Phytochemistry, 1981, Vol. 20, p. 180. © Pergamon Press Ltd. Printed in England. 0031-9422/81/0101-0180 $02.00/0

PROPACIN, A COUMARINOLIGNOID FROM *PROTIUM OPACUM*

M. DAS GRAÇAS B. ZOGHBI,* NÍDIA F. ROQUE† and OTTO R. GOTTLIEB†

*Instituto Nacional de Pesquisas da Amazônia, Conselho Nacional de Desenvolvimento Científico e Tecnológico, 69000 Manaus, AM, Brazil; †Instituto de Química, Universidade de São Paulo, 05508 São Paulo, SP, Brazil

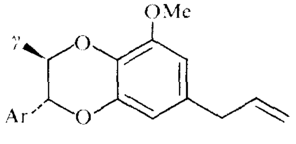
(*Received* 28 *April* 1980)

Key Word Index—*Protium opacum*; Burseraceae; propacin; coumarinolignoid; (*E*-1′-guaiacyl-2′-methylethylenedioxy)-1′,2′: 8,7 or 1′,2′: 7,8-6-methoxycoumarin.

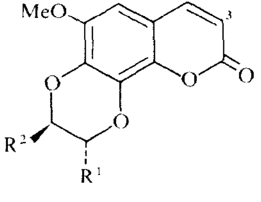
The C_6C_3 units of the benzodioxan flavonolignoids, such as sylibin [1], and xanthonolignoids, such as kielcorin [2, 3], show an oxygenated γ-carbon. With the exception of the neolignans of the eusiderin group (**1**) [4], as far as we know no comparable benzodioxans with an unoxygenated γ-carbon have yet been identified. In the present note we wish to report the isolation of such a coumarinolignoid from *Protium opacum*.

The compound, designated propacin (**2a** or **2b**), $C_{20}H_{18}O_7$, is reminiscent of the eusiderins with respect to the C_6C_3 unit, which not only causes the base peak in the MS by retro-Diels–Alder fragmentation to $[C_6H_3\cdot OH\text{-}\cdot OMe\cdot CH{=}CHMe]^{+\cdot}$, but also shows the expected ^1H NMR signals [4]. The *trans* relation of the substituents of the benzofuran is thus assured. The three aromatic protons are represented by a broad singlet (δ 6.93) as expected for a 3,4-dioxyphenyl residue. In the spectrum of the acetate, this signal is resolved into a two-proton multiplet at lower field and a doublet ($J = 2$ Hz) at higher field. A proton, *meta*-related to the original OH, is thus vicinal to two substituted positions, a fact which points to the 4-hydroxy-3-methoxy pattern.

The existence of a coumarin unit in propacin is consistent with the IR (ν_{max}^{KBr} 1710 cm^{-1}), UV (λ_{max}^{MeOH} 323 nm, ε 13 950) and ^1H NMR (δ 6.33 and 7.63, AB system, $J = 9.5$ Hz) spectra. The symmetry of the A and B parts of this NMR signal reveals C-8 to be substituted [5]. Indeed, the lone aromatic proton (δ 6.55, *s*) is situated at C-5 in view of the characteristic chemical shift of the H-4 doublet: δ 7.63 vs. *ca* 8 expected for a 5-methoxycoumarin [5, 6]. The OMe must be located at the vicinal position 6, since considerable C_6H_6-induced upfield shifts (Δ 0.44, 0.56) occur with respect to both OMe signals of propacin acetate.



1a Ar = 3,4,5-trimethoxyphenyl
1b Ar = 3,4-methylenedioxyphenyl



2a R¹ = 4-hydroxy-3-methoxyphenyl, R² = Me
2b R¹ = Me, R² = 4-hydroxy-3-methoxyphenyl

EXPERIMENTAL

Powdered trunk wood (5.5 kg) of *P. opacum* Swart. (voucher INPA herbarium No. 63341) from the region of River Canumã, an affluent of River Madeira, Municipality of Nova Olinda, Amazonas State, was percolated with EtOH. The extract (38 g) was fractionated by successive washings into petrol- (15 g), $CHCl_3$- (8 g) and EtOAc- (1 g) soluble parts. The $CHCl_3$ extract was chromatographed on a dry Si gel (80 g deactivated with 10 % H_2O) column developed with C_6H_6–Me_2CO (9:1). The more polar fractions (900 mg) were submitted to Si gel column chromatography. Elution with $CHCl_3$–MeOH of gradually increasing polarity gave sitosterol (300 mg) and **2** (50 mg).

Propacin (**2a** *or* **2b**), colourless crystals, mp 226–228 ($CHCl_3$–MeOH) (M found: 370.1040; $C_{20}H_{18}O_7$ requires: 370.1053). ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1615, 1565, 1450, 1290, 1145, 1050, 840. λ_{max}^{MeOH} nm: 231, 257 inf., 286, 323 (ε 33 000, 4650, 7800, 13 950). ^1H NMR (60 MHz, $CDCl_3$): δ 6.33, 7.63 (AB system, $J = 9$ Hz, H-3, H-4), 6.55 (*s*, H-5), 6.93 (*s*, H-2′, H-5′, H-6′), 4.7 (*d*, $J = 7.5$ Hz, H-7′), 4.3 (*m*, H-8′), 1.33 (*d*, $J = 6.5$ Hz, Me-8′), 3.95, 3.9 (2*s*, 2 OMe). MS *m/e* (rel. int.): 370 M^+ (40), 327 (10), 233 (30), 164 (100). *Acetate*, mp 202–205 (C_6H_6). ν_{max}^{KBr} cm^{-1}: 1770, 1730, 1640, 1610, 1470, 1320, 1225, 1160, 1065, 850. ^1H NMR (60 MHz, $CDCl_3$): δ 6.33, 7.65 (AB system, $J = 9.5$ Hz, H-3, H-4), 6.55 (*s*, H-5), 6.8 (*d*, $J = 2$ Hz, H-2′), 7.1–7.07 (*m*, H-5′, H-6′), 4.78 (*d*, $J = 7.5$ Hz, H-7′), 4.25 (*m*, H-8′), 1.3 (*d*, $J = 6.5$ Hz, Me-8′), 3.87, 3.83 (2*s*, 2 OMe), 2.33 (*s*, OAc).

Acknowledgements—We are indebted to Mr. Osmarino Monteiro, Dr. William A. Rodrigues and Prof. Ayssor P. Mourão for the collection, the identification and the extraction of the plant material respectively.

REFERENCES

1. Hänsel, R., Schulz, J. and Pelter, A. (1975) *Chem. Ber.* **108**, 1482.
2. Castelão, J. F. Jr., Gottlieb, O. R., Lima, R. A. de, Mesquita, A. A. L., Gottlieb, H. E. and Wenkert, E. (1977) *Phytochemistry* **16**, 735.
3. Nielsen, H. and Arends, P. (1978) *Phytochemistry* **17**, 2040.
4. Braz Filho, R., Mourão, J. C., Gottlieb, O. R. and Maia, J. G. S. (1976) *Tetrahedron Letters* 1157.
5. Lassak, E. V. and Pinhey, J. T. (1967) *J. Chem. Soc. C* 2000.
6. Nielsen, B. E. (1970) *Coumarins of Umbelliferous Plants*, p. 52. The Royal Danish School of Pharmacy, Copenhagen.