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A PHLORACETOPHENONE GLUCOSIDE FROM *RHODODENDRON FERRUGINEUM*

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Key Word Index—*Rhododendron ferrugineum*; Ericaceae; acetophenone.

Abstract—The new phloracetophenone 4′-glucoside was isolated from dried flowers of *Rhododendron ferrugineum* L. © 1997 Published by Elsevier Science Ltd

INTRODUCTION

In the course of a study of polyphenols of *Rhododendron ferrugineum* L., a new acetophenone glycoside phloracetophenone 4′-glucoside (**2**) was identified from dried flowers. The already known phloracetophenone (**1**) was also identified. Their structures were established by spectroscopic methods.

RESULTS AND DISCUSSION

The ^{13}C NMR spectrum of **1** and **2** showed signals due to a phloroglucinol-type aromatic ring (between 95 and 167 ppm) and an acetyl group [1]. The former structure was confirmed by UV spectra obtained with classical $AlCl_3$–HCl reagents. Compound **1** was easily identified as the known phloracetophenone [2]. Its presence could result from hydrolysis of the corresponding glycoside during desiccation of the plant material. Analysis on fresh flowers which is in progress in our laboratory would remove this ambiguity. Compound **2** differed from **1** by the presence of 6 ^{13}C NMR signals between 60 and 105 ppm attributable to an *O*-glycosidically linked hexose residue. The 2,4,6-trihydroxyacetophenone *O*-glycoside structure was confirmed by the positive and negative ion FAB mass spectral data, which showed the $[M-H]^-$ peak at *m/z* 329 and $[M+H]^+$ peak at *m/z* 331. The hexose residue was considered to be β D-glucopyranose because the chemical shifts of sugar carbon were in good agreement with those measured by Agrawal [3]. The anomeric proton coupling constant ($J = 7$ Hz) confirmed the β configuration [4]. Since ^{13}C and ^1H NMR signals of **2**, which were present in **1** spectra, were symmetrically shifted, it could be deduced that the glucose residue is at carbon **4**. Thus, **2** is phloracetophenone 4′-β-D-glucopyranoside. In the plant kingdom, few acetophenone glycosides co-occurring with their aglycones have been described. In the Ericaceae, the 2′-glucoside of phloracetophenone 4′-methyl ether [5] and particularly picein ((4′-β-D-glucopyranosyloxy)-acetophenone) [6–8] were reported. Compound **2** is thus, the first phloracetophenone 4′-glycoside to be found in Ericaceae. In other families, methoxylated derivatives of phloracetophenone glycosides seem to be predominant [9–11].

EXPERIMENTAL

General. Polyamide SC-6 (Macherey–Nagel), Sephadex LH20 (Pharmacia). MPLC: silica gel C 60 RP 18, 20–40 μm (Sorbsil Prolabo), (230 mm × 15 mm); Büchi 681 pump; detection, UV 290 nm, Waters UV detector 490E. Semi-prep. HPLC: Waters C18 μBondapak column (7.8 mm × 300 mm); detection, UV 290 nm, Waters UV detector 490E. FABMS: Nermag spectrometer glycerol as matrix. NMR: ^1H and ^{13}C, 200 MHz.

Plant material. Rhododendron ferrugineum L., identified by Prof. J. Raynaud, was collected in the French Alps in July 1995. Voucher specimens were deposited in our department (RFe 95 and RF1 95).

Extraction and isolation. 600 g of dried flowers were extracted with MeOH at room temp. The concd methanolic soln was extracted successively with hexane, $CHCl_3$, and EtOAc. The chloroformic phase, chromatographed over polyamid with toluene containing increasing amounts of MeOH, gave 12 frs. Fr. 4 was applied to a column of Sephadex LH20. Elution with

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MeOH gave 6 frs. Chromatography of fr. 6 on a μBondapak C18 column with MeOH–H_2O (3:7) afford compound **1**. The EtOAc extract was also chromatographed over polyamid with toluene containing increasing amount of MeOH and gave 14 frs. Fr. 7 was sepd on a Sephadex LH20 column with MeOH as eluent. Nine frs were collected. Fr. 1 was subjected to RP18 MPLC using MeOH–H_2O (1:4) to give Compound **2**.

Phloracetophenone (**1**). UV λ_{max}^{MeOH} 284, 314 sh; ($AlCl_3$): 305, 365; ($AlCl_3$–HCl): 304, 365. Negative FAB-MS: *m/z* 167 $[M-H]^-$; positive FAB-MS *m/z* 169 $[M+H]^+$. ^1H NMR (CD_3OD): δ 2.59 (3H, *s*, Me), 5.79 (2H, *s*, H-3 and H-5). ^{13}C NMR (CD_3OD): δ 32.68 (Me), 95.63 (C-3 and C-5), 106.0 (C-1), 165.90 (C-2 and C-6), 166.33 (C-4), 204.60 (COMe).

Phloracetophenone 4′-glucoside (**2**). UV λ_{max}^{MeOH} 281, 310sh; ($AlCl_3$): 302, 374; ($AlCl_3$–HCl): 300, 373. Negative FAB-MS: *m/z* 329 $[M-H]^-$, 167 $[M\text{-glc}-H]^-$; positive FAB-MS: *m/z* 331 $[M+H]^+$, 169 $[M\text{-glc}+H]^+$. ^1H NMR (CD_3OD): δ 2.62 (3H, *s*, Me), 3.40–3.43 (4H, *m*, sugar-H), 3.71 (1H, *dd*, $J = 11.7$, 4.4 Hz, glc-H-6B), 3.89 (1H, *dd*, $J = 11.8$, 1.6, H-6A), 4.91 (1H, *d*, $J = 7$ Hz, anomeric-H), 6.07 (2H, *s*, H-3 and H-5). ^{13}C NMR (CD_3OD): δ 32.94 (Me), 62.40 (glc-C-6), 71.18 (glc-C-4), 74.64 (glc-C-2), 77.94 (glc-C-5), 78.30 (glc-C-3), 96.30 (C-3 and C-5), 101.16 (anomeric C), 105.0 (C-1), 165.19 (C-4), 165.52 (C-2 and C-6), 204.0 (COMe).

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