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A PYRONE GLYCOSIDE FROM *ERIGERON KARWINSKYANUS*

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Key Word Index—*Erigeron karwinskyanus*; Compositae; pyrone glucoside; 3-hydroxy-4-pyrone 3-α-D-glucopyranoside.

Abstract—The aerial parts of *Erigeron karwinskyanus* yielded 3-hydroxy-4-pyrone 3-α-D-glucopyranoside, a new glycoside. The structure was elucidated from a combination of spectral data.

INTRODUCTION

Erigeron karwinskyanus DC. (Compositae) is a perennial herb, found in the mountainous region of Nainital. Some *Erigeron* species have been found to show biological activity and the pyrone β-glycosides, erigeroside and 4-pyrone-3-β-D-glucopyranoside have been reported in their extracts [1, 2]. No previous chemical studies have been reported on *E. karwinskyanus*. This communication reports 3-hydroxy-4-pyrone 3-α-D-glucopyranoside (**1**), a new glycoside isolated from an ethanolic extract of *E. karwinskyanus*.

RESULTS AND DISCUSSION

The ethanolic extract of aerial parts of *E. karwinskyanus* was subjected to column chromatography (silica gel). Elution with methanol yielded an amorphous solid which was purified by HPLC and recrystallized from methanol to white needles. This compound ($C_{11}H_{14}O_8$) was found to be a 3-hydroxy-4-pyrone 3-α-D-glycopyranoside ($M^+ + 1$ at m/z 275) and its structure was established on the basis of spectral data. Complete structural information was obtained from the IR, ^{1}H NMR and mass spectra, and hydrolysis of the glycoside. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3550–3320 indicated the presence of a polymeric hydroxyl group. Diagnostic bands of γ-pyrone were at 1662 and 1610 [3]. Absorptions at 1240, 1150–1130 and 780 are due to =C–O– and C–O–C in the pyrone ring. Its UV absorptions at 216 and 262 nm also indicated an α,β-unsaturated keto group in the pyrone ring. Bands at 770 and 840 in the IR spectrum suggested the presence of an α-glucoside. The protons at δ6.8 (*d*, 1H, H-5), 8.32 (*d*, 1H, H-6) and 8.5 (*s*, 1H, H-2) in the 90 MHz ^{1}H NMR spectrum of the glycoside also indicated a pyrone aglycone. MS: m/z 275 $[M+1]^+$ and base peak at 112. The fragments at 112, 86, 85, 84 and 55 showed a γ-pyrone, the degradation occurring with the loss of C_2H_2 or CO [4]. The ion peaks at 163, 145, 127, 73 and 57 are from the sugar part of the molecule.

The fragment ion m/z 331 in the MS of the acetylated glycoside ($[M]^+$ 442) indicated the formation of a tetra-acetyl glucose oxonium ion after separation of the aglycone. Further fragmentation at C-1 would give fragments at 169 and 109 by the loss of acetic acid or ketene and 43 due to an acylium ion. The fragments at 169 and 109 confirmed the pyranose carbohydrate ring [5, 6] and the high intensity of m/z 331 (87%) suggested an α-glucoside. This is also supported by the observation of Biemann *et al.*, who have reported that the intensity of fragment m/z 331 is very low in a β-anomer but high in the α-anomer, and they have also used this observation for deducing the stereochemistry at C-1 in anomeric acetates [5].

Failure of **1** to undergo emulsin hydrolysis indicated an α-linkage between sugar and aglycone. Compound **1** $[\alpha]_D^{20}$ +162° (H_2O), showed a 'downward' mutarotation on addition of 6% methanolic hydrochloric acid to an aqueous solution, further confirming that the glycoside is the α-anomer.

EXPERIMENTAL

Mps are uncorr. The UV spectrum was recorded in EtOH and the IR spectrum in KBr. ^{1}H NMR spectra were obtained at 90 MHz in D_2O with TMS as int. standard. MS were recorded at 70 eV.

Plant material. The plants were collected locally from Nainital. A voucher No. H 257/79, has been deposited at the Herbarium of the Royal Botanic Gardens, Kew.

Isolation of 3-*hydroxy*-4-*pyrone* 3-*α*-D-*glucopyranoside* (**1**). Air dried plants (aerial parts, 3 kg) were ground to a fine powder which was extracted with EtOH in a Soxhlet. The extract was concd to 200 ml under red. pres. and extracted with hot distilled H_2O. The H_2O soluble portion was treated successively with $CHCl_3$ and EtOAc, concd and chromatographed on silica gel. Elution with MeOH yielded an amorphous compound which crystallized from MeOH and when further purified by HPLC afforded crystals, mp 188–189° (Found: C, 48.42; H, 5.15. $C_{11}H_{14}O_8$ requires C, 48.17; H, 5.11%); $[\alpha]_D^{20}$ +162° (H_2O); slightly bitter in taste. Compound **1** is soluble in H_2O, sparingly soluble in cold EtOH, and insoluble in Et_2O. It gave no colour with NaOH or $FeCl_3$ soln, did not absorb Br_2–H_2O but gave a positive Molisch test. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}; 3550–3320, 3100, 1662, 1610, 1240, 1150–1130, 780, 770 and 840; ^{1}H NMR (90 MHz) (D_2O): δ3.7–3.8 (*m*, 4H, H-2′, H-3′, H-4′, H-5′), 3.98 and 4.05 (2H, H-6′), 5.1 (1H, H-1′), 6.8 (*d*, 1H, H-5), 8.32 (*d*, 1H, H-6) and 8.5 (*s*, 1H, H-2); MS *m/z*: 275 $[M+1]^+$, 183, 163, 162, 145, 141, 86, 85, 84, 73, 60, 57 and 55.

Glucoside tetra-acetate. Compound **1** on acetylation (Ac_2O–pyridine) and recrystallization from MeOH gave a glucoside tetra-acetate; MS *m/z* (rel. int.): 442 $[M]^+$, 169 (100), 331 (87), 109 (62), 211 (30), 271 (22), 42 (13) and 112 (11).

Acid hydrolysis of **1**. Acid hydrolysis (6% methanolic H_2SO_4, 5 hr) gave only a small quantity of white amorphous aglycone from the EtOAc extract, which gave a red colour with $FeCl_3$. MS *m/z*: 112 $[M]^+$; IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1662 and 1610 (diagnostic bands of γ-pyrone). The remaining aq. layer reduced Fehlings soln and Tollen's reagent, and the sugar was identified as D-glucose by co-PC in *n*-BuOH–HOAc–H_2O (4:1:5), EtOAc–pyridine–H_2O (5:2:7), *n*-BuOH–pyridine–H_2O (6:4:3) and EtOAc–HOAc–H_2O (5:2:2).

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3-BENZYL-4-CHROMANONES FROM *MUSCARI COMOSUM*

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Key Word Index—*Muscari comosum*; Liliaceae, 3-benzyl-4-chromanones; homoisoflavanones; 5-hydroxy-3-(*p*-hydroxybenzyl)-7,8-dimethoxy-4-chromanone; 5,8-dihydroxy-3-(*p*-hydroxybenzyl)-7-methoxy-4-chromanone; 5,7-dihydroxy-3-(*p*-hydroxybenzyl)-6-methoxy-4-chromanone.

Abstract—From the bulbs of *Muscari comosum* two novel 3-benzyl-4-chromanones, 7-*O*-methyl-3,9-dihydropunctatin and 8-*O*-demethyl-7-*O*-methyl-3,9-didropunctatin, were isolated.

INTRODUCTION

The bulbs of *Muscari comosum* have been shown to be a rich source of both triterpene glycosides [1] and free triterpenes [2]. One of these latter compounds, eucosterol, was found for the first time in some *Eucomis* species of the Liliaceae family [3] which were also shown [4] to contain some members of a new class of natural compounds, 3-benzyl(idene)-4-chromanones (or 'homoisoflavanones'). This prompted us to investigate the occurrence of this type of compound in *M. comosum*. This study led us to isolate two novel 3-benzyl-chromanones, namely 7-*O*-methyl-3,9-dihydropunctatin **1** and 8-*O*-demethyl-7-*O*-methyl-3,9-dihydropunctatin **2**, in addition to the already known [5] 3,9-dihydroeucomnalin **3**. The structures of **1** and **2** were elucidated by spectral analysis and chemical correlation.

RESULTS AND DISCUSSION

Compound **1** possesses the molecular formula $C_{18}H_{18}O_6$ (high-resolution mass spectrum). In the ^{1}H NMR spectrum (Table 1) the signals of the $-(2)CH_2-(3)CH-(9)CH_2-$ grouping were clearly seen; they were easily assigned by comparison to the reported chemical shift values for similar groupings in 3-benzyl-4-chromanones [4]. The presence of a hydroxytropylium

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