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A FLAVANONE GLYCOSIDE FROM *DIPLAZIUM ESCULENTUM*

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Key Word Index—*Diplazium esculentum*; Polypodiaceae; a new flavanone glycoside; eriodictyol 5-*O*-methyl ether 7-*O*-β-D-xylosylgalactoside.

Abstract—We report in this paper the isolation and identification of a new glycoside, eriodictyol 5-*O*-methyl ether 7-*O*-β-D-xylosylgalactoside from whole plant of the fern *Diplazium esculentum*.

INTRODUCTION

The UV spectra and diagnostic shifts [1] of the glycoside were characteristic of a 5,7-disubstituted eriodicytol. Acid hydrolysis showed the presence of an aglycone, xylose and galactose. The aglycone on demethylation (48% HBr–AcOH) afforded eriodictyol (mp, mmp, UV, ^{1}H NMR MS, IR spectra and co-chromatography) [2]. KOH degradation [3] of the aglycone gave the mono-methyl ether of phloroglucinol (mp and co-TLC) and protocatechuic acid (mp and co-TLC) which determined the hydroxyls at C-7, C-3′ and C-4′ and a methoxyl at C-5. The UV spectrum of the aglycone confirmed the presence of a free OH at C-7 (bathochromic shift with NaOAc) and an OMe at C-5 (unaffected by $AlCl_3$). Hence the aglycone is eriodictyol 5-*O*-methyl ether (mp, mmp, ^{1}H NMR, MS, IR spectra and co-chromatography) [4] Methylation [5, 6] and hydrolysis gave 2,3,6-trimethylgalactose, 2,3,4-trimethylxylose [7] and eriodictyol 5,3′,4′-tri-*O*-methyl ether (mp, mmp, UV, IR spectra and co-chromatography) showing that the sugars were linked at position-7 of the aglycone. Partial acid hydrolysis of the glycoside liberated xylose first as terminal sugar and emuslin enzymatic hydrolysis revealed the presence of a β-linkage between the sugars as well as to the aglycone. Thus it was identified as eriodictyol 5-*O*-methyl ether 7-*O*-β-D-xylosylgalactoside.

EXPERIMENTAL

Diplazium esculentum (2 kg) (whole plant) were extracted 2 × with EtOH under reflux; the combined extracts (10 l.) were concd under red. pres. to *ca* 300 ml and successively extracted with petrol, C_6H_6 EtOAc and Me_2CO. The Me_2CO extract afforded a brownish yellow solid which was further rechromatographed over Si-gel column; furnished a dark yellow solid; crystallized from EtOAc: petrol as yellow needles (800 mg), mp 62–4°. TLC, Si-gel, R_f 0.62 (MeOH–$CHCl_3$, 6:4); PC, R_f 0.92 (BuOH–AcOH–H_2O, 4:1:5). UV, λ_{max}^{MeOH} nm 288, 330 (sh); +$AlCl_3$, 290, 335 (sh); +NaOAc, 290, 332 (sh). 500 mg of the glycoside was hydrolysed with H_2SO_4 (7%, 40 ml) and gave an aglycone, xylose and galactose. The aglycone was purified over a Si-gel column (MeOH–MeCOMe, 9:1) and crystallized as yellow needles (EtOH); mp 110° (d), $C_{16}H_{14}O_6$ (M^+ 302). (Found; C, 63.50; H, 4.63; required for $C_{16}H_{14}O_6$; C, 63.57; H, 4.63%). TLC, Si-gel R_f 0.71 (MeOH–$CHCl_3$, 7:3); PC, R_f 0.94 (BuOH–AcOH–H_2O, 4:1:5). UV, λ_{max}^{MeOH} nm 290, 330 (sh); +$AlCl_3$, 288, 335 (sh); +NaOAc, 325, 332 (sh). ^{1}H NMR (90 Hz,), δ, 7.25 (*d*, C-6′ and C-2′); 7.20 (C-5′); 6.30 (*d*, C-6 or C-8); 6.00 (*s*, 3H of 3-OH); 2.75 (H-1 and H-2). MS (*m/e*) 302 (M^+), 287 (M^+ −15), 259 (M^+ −43), 192 (M^+ −110) and 109 (M^+ −193).

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