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J. Nat. Prod., **1994**, 57 (5), 663-664• DOI:
10.1021/np50107a018 • Publication Date (Web): 01 July 2004

Journal of Natural Products
Vol. 57, No. 5, pp. 663-664, May 1994

SYNTHESIS AND PROPERTIES OF PHASEOLLIDIN ISOFLAVAN

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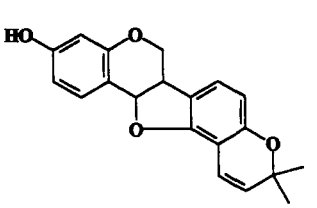
ABSTRACT.—Phaseollidin isoflavan [**3**] has been synthesized by the reduction of phaseollin [**1**] in 64% yield. The ^{1}H- and ^{13}C-nmr spectra are reported for this novel compound.

Phaseollidin isoflavan [**3**], a presumed intermediate in the biosynthesis of the pterocarpan phytoalexins, was unexpectedly obtained in 64% yield in the attempted reduction of phaseollin [**1**] to phaseollidin [**2**] by the method of Dewick and Steele (1). Previously, reduction of **1** by this method resulted in the cleavage of the *gem*-dimethyl chromene moiety. The present work describes reduction of both the allylic and benzylic ethers and gives a detailed spectral characterization of **3**.

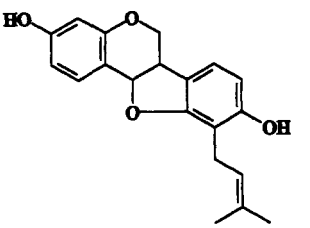
Phaseollidin isoflavan is a novel compound. The related compound, 2′-OMe-phaseollidin isoflavan [**4**] has previously been isolated from *Vigna unguiculata* (2). Isoflavans isolated from *Lotus corniculatus* and *Phaseolus vulgaris* have been shown to be present as both the 2′-OH and 2′-OMe compounds (3–5). The identification of 2′-OMe-phaseollidin isoflavan [**4**] from *Vigna unguiculata* would suggest the corresponding 2′-OH isoflavan, viz. phaseollidin isoflavan [**3**] is also likely to occur as a natural product. In confirming the structure of **3** we became aware of the paucity of published spectral information relating to B-ring prenylated isoflavans.

EXPERIMENTAL

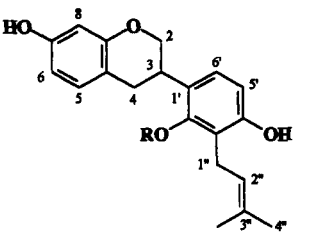
GENERAL EXPERIMENTAL PROCEDURES.—Nmr spectra were recorded on a Bruker AC300 (300 MHz) spectrometer in $CDCl_3$. Nmr data are reported in ppm (δ) and referenced to TMS δ 0.0 for both ^{1}H- and ^{13}C-nmr spectra. Mass spectra were obtained with a VG70-250S spectrometer at 70



1



2



3 R=H
4 R=Me

eV. Uv spectra were recorded on a Cary 1 spectrophotometer.

Tlc was performed on aluminum foil-backed Si gel plates (0.2 mm) (Merck), and developed by lightly spraying with a solution of vanillin (1.0 g) in concentrated H_2SO_4 (50 ml) and charring at 150°. Prep. centrifugal chromatography (Chromatotron apparatus) was performed on 1 mm Si gel rotors (Merck GF-254 type 60) with $CHCl_3$ (2% EtOH). Hplc was carried out on a Waters RCM 8×100 5 μm C-18 Resolve column at 700 psi; MeOH-H_2O (55:45) to MeOH-H_2O (65:35) from 0–6 min, MeOH-H_2O (65:35) to MeOH-H_2O (55:45) 10–12 min, MeOH-H_2O (55:45) to 17 min at 1 ml/min; R_t of **3** 10.0 min; uv detector, 280 nm.

Phaseollin was obtained from an earlier isolation (6). All reagents were obtained from the Aldrich Chemical Company and were used without further purification unless stated. 1,2-Dimethoxyethane (DME) was freshly distilled from Na/benzophenone "blue" under dry N_2. Liquid NH_3 was anhydrous and distilled from glass. Ether was Et_2O (BDH Analar). Room temperature was 18–23°.

PHASEOLLIDIN ISOFLAVAN [**3**].—To a solution of phaseollin [**1**], (11.3 mg, 0.035 mmol) in DME (9 ml), under dry N_2, was added liquid NH_3 (14 ml) and freshly cut Li metal (25 mg, 3.5 mmol). After stirring for 3 min, the blue reaction mixture was quenched with H_2O (15 ml) and allowed to warm to room temperature over 1 h. The pH was adjusted (6) by the dropwise addition of concentrated HCl, concentrated *in vacuo* to remove DME, diluted with H_2O (20 ml), and extracted with Et_2O (3×30 ml). The combined Et_2O extracts were dried ($MgSO_4$), filtered (vac.), concentrated *in vacuo*, and chromatographed (prep. centrifugal) to yield phaseollidin isoflavan [**3**] as a white amorphous solid, 7.3 mg, 64.2%. This material was further purified by hplc. Uv λ max (MeOH) (log ε) 206 (4.79), 227 (sh) (4.22), 250 (2.67), 283 (3.68), 289 (sh) (3.51) nm; λ max (MeOH+NaOAc) no spectral changes; λ max (MeOH+NaOMe) (log ε) 210 (5.10), 244 (sh) (4.07), 265 (3.28), 292 (3.76) nm; effect reversible by acid; eims (probe) 70 eV, *m/z* 326.1509 $[M]^+$ (100) (calcd for $C_{20}H_{22}O_4$ 326.1518), 204 (97), 192 (21), 191 (74), 149 (69), 148 (96), 147 (56), 136 (27), 135 (71), 123 (59); ^1H nmr (300 MHz, $CDCl_3$) δ 1.78 (3H, s, $-CH_3$), 1.85 (3H, s, $-CH_3$), 2.83–3.00 (2H, m, H-4), 3.44 (2H, br d, J=6.9 Hz, H-1″), 3.48 (1H, m, H-3), 4.00 (1H, t, J=10.1 Hz, H-2), 4.31 (1H, ddd, J=10.4, 3.4, and 1.7 Hz, H-2), 5.26 (1H, tt, J=7.1 and 1.3 Hz, H-2″), 6.33–6.39 (3H, m, H-5′, H-6, and H-8), 6.81 (1H, d, J=8.3 Hz, H-6′), 6.92 (1H, d, J=8.1 Hz, H-5); ^{13}C nmr (75.5 MHz, $CDCl_3$) δ 17.9 (q, C-5″), 22.8 (t, C-1″), 25.8 (q, C-4″), 30.5 (t, C-4), 31.9 (d, C-3), 70.1 (t, C-2), 103.3 (d, C-8), 107.7 (d, C-5′), 107.9 (d, C-6), 113.3 (s, C-4a), 114.8 (s, C-1′), 120.5 (s, C-3′), 121.2 (d, C-2″), 125.2 (d, C-6′), 130.4 (d, C-5), 136.4 (s, C-3″), 152.9 (s, C-2′), 153.7 (s, C-4′), 154.9 (s, C-8a), 155.3 (s, C-7).

ACKNOWLEDGMENTS

The authors are grateful for funds provided by the New Zealand Lottery Grants Board to purchase the Cary 1 spectrophotometer; to H. Wong, The New Zealand Institute For Industrial Research and Development Ltd., Lower Hutt, for nmr; and to D.D. Rowan, The Horticulture and Food Research Institute of New Zealand Ltd., Palmerston North, and G.A. Lane, New Zealand Pastoral Agriculture Research Institute Ltd., Palmerston North, for helpful discussions.

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Received 16 November 1993