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## AN ARYLTETRALIN LIGNAN FROM *PERSEA LINGUE*

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Key Word Index—*Persea lingue*; Lauraceae; stem bark; aryltetralin lignan; lingueresinol.

**Abstract**—The stem bark of *Persea lingue* afforded a new aryltetralin lignan, named lingueresinol, which was shown to be a positional isomer of *epi-lyoniresinol*.

*Persea lingue* (Ruiz et Pav.) Nees is the southernmost representative of the Lauraceae, with a range extending from the Andean foothills and coastal cordillera of semi-arid central Chile into the temperate forest as far as 42°S latitude [1]. Its wood is used to make furniture and its fruit is reputedly toxic to livestock [1]. The bark is employed in traditional medicine for the treatment of dysentery, leucorrhoea, endometritis and some kinds of tumours [2].

A methanol extract of the defatted trunk bark yielded 0.023% of a crystalline substance with the composition  $C_{22}H_{28}O_8$  by high resolution mass spectrometry. Its UV spectrum showed a shoulder near 240 nm, an absorption maximum at 275 nm and a slightly weaker shoulder at 282 nm, the two latter undergoing batho- and hyperchromic changes upon addition of base, indicating the presence of one or more phenol functions. The  $^1H$ NMR spectrum exhibited several one- and two-proton multiplets in the upfield region, a three-proton singlet at  $\delta$ 3.46, another singlet, integrated for six protons, at  $\delta$ 3.82 and a typical methoxyl signal at  $\delta$ 3.92; the downfield region only contained a two-proton singlet at  $\delta$ 6.43 and a one-proton singlet at  $\delta$ 6.61. The  $^{13}C$ NMR spectrum showed the methoxyl signals at  $\delta$ 55.9, 56.3 (double intensity) and 59.1, as well as six other aliphatic carbon resonances and 10 aromatic carbon signals, two of which corresponded to two carbons each.

The above data appeared to agree reasonably well with those published for the aryltetralin lignan lyoniresinol [3-7]. Some of the aromatic ring  $^{13}C$ NMR resonances and a methoxy signal at  $\delta$ 67.9, however, differed by several ppm from the published values [7]. Two-dimensional chemical shift-correlated  $^1H$ - $^1H$  and  $^1H$ - $^{13}C$ NMR spectra were recorded and analysed (Table 1), leading to the conclusion that the relative stereochemistry of the *P. lingue* compound differs from that of lyoniresinol in that the two methoxy groups bear a *cis* relationship to each other and are *trans* with respect to the pendent aryl ring, as in the semisynthetic *epi-lyoniresinol* dimethyl ether [5]. Furthermore, the  $^{13}C$  resonances could be accommodated more satisfactorily by placing the downfield methoxyl group at C-4', between the two magnetically equivalent methoxyls [8], instead of assuming that it lies at C-8, compressed between the C-7 hydroxyl group and ring B. The implication that a

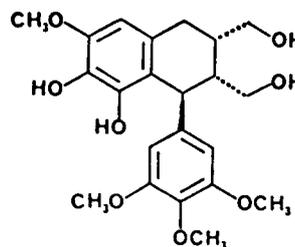


Table 1.  $^1H$  and  $^{13}C$ NMR chemical shifts of lingueresinol (1) in  $DMSO-d_6$  ( $\delta$  ppm)

| Atom             | H         | C     |
|------------------|-----------|-------|
| H-1; C-1         | 4.36      | 40.1  |
| H-2; C-2         | 1.98      | 46.8  |
| H-2a; C-2a       | 3.64      | 67.9  |
| H-3; C-3         | 1.65      | 39.3  |
| H-3a; C-3a       | 3.52      | 64.3  |
| H-4; C-4         | 2.62/2.75 | 32.3  |
| C-4a             | —         | 128.8 |
| H-5; C-5         | 6.61      | 106.9 |
| C-6              | —         | 147.0 |
| C-7              | —         | 137.3 |
| C-8              | —         | 137.9 |
| C-8a             | —         | 125.1 |
| C-1'             | —         | 133.6 |
| H-2'/6'; C-2'/6' | 6.43      | 106.2 |
| C-3'/5'          | —         | 147.7 |
| C-4'             | —         | 146.6 |
| MeO-6            | 3.92      | 55.9  |
| MeO-3'/5'        | 3.82      | 56.3  |
| MeO-4'           | 3.46      | 59.1  |

catechol grouping is present in the molecule was confirmed by a weak shoulder appearing in the UV spectrum in methanol after adding aluminium trichloride. The positive optical rotation, as in (+)-lyoniresinol and *epi-lyoniresinol*, suggests that the steric arrangement of the aromatic rings is the same in the *Persea* lignan, which should

therefore have the (1 $\beta$ ,2 $\alpha$ ,3 $\alpha$ ) configuration. We consequently propose structure **1** and the name *lingueresinol* for this compound from *P. lingue*.

#### EXPERIMENTAL

**General.** Plant material was collected in the grounds of 'El Principal' estate, in the Clarillo valley, SE of Santiago, in January (summer). A voucher specimen is preserved in the herbarium of the National Museum of Natural History, Santiago, Chile. Chromatographic columns were packed with silica gel 60 or Sephadex LH-20. NMR were run at 400 MHz ( $^1\text{H}$ ) and 100.6 MHz ( $^{13}\text{C}$ ); chemical shifts are given in ppm ( $\delta$ ) from TMS, using the solvent multiplet (DMSO- $d_6$ ) as int. standard.

**Extraction and isolation.** Powdered air-dried trunk bark (900 g) was extracted successively (Soxhlet) with petrol,  $\text{CHCl}_3$  and MeOH. The MeOH extract was concd and the residue (35 g) fractionated by CC on silica gel eluting with  $\text{CHCl}_3$ -MeOH. One of the latter frs (3.8 g) was sepd further by gel filtration on Sephadex with MeOH followed by chromatography on silica gel as before to yield 210 mg pure *lingueresinol*.

**Lingueresinol (1).** Recrystallized from MeOH; mp 179–183°;  $[\alpha]_D^{25} + 35.9^\circ$  (MeOH;  $c$  1.255). MS  $m/z$  (rel. int.): 420.1778 ( $[\text{M}]^+$ , calc.  $\text{C}_{22}\text{H}_{28}\text{O}_8$  420.1784) (100), 402 [ $\text{C}_{22}\text{H}_{26}\text{O}_7$ ] $^+$  (13), 371 [ $\text{C}_{21}\text{H}_{23}\text{O}_6$ ] $^+$  (27), 248 [ $\text{C}_{14}\text{H}_{16}\text{O}_4$ ] $^+$  (25), 217 [ $\text{C}_{13}\text{H}_{13}\text{O}_3$ ] $^+$  (56), 210 [ $\text{C}_{11}\text{H}_{14}\text{O}_4$ ] $^+$  (21), 205 [ $\text{C}_{12}\text{H}_{13}\text{O}_3$ ] $^+$  (69), 183 [ $\text{C}_9\text{H}_{11}\text{O}_4$ ] $^+$  (64), 173 [ $\text{C}_{11}\text{H}_9\text{O}_2$ ] $^+$  (46), 167 [ $\text{C}_9\text{H}_{11}\text{O}_3$ ] $^+$  (70).

IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 1630, 1538, 1518, 1470. UV  $\lambda_{\text{max}}^{\text{MeOH}}$  (log  $\epsilon$ ): 240sh (3.8), 275 (3.34), 282sh (3.33). UV  $\lambda_{\text{max}}^{\text{MeOH} + \text{MeONa}}$  (log  $\epsilon$ ): 283sh (3.43), 296sh (3.28). UV  $\lambda_{\text{max}}^{\text{MeOH} + \text{AlCl}_3}$  (log  $\epsilon$ ): 275 (3.34), 282 (3.33), 317sh (2.76).  $^1\text{H}$  and  $^{13}\text{C}$  NMR, see Table 1.

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## A FLAVANONE GLYCOSIDE FROM *HAMELIA PATENS*

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**Key Word Index**—*Hamelia patens*; Rubiaceae; flavanone glycosides; rosmarinic acid.

**Abstract**—A new glycoside, 5,7,2',5'-tetrahydroxyflavanone 7-rutinoside, together with narirutin and rosmarinic acid were isolated from the aerial parts of *Hamelia patens*. The structures were assigned by spectral ( $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT  $^{13}\text{C}$  NMR and FABMS) methods and the absolute configurations determined by CD in conjunction with NMR data.

#### INTRODUCTION

*Hamelia patens* Jacq. (Rubiaceae) is a herbaceous perennial plant used in Peruvian folk-medicine as an anti-inflammatory, antirheumatic and antipyretic remedy [1]. Previous phytochemical investigations of this species reported the isolation of ursolic acid, sitosterol glucoside,

apigenin, rutin and oxindole alkaloids [2–4]. As a part of our continuing study on the biologically active metabolites from South American Rubiaceae [5–8], we report here the isolation of a new flavanone glycoside **2**; besides the already known (2S)-narirutin **1**, a mixture of (2S)- and (2R)-narirutin **1a** and rosmarinic acid **3**, from a methanol extract of *H. patens*.