gave an oil (1 kg) which was distilled under vacuum in order to remove volatile compounds. The residue (332 g) was submitted to column and prep. TLC to yield 102 mg of **4** (system 1, R_f 0.55; system 2, R_f 0.46) and 0.7 mg of **5** (system 1, R_f 0.61; system 2, R_f 0.52), identified by comparison with authentic samples (TLC, IR, mmp). **4** was also found in the EtOH extract (4 mg).

Aristolochic acid Ia methyl ester methyl ether (**4**). The fraction containing the aristolochic acids from 13.3 kg dried roots was fractionated in phenolic and nonphenolic acids by countercurrent distribution as previously reported [1]. A portion of the phenolic acid mixture, after the removal of the main components by crystallization (dioxane), was treated with CH_2N_2 and submitted to prep. TLC (system 1, R_f 0.55; system 2, R_f 0.46) yielding the methyl ester of O-methylaristolochic acid Ia, 2.4 mg, identical to aristolochic acid I methyl ester (**4**).

Aristolochic acid Ia ethyl ester ethyl ether (**6**). Methylation of the remaining portion of phenolic acids with CHN_2 and separation of the products by prep. TLC (system 1, R_f 0.60; system 2, 0.51) afforded the ethyl ester of *O*-ethylaristolochic acid Ia (**6**), 7.6 mg, mp 266°. UV λ_{max}^{EtOH} nm (log ϵ): 252 (4.4), 319 (4.0), 392 (3.8); IR ν_{max}^{KBr} cm^{-1}: 1709 (C=O), 1592, 1506 (NO_2), 1460, 1383, 1326, 1274, 1221, 1145, 1047, 933 (CH_2O_2), 806, 753; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.47 (6H, *m*, 2 × Me), 4.28 (4H, *m*, 2 × CH_2O), 6.31 (2H, *s*, CH_2O_2), 7.02 (1H, *d*, $J_{6,7}$ = 8 Hz, H-7), 7.62 (1H, *t*, $J_{5,6}$ and $J_{6,7}$ = 8.3 Hz, H-6), 7.73 (1H, *s*, H-2), 8.57 (1H, *dd*, $J_{5,6}$ = 8.5 Hz, $J_{5,7}$ = 1 Hz, H-5), 8.79 (1H, *s*, H-9); EIMS, 70 eV, *m/z* (rel. int.): 383 $[M]^+$ (30), 338 $[M - OCH_2Me]^+$ (17), 337 $[M - NO_2]^+$ (54), 310 (24), 309 $[M - NO_2 - CH_2{=}CH_2]^+$ (100), 308 (9), 281 (17), 280 (39), 279 (15), 251 (9).

REFERENCES

1. Priestap, H. A., Ruveda, E. A., Mascaretti, O. A. and Deulofeu, V. (1971) *An. Asoc. Quim. Argent.* **59**, 245.
2. Rothschild, M., von Euw, J. and Reichstein, T. (1972) *Insect Biochem.* **2**, 334.
3. Pakrashi, S. C., Ghosh-Dastidar, P., Basu, S. and Achari, B. (1977) *Phytochemistry* **16**, 1103.

Phytochemistry, Vol. 21, No. 11, pp. 2756–2758, 1982.
Printed in Great Britain.

0031-9422/82/112756-03$03.00/0

AN UNUSUAL POROSIN TYPE NEOLIGNAN FROM *LICARIA CHRYSOPHYLLA**

ZENAIDE S. FERREIRA, NIDIA C. ROQUE, OTTO R. GOTTLIEB and HUGO E. GOTTLIEB†

Instituto de Quimica, Universidade de São Paulo, 05508 São Paulo, Brazil; †Isotope Department, The Weizmann Institute of Science, Rehovot, Israel

(*Received* 1 *March* 1982)

Key Word Index—*Licaria chrysophylla*; Lauraceae; chrysophyllin A; chrysophyllin B; benzofuranoid neolignans.

Abstract—The trunk wood of *Licaria chrysophylla* contains rel-(7*S*, 8*R*, 1′*S*, 5′*S*)-$\Delta^{8'}$-3,3′,5′-trimethoxy-4,5-methylenedioxy-1′,4′,5′,6′-tetrahydro-4′-oxo-7.1′,8.0.2′-neolignan (chrysophyllin A), which differs from all other known benzofuranoid neolignans by showing 7.1′ (rather than 8.1′) and 8.0.2′ (rather than 7.0.2′) linkages between the propenylphenol and allylphenol derived moieties.

The trunk wood of *Licaria chrysophylla* gave a considerable proportion of a novel neolignan, $C_{22}H_{26}O_7$, designated chrysophyllin A (**1a**). The base peak of its mass spectrum (*m/z* 192) was assigned to ion **2**. If the signals due to such a molecular unit are deleted from the ^{1}H and ^{13}C NMR spectra, all remaining signals are comparable with the analogous signals of the cyclohexenone moiety of 3′-methoxyporosin (**3a**) from *Aniba ferrea* [2] (Table 1). Nomenclature and numbering of neolignans follow the rules outlined in a recent review [6].

*Part LXVIII in the series "The Chemistry of Brazilian Lauraceae". For Part LXVII see ref. [1].

Such is the similarity of the spectral data that even stereochemical identity can be assumed to exist. Thus, the reciprocal γ-effect between C-5′ and C-7′ noted for porosin (**3b**) [5] is reproduced by **1a** which must also bear H-5′ and the allyl group in a *cis* relationship. The sole significant differences in the spectra refer to the NMR signals of all allyl protons, which appear at a consistently higher field in **1a** than in **3a** and **3b**, and of the carbon at position 6′, which appears at lower field in **1a** than in **3a** and **3b**. The signal of C-6′ of **3a** and **3b** is located at a relatively high field due to the protective γ-effect of the *cis*-methyl on C-8. Since no such protection of C-6′ occurs in **1a**, the existence of a *trans*-methyl could be suspected. In this case C-7′

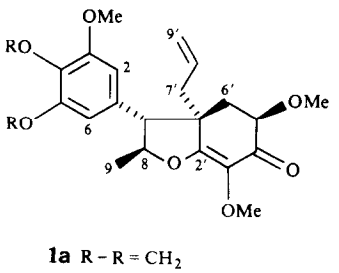
Table 1. NMR spectral data of neolignans*

Position	^{1}H data†			^{13}C data‡		
	1a	**3a** [2]	**3b** [3, 4]	**1a**	**3a** [2]	**3b** [5]
1	—	—		136.1	129.8	128.3
2	6.32*d*, 1.5	6.5–6.8*m*	6.76*d*, 2	102.3	106.2	108.6
3	—	—	—	149.7	147.8	148.5
4	—	—	—	130.2	147.8	148.5
5	6.39*d*, 1.5	6.5–6.8*m*	6.83*dd*, 8, 2	143.4	108.2	110.9
6	—		6.93*d*, 8	109.1	118.7	117.8
7	2.90*d*, 10.5	5.75*d*, 5.5	5.89*d*, 5.5	62.1	87.4	87.2
8	5.05*m*,	2.6*m*	2.6*m*	82.2	42.8	42.5
9	1.48*d*, 6	0.55*d*, 7.5	0.52*d*, 7.5	18.9	11.6	11.6
1′	—	—	—	48.3	48.7	50.2
2′	—	—	—	169.6	167.0	183.4
3′	—	—	5.59*s*	127.4	126.6	100.1
4′	—	—	—	192.7	192.3	196.6
5′	3.94*dd*, 12, 5	3.80*dd*, 12, 5	4.02*dd*, 12, 5	77.2	77.3	76.8
6′	2.45, 12, 5	1.7–2.7*m*	2.22*dd*, 12, 5	37.8	32.2	32.0
	1.89*t*, 12		1.92*t*, 12	—	—	—
7′	2.42*br dd*, 14.5, 5.5		2.69*dd*, 14.7, 7	39.1	39.8	39.0
	2.24*dd*, 14.5, 8		2.36*dd*, 14.7, 7	—	—	—
8′	5.2*m*	5.5–5.9*m*	6.0*m*	133.7	132.7	132.5
9′	5.05*m*	4.9–5.3*m*	6.35*m*	118.8	119.8	119.8
OMe	3.58*s*	3.62*s*	3.62*s*	57.1	59.2	57.8
OMe	3.76*s*	3.80*s*	3.90*s*	59.3	60.4	55.9
OMe	3.93*s*	—	3.90*s*	60.3	—	55.9
O_2CH_2	6.01*s*	5.92*s*	—	101.7	101.1	—

*Chemical shifts in ppm from internal TMS for $CDCl_3$ solutions at 270 MHz (**1**), 60 MHz (**3a**) and 220 MHz (**3b**) for ^{1}H spectra; at 20 MHz for ^{13}C spectra. Coupling constants (J) in Hz.

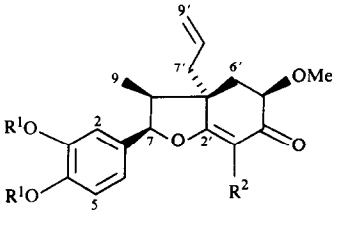
†δ Values, multiplicity, coupling constant [J(Hz)].

‡δ Values.



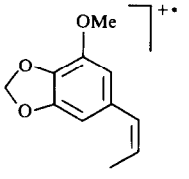
1a R–R = CH_2

1b R = Me

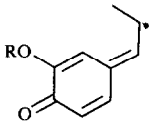


3a R^1–R^1 = CH_2, R^2 = OMe

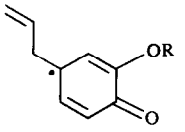
3b R^1 = Me, R^2 = H



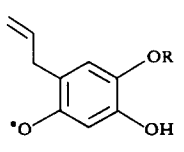
2



4



5



6

should suffer the γ-effect. This also does not happen. The chemical shifts for C-7′ of all three compounds are practically identical (δ 39.4 ± 0.4). Thus in comparison with **3a** and **3b**, in **1a** methyl and aryl must be interchanged. The carbon of position 1 of the aryl not substituted by hydrogen, is not expected to protect significantly either C-6′ or C-7′. Indeed, the presence of the aryl group in close proximity of the allyl protons is the sole reasonable explanation for their absorption at relatively high fields.

The location of the aryl–methyl substituents at interchanged positions is confirmed by further observations. Double irradiation of H-8, clearly a carbinolic proton (δ 5.05), in **1a** causes the collapse of the methyl-doublet (δ 1.48) to a singlet; and vice-versa, irradiation of H-9 causes the change of the H-8 multiplet to a doublet of $J = 10.5$ Hz. This coupling constant, much larger than $J_{H\text{-}7,H\text{-}8}$ (= 5 Hz) in the porosins (**3a**, **3b**), as well as the chemical shift of the methyl protons (δ 1.48), which are more shielded ($\delta_{Me} = 0.5$) in the porosins, points to a *trans*-aryl–methyl relationship in **1a**. All other possible decoupling experiments were performed and led to the expected results.

The presence of a small amount of chrysophyllin B (**1b**) in the extract was detected by ^{1}H NMR spectral means.

The biosynthesis of the porosin type neolignans (**3**) was postulated to involve coupling of the propenylphenol and the allylphenol derived radicals **4** and **5** [6]. By analogy, the biosynthesis of the chrysophyllin type neolignans would require the coupling of **4** with the 2,4-dihydroxy-5-methoxyallylbenzene derived radical, **6**. A biomimetic synthesis of a bicyclo (3.2.1) octanoid neolignan with the aryl and methyl substituents at analogously abnormal positions as in the chrysophyllins has been achieved by the concerted [2 + 4] cycloaddition of (*E*)-isosafrole to a 2,3-dimethoxy-6-hydroxyallylbenzene derived molecular species [7].

EXPERIMENTAL

Isolation of constituents. A sample of trunk wood of *L. chrysophylla* (Meissn.) Kosterm. (voucher Xyl. 7265, Herb 92081, INPA, Manaus) from the Negro–Marié Rivers, Amazonas, was reduced to powder (15 g) and percolated with petrol. Partial evaporation of the solvent and cooling to room temp. gave a ppt (0.1 g). This was purified by TLC (Si gel, C_6H_6–EtOAc, 1:1) to **1a** (66 mg) and a mixture of **1a** and **1b** (19 mg).

Rel-(7S,8R,1′S,5′S)-Δ^{8}-3, 3′, 5′-*trimethoxy*-4,5-*methylenedioxy*-1′, 4′, 5′, 6′-*tetrahydro*-4′-*oxo*-7.1′, 8.0.2′-*neolignan* (*chrysophyllin* A, **1a**). Mp 183–185° (C_6H_6). (Found: 402.1683; $C_{22}H_{26}O_7$ requires: 402.1679.) UV λ_{max}^{MeOH} nm: 258 inf., 273 (ε 14 250, 20 100). IR ν_{max}^{KBr} cm^{-1}: 1680, 1645, 1635, 1515, 1450, 1200, 1070, 1035, 950, 830, 790. ORD (*c*, 0.5 mg/10 ml MeOH): $[\phi]_{370}$ 0, $[\phi]_{324}^{pk}$ + 22 510, $[\phi]_{305}$ 0, $[\phi]_{280}^{tr}$ − 55 500, $[\phi]_{255}$ 0, $[\phi]_{245}^{pk}$ + 8040, $[\phi]_{225}$ 0. MS *m/z* (rel. int.): 402 (6), 361 (15), 331 (5), 301 (31), 192 (100), 179 (20), 165 (11), 118 (11), 91 (18), 77 (11). *Dihydro derivative.* Hydrogenation of **1a** in MeOH over Pd–C and purification of the product by TLC gave an oil, ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.40 (*d*, $J = 2$ Hz, H-2, H-5), 2.90 (*d*, $J = 11$ Hz, H-7), 5.15 (*m*, $J = 11$, 6.5 Hz), 1.55 (*d*, $J = 6.5$ Hz, 3H-9), *ca* 3.9 (superimposed, H-5′), 2.50 (*dd*, $J = 12$, 6 Hz, H-6′), 1.85 (*t*, $J = 12$ Hz, H-6′), 1.5 (*m*, superimposed, 2H-7′), 1.2 (*m*, 2H-8′), 0.8 (*t*, $J = 7$ Hz, 3H-9′), 3.61, 3.73, 3.93 (3*s*, 3OMe), 5.97 (*s*, O_2CH_2). MS *m/z*: 404 $[M]^+$.

Acknowledgements—We are grateful to Professor Klaus Kubitzki, Universität, Hamburg, and to Dr. Arthur A. Loureiro, Instituto Nacional de Pesquisas da Amazonia, Manaus, for collection and classification of the plant material.

REFERENCES

1. Dias, A. de F., Giesbrecht, A. M. and Gottlieb, O. R. (1981) *Phytochemistry* **21**, 1137.
2. Andrade, C. H. S., Braz Fo., R. and Gottlieb, O. R. (1980) *Phytochemistry* **19**, 1191.
3. Aiba, C. J., Braz Fo., R. and Gottlieb, O. R. (1973) *Phytochemistry* **12**, 413.
4. Aiba, C. J., Gottlieb, O. R., Yoshida, M., Mourão, J. C. and Gottlieb, H. E. (1976) *Phytochemistry* **15**, 1031.
5. Wenkert, E., Gottlieb, H. F., Gottlieb, O. R., Pereira, M. O. da S. and Formiga, M. D. (1976) *Phytochemistry* **15**, 1547.
6. Gottlieb, O. R. (1978) *Prog. Chem. Org. Nat. Prod.* **35**, 1.
7. Büchi, G. and Chu, P.-S. (1978) *J. Org. Chem.* **43**, 3717.