

CHEMISTRY IN THE ANNONACEAE, XVII.¹
PHENYLPROPENES FROM *UVARIODENDRON CONNIVENS* SEEDS

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Uvariodendron connivens (Benth.) R. E. Fries, an understory tree found in the rain-forest zone of Nigeria and Cameroun (1), does not appear to have been a subject of previous phytochemical analysis (2). We report here the findings of an examination of a small sample of ripe seeds from which the phenylpropene derivatives **1**, **2**, and **3** were isolated in yields of 0.19%, 0.10%, and 0.13%, respectively. Accurate mass

$C_{12}H_{16}O_4$, and 1H nmr (Table 1) indicated that each had two equivalent aromatic protons and three methoxyl substituents.

The identity of the major compound as elemicin (**1**) was established from full analysis of both 1H - and ^{13}C -nmr data (Table 1) which clearly required the 3-phenylprop-1-en system. The ^{13}C -nmr data was of particular value in placement of the three methoxyl resonances at C-

TABLE 1. 1H - (90 MHz) and ^{13}C -nmr (62.5 MHz) Spectra^a of Isolated Compounds

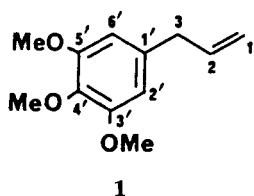
Atom	1H nmr			^{13}C nmr	
	1	2	3	1	3
C-1'				135.76	132.48
C-2'	6.40 s	6.80 s	6.60 s	105.76	103.82
C-3'				153.26	153.40
C-4'				136.64	138.18
C-5'				153.26	153.40
C-6'	6.40 s	6.80 s	6.60 s	105.76	103.82
C-3	3.28 d (6) ^b	7.40 d (16)	6.59 d (16)	40.51	131.14
C-2	5.90 ddt (15,7,6)	6.81 dd (16,8)	6.34 dt (16,5)	137.28	128.11
C-1	5.06 dd (15,2) 5.14 dd (7,2)	9.66 d (8)	4.30 d (5)	115.92	63.63
3'-OMe	3.70 s	3.88 s	3.84 s	56.10	56.17
4'-OMe	3.80 s	3.88 s	3.82 s	60.70	60.92
5'-OMe	3.70 s	3.88 s	3.84 s	56.10	56.17

^aAll spectra run in $CDCl_3$.^bJ values in parentheses.

measurements for the three compounds revealed molecular ions corresponding to $C_{12}H_{16}O_3$, $C_{12}H_{14}O_4$, and

3', C-4', and C-5' (C-4' at 136.64 ppm, shielded by two adjacent oxygen substituents, and 4'-OMe at 60.70 ppm, deshielded due to C-3' and C-5' both being substituted) rather than C-2', C-4', and C-6', a pattern which would also have led to two equivalent

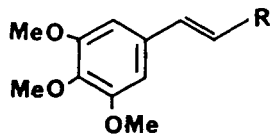
¹For part XVI, see M.A. Meek, C.H. Schwalbe, P.G. Waterman, and I. Mohammad, *Acta Cryst.*, (in press).



aromatic protons. The corresponding phenylprop-2-en, *trans*-isoelemicin, has previously been reported from another plant of the Annonaceae, *Gutteria gaumeri* (3).

Compound **2** gave ^1H -nmr resonances typical of a *trans*-cinnamaldehyde. The substitution pattern of the aromatic ring was established by its reduction to give the alcohol **3** in which the 3',4',5'-substitution pattern had been established by ^{13}C nmr (see below). Compound **2** was therefore identified as 3',4',5'-trimethoxycinnamaldehyde, previously reported from *Zanthoxylum procerum* (Rutaceae) (4).

Compound **3** was established as 3',4',5'-trimethoxycinnamyl alcohol by analysis of nmr spectra (Table 1), which indicated the occurrence of an oxymethylene group, a *trans* double bond and the 3',4',5'-substitution pattern. Compound **3** was obtained on reduction of **2** and on acetylation readily gave the corresponding acetate (**4**). Surprisingly, **3** does not appear to have been reported previously as a natural product.



- 2** R=CHO
3 R=CH₂OH
4 R=CH₂OAc

EXPERIMENTAL

PLANT MATERIAL.—Seeds of *U. connivens* were collected in the Korup National Park, Cameroun, during the summer of 1983. A voucher specimen, D. W. Thomas—2264, has been deposited at the herbarium of the Missouri Botanic Gardens, St. Louis, MO.

EXTRACTION AND ISOLATION.—The milled seeds (180 g) were extracted in a Soxhlet apparatus with petroleum ether (40–60°) for 3 days. The concentrated extract was chromatographed over a silica gel column eluting with toluene to give **1** (342 mg) and then with toluene-EtOAc-HOAc (95:5:0.1) to give **2** (180 mg). Further elution with a 90:10:0.1 mixture of the above solvents gave **3** (234 mg).

ELEMICIN (1).—Oil: ms m/z 208.1091 (M^+) (calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$, 208.1099). ^1H and ^{13}C nmr (see Table 1). Physical and spectral data in close agreement with that published (5).

3',4',5'-TRIMETHOXYCINNAMALDEHYDE (2).—Oil: ms m/z 222.0876 (M^+) (calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4$, 222.0892). ^1H nmr (see Table 1). Physical and chemical data in close agreement with that published (4, 6).

3',4',5'-TRIMETHOXYCINNAMYL ALCOHOL (3).—Mp, 110°; uv max, nm (MeOH) (log ϵ), 230 (3.95), 267 (4.06); ir (KCl) 3400, 1580, 1450 cm^{-1} ; ms m/z (rel. int.) 224.1035 (M^+ , 100) (calcd for $\text{C}_{12}\text{H}_{16}\text{O}_4$, 224.1048), 195 (31), 193 (13), 181 (26), 179 (4). ^1H and ^{13}C nmr (see Table 1).

3',4',5'-TRIMETHOXYCINNAMYL ACETATE (4).—Compound **3** (50 mg) in pyridine (5 ml) treated with Ac_2O (2 ml) at room temperature gave **4** (35 mg) as a gum; ir (KCl) 1740 cm^{-1} . ^1H nmr (90 MHz, CDCl_3) 6.60 (2H, s, H-2', H-6'), 6.56 (1H, d, $J=16$ Hz, H-3), 6.24 (1H, dt, $J=16, 4$ Hz, H-2), 4.70 (2H, d, $J=4$ Hz, CH_2 -1), 3.83 (6H, s, OMe-3', OMe-5'), 3.81 (3H, s, OMe-4'), 2.07 (3H, s, COMe).

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