6-O-VERATRYL CATALPOSIDE: A NEW IRIDOID GLUCOSIDE FROM TECOMELLA UNDULATA

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Key Word Index-Tecomella undulata; Bignoniaceae; iridoid glucoside; 6-O-veratryl catalposide.

Plant. Tecomella undulata (G. Don) Seem; Voucher specimen No. 8257 deposited in the R.U.B.L. Herbarium. Source. University Reserve Forest of Rajasthan. Uses. In indigenous system of medicine [1].

Previous work. T. undulata [2–5]. On sister species T. mollis [6], T. radicans [7], T. indica [8], T. capensis [9] and T. stans [10].

Present work. From the acetone extract of the heartwood, we have isolated a new glucoside 6-O-veratryl catalposide (1) characterized (IR, UV, NMR, MS and hydrolysis products) as belonging to the group of iridoid glucosides.

EXPERIMENTAL

Isolation. Defatted heartwood (500 g) was extracted with C_3H_6O ; the compound separated out on concentration and was crystallized from MeOH–Et₂O (4:1) as colourless needles. m.p. 218–219°. [α] $_{15}^{35}$ – 179 (pyridine). Found: C, 52:53; H, 5:99; OMe, 11:50. Calc. for $C_24H_{30}O_{13}H_2O$: C, 52:94; H. 5:88; OMe, 11:40%). UV λ_{max} (EtOH) 225, 262, 293 nm was identical to that of veratric acid [11] indicating that the main chromophores of glucoside are due to a veratryl moiety. IR ν_{max} (KBr) 3509–3226 (broad, –OH), 1712 (aromatic ester carbonyl), 1653 (enolic double bond) and 1603 cm $^{-1}$ (aromatic). It formed a pentacetyl derivative (2), m.p. 123–124° (Pyridine–Ac₂O), needles from EtOH.

Hydrolysis. Acid hydrolysis (7% H₂SO₄ for 7 min and 10%

HCl for 30 mins) yielded a black product insoluble in all organic solvents showing behaviour similar to that of other iridoid glucosides [12, 13]. It gave positive Godin's test [14, 15]. The sugar moiety was identified as D-glucose by PC.

Basic hydrolysis with Ba(OH)₂ yielded veratric acid, m.p. $181-182^{\circ}$ and catalpol (4), m.p. $199-201^{\circ}$. The absence of veratryl moiety in glucose was shown by MS of the acetate (2) (m/e 331, tetra acetyl glucose moiety [11]) and was supported by the isolation of p-glucose by β -glucosidase hydrolysis of (1).

The NMR spectrum of (2) and catalposide hexacetate [16] (3) exhibited a general similarity in the disposition of protons. The spectrum of (2) (60 Mc, CDCl₃, δ values) showed the expected aromatic protons [7·75 (H_x, d, J_{xz} 2 H_z), 7·08 (H_y, d, J_{yz} 9 H_z), 7·93 (H_z, dd, J_{yz} 9 H_z and J_{xz} 2 H_z)]. Taking the viryl signal at 6·51 [C-3(H), d, J 6 H_z] as reference, the region between 4·6-5·4 showed 8 protons [C-1, C-1', C-4, C-6, C-10(1 H), C-2', C-3', C-4'], the region between 3·5-4·6, 11 protons [C-6'(2 H), C-10(1 H), C-7(epoxide proton, 1 H), C-5'(1 H) and 2 × OMe(6 H)], the region 2·0-2·25 was assigned to the acetyl protons and integrated for 15 protons (5 × COMe, 15 H) and the two multiplet between 2·61–2·90 assigned to C-9 and C-5 protons. The NMR spectrum, thus confirmed (1), to be derivative of catalpol (4).

In the MS of (1), the largest fragment observed at m/e 364 correspond to the aglucone of (1), as expected [15]. The location of veratryl moiety, as in (1), was finally indicated by a study of products, obtained after acid hydrolysis [17] of the dihydro derivative [hydrogenated with Pd/C in EtOH-H₂O (5:3)], m.p. 130-131°.

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O-METHYLPELLOTINE, A NEW PEYOTE ALKALOID FROM LOPHOPHORA DIFFUSA*

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The Mexican cactus Lophophora diffusa (Croizat) H. Bravo has only recently been recognized as a Lophophora species in its own right [1,2]. Scores of chemical papers [3,4] have been published on its sister species L. williamsii (Lem.) Coulter, the mescaline-containing and vision-producing "peyote". L. diffusa, which is also called "peyote", has however not been extensively investigated.

In a TLC investigation of *Lophophora* populations, Todd [5] found pellotine to be the major alkaloid of *L. diffusa* and reported low amounts of lophophorine and anhalamine, and traces only of anhalonidine and mescaline. During a recent reinvestigation of *L. williamsii* and *L. diffusa* (Bruhn and Holmstedt. to be published) we were able to largely confirm Todd's findings, but we also found some minor unknown compounds. In the present communication we wish to report the identification of one of these unknown compounds as the tetrahydroisoquinoline alkaloid *O*-methylpellotine, not previously known to occur in nature.

The extremely low yields of non-phenolic alkaloids from *L. diffusa* did not permit the isolation of any compound. However, comparison with reference materials using TLC and GC indicated the presence of *O*-methylpellotine. After purification

by preparative TLC the band corresponding to reference O-methylpellotine was used for GC-MS. The identification of O-methylpellotine is based on identical MS and the same chromatographic behaviour (TLC, GC) as an authentic sample. O-Methylpellotine (1,2-dimethyl-6,7.8-trimethoxytetrahydroisoquinoline) has not earlier been identified in Lophophora species, although its presence could be expected, several closely related alkaloids already being found [3].

EXPERIMENTAL

Plant material. Lophophora diffusa (Croizat) H. Bravo was collected north of Vizarrón, Querétaro, on 29 June 1971 by Jan G. Bruhn and Sr. Hernando Sánchez-Mejorada, Departamento de Botánica, Instituto de Biología, Universidad Nacional Autónoma de México. Mexico City, who also identified the plants. A herbarium specimen has been placed in the Department of Pharmacognosy, Biomedicum, Uppsala.

Isolation of alkaloids. Experimental details have been described in earlier publications [6,7]. A part of the purified alkaloid extract (500 mg) was fractionated on an ion-exchange column (IRA 400) into phenolic and non-phenolic alkaloids. These fractions were then studied by TLC and GC. Only 2% (10 mg) of the total alkaloids were recovered as non-phenolic alkaloids. The non-phenolic alkaloids were subjected to preparative TLC on Si gel G plates. System: CHCl₃--EtOH-NH₃ conc (80:20:0,4). The band corresponding to O-methylpelotine was scraped off and eluted with hot EtOH. After filtration and evaporation, the residue was dissolved in a small amount of abs. EtOH and studied by GC.

Identification of O-methylpellotine. GC on 2 columns (5% SE-30 and 5% XE-60 on Gas Chrom Q, 100/120 mesh. col. temp. 150°) showed a peak with the same retention times as O-methyl-

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