyl, $\Delta^{5',6'}$



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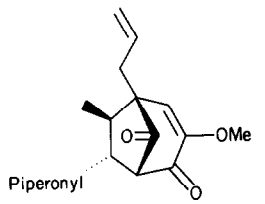

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