

ISOPREGOMISIN, A 1,4-BIS(PHENYL)-2,3-DIMETHYLBUTANE  
LIGNAN FROM *PORLIERIA CHILENSIS*

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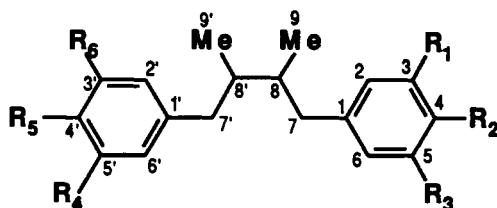
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ABSTRACT.—From twigs of a Chilean Zygophyllaceae species named *Porlieria chilensis* a new symmetrical 1,4-bis(phenyl)-2,3-dimethylbutane type lignan was isolated. This new compound was accompanied by the known lignan meso-dihydroguaiaretic acid (**1**) and the name isopregomisin (**2**) was proposed for it. The structural determination of **2** was accomplished by careful analysis of spectral data.

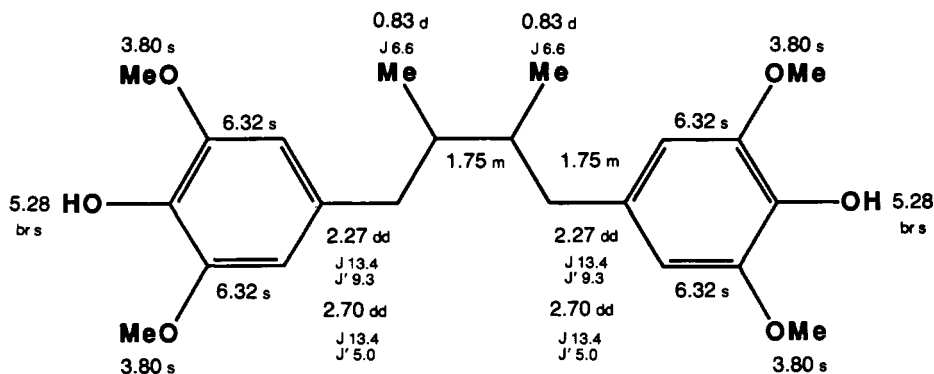
An investigation of the twigs of *Porlieria chilensis* Johnston (Zygophyllaceae) has supplied the known lignan, meso-dihydroguaiaretic acid [**1**], (**1,2**) together with the new compound, isopregomisin [**2**].

Isopregomisin [**2**] was obtained as a white crystalline solid, mp 110–112°, [ $\alpha$ ]<sub>D</sub><sup>0</sup> ( $c = 0.48$ , CHCl<sub>3</sub>). Combustion analysis and accurate mass measurements provided a molecular formula of C<sub>22</sub>H<sub>30</sub>O<sub>6</sub>. The uv spectrum of **2** is very similar to that of meso-dihydroguaiaretic acid [**1**]. It underwent a bathochromic

shift in basic solution. The mass spectrum was almost identical to that of pregomisin [**3**], isolated from *Schizandra chinensis* Baill. (Schizandraceae) (3,4). The cd spectrum, which showed no absorption between 200–400 nm, suggested that **2** has the meso form. The 200 MHz <sup>1</sup>H-nmr spectrum (CDCl<sub>3</sub>) is indicated around expression **4** and shows that the compound is a symmetrical 1,4-bis(phenyl)-2,3-dimethylbutane type lignan, with two methoxys and one phenolic hydroxyl group in each aromatic ring also in a symmetrical position.



- 1** R<sub>1</sub>=R<sub>6</sub>=OMe, R<sub>2</sub>=R<sub>5</sub>=OH, R<sub>3</sub>=R<sub>4</sub>=H  
**2** R<sub>1</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>6</sub>=OMe, R<sub>2</sub>=R<sub>5</sub>=OH  
**3** R<sub>1</sub>=R<sub>6</sub>=OH, R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=R<sub>6</sub>=OMe



The  $^{13}\text{C}$ -nmr spectrum of **2** (Table 1) is in complete agreement with a highly symmetric compound and shows signals for eight carbon atoms. Consequently, the structure of **2** is isomeric with pregomisin [**3**], and it was named isopregomisin.

TABLE 1.  $^{13}\text{C}$ -nmr Spectral Data of Isopregomisin [**2**] ( $\text{CDCl}_3$ ,  $\delta$  ppm).

Carbon	Compound <b>2</b>
3,5,3',5' . . . . .	146.8
1,1' . . . . .	132.9 <sup>a</sup>
4,4' . . . . .	132.7 <sup>a</sup>
2,6,2',6' . . . . .	105.6
OMe . . . . .	56.3
7,7' . . . . .	39.4 <sup>b</sup>
8,8' . . . . .	39.0 <sup>b</sup>
9,9' . . . . .	16.3

<sup>a</sup>Values may be interchanged.

<sup>b</sup>APT test.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were determined on a Kofler hotstage microscope and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were obtained with a Bruker WP-200 spectrometer using TMS as internal standard. Ir spectra were recorded on a Perkin-Elmer 735 B spectrometer. Uv spectra were recorded on a Carl Zeiss DMR 22 spectrometer. High resolution mass spectra were obtained with a VG Micromass ZAB-2F spectrometer operating at 70 eV and 200°. Optical activities were measured on a Perkin-Elmer 241 polarimeter.

PLANT COLLECTION.—*P. chilensis* was collected in Maipo Canyon (Región Metropolitana) in April 1985. A voucher specimen is deposited in the Museo de Historia Natural, Santiago de Chile.

EXTRACTION AND ISOLATION.—A sample of *P. chilensis* (6.0 kg, dry twigs) was dried, pow-

dered, and extracted with petroleum ether at room temperature. The extracts were concentrated and partitioned between MeOH-H<sub>2</sub>O (9:1) and petroleum ether. The MeOH layer was stripped of solvent, leaving a residue of 10 g. Part of the residue (5 g) was fractionated by cc over Si gel 60 (Merck), using hexane gradually enriched with EtOAc. The fractions were monitored by tlc on glass plates of Si gel 60 F<sub>254</sub> (Merck), using the system hexane-EtOAc (9:1) and spraying with 33% H<sub>2</sub>SO<sub>4</sub>. Final purification was achieved on glass plates of Si gel 60 F<sub>254</sub> + 366, 2mm (Merck), using hexane-EtOAc (9:1) and by crystallization from hexane.

*meso*-DIHYDROGUAIARETIC ACID [**1**].—Crystalline solid (1.5 g): mp 90°;  $[\alpha]^{22\text{D}}_0$  0° (0.35, CHCl<sub>3</sub>); spectral data identical with those reported in the literature (4).

ISOPREGOMISIN [**2**].—Crystalline solid (130 mg): mp 110–112°;  $\nu$  max (KBr) 3370, 1610, 1510 cm<sup>-1</sup>;  $\lambda$  max (MeOH), 225 (sh), 273 nm (log  $\epsilon$  4.3, 3.6);  $\lambda$  max (MeOH + OH<sup>-</sup>) 251, 290 nm (log  $\epsilon$  4.1, 3.7); eims  $m/z$  [M]<sup>+</sup> 390 (87), 168 (60), 167 (100); hreims  $m/z$  [M]<sup>+</sup> 390.2047 (C<sub>22</sub>H<sub>30</sub>O<sub>6</sub>, -0.5 mmu deviation), 167.0706 (C<sub>9</sub>H<sub>11</sub>O<sub>3</sub>, 0.2 mmu deviation); combustion anal. calcd for C<sub>22</sub>H<sub>30</sub>O<sub>6</sub>, C 67.67, H 7.74, found C 67.95, H 7.76.

## ACKNOWLEDGMENTS

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