

LIGNOIDS FROM *NECTANDRA AMAZONUM* AND *N. GLABRESCENS**

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Key Word Index—*Nectandra amazonum*; *N. glabrescens*; Lauraceae; furofuran lignans; benzofuran neolignans.

Abstract—The fruit calyces of *Nectandra amazonum* contain the furofuran lignans sesamin and *O*-methylpiperitol, while the fruits of *N. glabrescens* contain the dihydrobenzofuran neolignans licarin-A and licarin-E.

Neither *Nectandra amazonum* Nees nor *N. glabrescens* Benth. both pertaining to the family Lauraceae, have been previously analysed chemically. In the present investigation calyces of the former species were found to contain nerolidol, stigmaterol, dulcitol, piperonylic acid and two furofuran lignans (+)-sesamin and (+)-*O*-methylpiperitol [2]. The fruits of the latter species were found to contain sitosterol, mannitol, kaempferol, quercetin, eugenol, isoeugenol, safrol, isosafrol and two dihydrobenzofuran neolignans licarin-A [3] and licarin-E.

Licarin-E, the sole new compound, and the known licarin B [3] have identical spectral properties and thus share the same constitutional formula. However, in view of the antipodal DC curves, $\theta_{298}^{\max} = +9250$ for licarin E, the structure of (2*R*,3*R*)-2,3-dihydro-7-methoxy-3-methyl-2-piperonyl-5*E*-propenylbenzofuran or, according to our proposed general system of nomenclature [4, 5], (7*R*,8*R*)-3'-methoxy-3,4-methylenedioxy- $\Delta^{7'}$ -8,5', 7*O*.4'-lignan, must be assigned to this compound. All other isolates were identified by spectral analysis extensive, when applicable to their acetates.

EXPERIMENTAL

Nectandra amazonum. Fruit calyces (410 g) gave an EtOH extract (32 g). Its suspension in 60% aq EtOH was extracted successively with hexane and CHCl₃. Upon addition of MeOH to the hexane extract (6.5 g) fatty material pptd. Addition of Me₂CO to the aq. EtOH ext (17 g) resulted in crystallization of dulcitol (100 mg). Chromatography of the defatted hexane ext gave nerolidol (200 mg) and stigmaterol (100 mg), that of the CHCl₃ ext (9 g) gave sesamin (60 mg), methylpiperitol (25 mg) and piperonylic acid (20 mg).

Nectandra glabrescens. Fruits (290 g) were submitted to the same procedure as above giving an EtOH extract (40 g) parti-

tioned into hexane (13.5 g), CHCl₃ (10 g) and aq. EtOH (17 g) extracts. The defatted hexane extract gave eugenol and isoeugenol (500 mg), safrol and isosafrol (1 g), and sitosterol (140 mg). The CHCl₃ ext gave licarin-E (100 mg), licarin-A (70 mg), kaempferol (sepd as the triacetate, 30 mg) and quercetin (sepd as the tetraacetate, 400 mg). The aq. EtOH ext gave mannitol (280 mg).

Licarin-E. Mp 83–85° (MeOH). IR ν_{\max}^{KBr} cm⁻¹: 1600, 1505, 1490, 1450, 1332, 1255, 1225, 1140, 1035, 960, 835. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 278, 295 inf. (ϵ 11.350, 6.150). ¹H NMR (60 MHz, CDCl₃) δ 1.35 (*d*, *J* = 7 Hz, 3H-9), 1.84 (*d*, *J* = 5 Hz, 3H-9'), 3.2–3.7 (*m*, H-8), 3.88 (*s*, OMe-3'), 5.15 (*d*, *J* = 9 Hz, H-7), 5.92 (*s*, O₂CH₂), 6.10 (*dq*, *J* = 16, 6.5 Hz, H-8'), 6.32 (*d*, *J* = 16 Hz, H-7'), 6.7–7.05 (*m*, H-2,4,5,2',6'). ¹³C NMR (20 MHz, CDCl₃) δ 17.9 (C-9), 18.3 (C-9'), 45.8 (C-8), 56.0 (OMe), 93.4 (C-7), 101.1 (O₂CH₂), 106.7 (C-2), 108.0 (C-5), 109.7 (C-2'), 113.4 (C-6'), 120.1 (C-6), 123.3 (C-8'), 131.1 (C-1', C-7'), 133.2 (C-5'), 134.4 (C-1), 144.1 (C-3'), 146.5 (C-4'), 147.9 (C-3, C-4). MS *m/z* (rel. int.): 324 (M, 100), 309 (8), 202 (2), 189 (8), 162 (5), 149 (9), 135 (15). CD (MeOH; *c* 0.01) $\theta_{298}^{\max} +9250$.

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REFERENCES

1. Silva, W. D. da, Braz-Filho, R. and Gottlieb, O. R. (1988) *Phytochemistry* 27, (in press).
2. Rao, C. B. S. (ed.) (1978) *Chemistry of Lignans*. Andhra University Press, Waltair.
3. Aiba, C. J., Corrêa, R. G. C. and Gottlieb, O. R. (1975) *Phytochemistry* 12, 1163.
4. Gottlieb, O. R. (1978) *Progr. Chem. Org. Nat. Prod.* 35, 1.
5. Gottlieb, O. R. and Yoshida, M. (1988) in *Natural Products of Woody Plants* (Rowe, J. W. and Kirk, C. H., eds), (in press). Springer, Berlin.

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