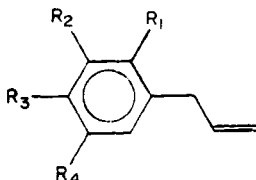


NEW C<sub>6</sub>-C<sub>3</sub> AND C<sub>6</sub>-C<sub>1</sub> COMPOUNDS FROM *PIPER LENTICELLOSUM*

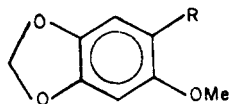
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The medicinal uses of *Piper* species are many and varied (1). *Piper lenticellosum* CDC, commonly known in Colombia as "cordoncillo oloroso" and/or "cordoncillo aromático," is used in folk medicine; published data indicate that it has dermatological, anti-diarrheal, and parasiticidal activity (2). The isolation of 3,4-methylenedioxypropenylbenzene, 3,5-dimethoxytoluene, and the allyl benzenes **1a**, **1b**, and **1d** were reported earlier from the essential oil of the leaves of *P. lenticellosum* (3). In this paper we report the isolation of the known allyl benzenes **1a-1d** and two new natural products **2a** and **2b**.



- 1a** R<sub>1</sub>=OMe, R<sub>2</sub>=H, R<sub>3</sub>=R<sub>4</sub>=OCH<sub>2</sub>O  
**1b** R<sub>1</sub>=R<sub>2</sub>=H, R<sub>3</sub>=R<sub>4</sub>=OMe  
**1c** R<sub>2</sub>=H, R<sub>1</sub>=R<sub>3</sub>=R<sub>4</sub>=OMe  
**1d** R<sub>1</sub>=H, R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=OMe



- 2a** R=CHO  
**2b** R=CH=CH-CHO

The low resolution mass spectrum ( $M^{+}$  180) and the <sup>1</sup>H-nmr spectrum indicated formula C<sub>9</sub>H<sub>8</sub>O<sub>4</sub> for compound **2a**. Absorption at 1660 cm<sup>-1</sup> in the ir spectrum is attributed to an aromatic -CHO, further evident from the uv absorption at 349 nm (ξ 4095). The <sup>1</sup>H-nmr spectrum contained signals due to two *para*-oriented aromatic protons (δ 6.50, s and δ 7.26, s), a methoxy group (δ 3.87, s), a methylenedioxy group (δ

6.00, s), and an aldehyde (δ 10.66, s). Structure **2a** was confirmed by comparison with the spectroscopic data published for the synthetic compound (4).

The uv spectrum of **2b** showed absorptions at 248, 300, and 376 nm (ξ 11330, 11330, and 16995) and the ir spectrum showed the presence of a conjugated carbonyl group (1665 cm<sup>-1</sup>) and an aromatic ring (1645-1480 cm<sup>-1</sup>). The <sup>1</sup>H-nmr spectrum was very similar to that of **2a**, except for the presence of a doublet at δ 9.79 (*J*=8.0 Hz) assignable to an aldehydic proton coupled to a olefinic proton which appeared as a double doublet at δ 6.60 (*J*=16.0 and 8.0 Hz). This last hydrogen was present in a typical *trans*-system with the remaining olefinic proton (δ 7.98, d, *J*=16.0 Hz). Further evidence for the structure of **2b** was provided by the  $M^{+}$  at *m/z* 206 in the mass spectrum.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded with the following instruments: ir, Perkin-Elmer 467 and 700; <sup>1</sup>H nmr, Varian Associates T-60; uv, Beckman 25; ms, Finnigan 3000.

PLANT MATERIALS.—A specimen from Tambo, Cauca, Colombia, was collected in March 1982, and identified by Prof. J.M. Idrobo. A voucher specimen is deposited at Herbario Nacional Colombiano U.N., Bogotá, 124071.

ISOLATION OF THE CONSTITUENTS.—A wood sample (835 g) was continuously extracted with EtOH giving an extract (32 g). The C<sub>6</sub>H<sub>6</sub>-CHCl<sub>3</sub> (1:1) soluble part (15 g) was chromatographed on silica (300 g) and eluted successively with petrol (40-60°) and C<sub>6</sub>H<sub>6</sub>. The petrol eluent yielded **1a** (4.59 g). The C<sub>6</sub>H<sub>6</sub> eluent yielded in order: **1b** (36 mg), **1c** (20 mg), **2a** (104 mg), **1d** (137 mg), and **2b** (285 mg). These compounds were purified by preparative tlc (silica gel HF<sub>254</sub>; the developing solvents were different mixtures of C<sub>6</sub>H<sub>6</sub> and CHCl<sub>3</sub>).

The compounds **1a-1d** were identified by di-

rect comparison of spectral data (uv, ir, <sup>1</sup>H nmr, and eims) with published data (3,5) and by direct comparison with authentic samples.

*2-Methoxy-4,5-methylenedioxybenzaldehyde (2a).*

—Crystals mp 107° (C<sub>6</sub>H<sub>14</sub>); uv λ<sub>max</sub> (EtOH) nm(ξ) 241 (7200), 277 (3240), 349 (4095); ir ν<sub>max</sub> (KBr) cm<sup>-1</sup> 3070, 3050, 3010, 2950, 2910, 2880, 1660, 1625, 1510, 1490, 1470, 1430, 1400, 1375, 1270, 1240, 1205, 1170, 1120, 1085, 1040, 1010, 940, 865, 850, 800, 760; <sup>1</sup>H nmr (60 MHz, CDCl<sub>3</sub>) δ 3.87 (s, OMe-2), 6.00 (s, OCH<sub>2</sub>O), 6.50 (s, H-3), 7.26 (s, H-6), 10.66 (s, CHO); eims *m/z* (rel. int.) 180 M<sup>+</sup> (100), 179 (88), 165 (25), 164 (20), 151 (16), 149 (26), 148 (8), 137 (18), 135 (12), 134 (47), 120 (22), 107 (39).

*Trans-2-methoxy-4,5-methylenedioxy-cinnamaldehyde (2b).*—Crystals mp 151-152° (CCl<sub>4</sub>); uv λ<sub>max</sub> (EtOH) nm (ξ) 248 (11330), 300 (1133), 376 (16995); ir ν<sub>max</sub> (KBr) cm<sup>-1</sup> 2970, 2960, 2920, 2850, 1665, 1625, 1615, 1510, 1500, 1480, 1460, 1440, 1390, 1370, 1315, 1290, 1260, 1250, 1205, 1185, 1170, 1140, 1090, 1040, 1010, 980, 940, 890, 860, 840, 765; <sup>1</sup>H nmr (60 MHz, CDCl<sub>3</sub>) δ 3.90 (s, OMe-2), 6.10 (s, OCH<sub>2</sub>O), 6.60 (dd, *J*=16.0 and 8.0 Hz, H-2'), 6.73 (s, H-3), 7.18 (s, H-6), 7.98 (d, *J*=16.0 Hz, H-1'), 9.79 (d, *J*=8.0 Hz, H-3');

eims *m/z* (rel. int.) 206 M<sup>+</sup> (68), 205 (5), 176 (13), 175 (100), 161 (8), 133 (26), 105 (10).

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