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PRUNETIN 5-*O*-β-D-GLUCOPYRANOSIDE, AN ISOFLAVONE FROM THE PEDUNCLE OF *PRUNUS AVIUM* AND *P. CERASUS*

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Key word Index—*Prunus avium*; *P. cerasus*; Rosaceae; cherry; peduncle; prunetin 5-glucoside; isoflavone.

Abstract—Prunetin 5-glucoside was isolated from cherry peduncle *Prunus avium* and *P. cerasus*. The structure was fully assigned on the basis of NMR evidence. It is the second 5-*O*-glycosylated isoflavonoid to be reported.

Prunetin-4′-*O*-glucoside has been reported previously from three species of *Prunus*, whereas the parent aglycone, prunetin, has been identified from eight species of this genus [1]. Unlike the isomeric flavones, *O*-glycosylation among the naturally occurring isoflavonoids seems to be largely restricted to the 7- and 4′-positions [1]. To date there is only one single isoflavone mentioned in the literature being 5-*O*-glycosylated [2]. This communication represents the second report of such glycosylation pattern. For this compound (**1**) we propose the trivial name prunetinoside.

The acetone extract of cherry peduncle *Prunus avium* and *P. cerasus* [3] (commercially availabe as Nicardin®) was subjected to chromatography to yield prunetinoside (**1**) which analysed for $C_{22}H_{21}O_{10}$. Its UV spectrum showed a prominent maximum at 259 nm indicative of an isoflavone nucleus. This was supported by a ^{13}C chemical shift of δ 153.3 for a methine carbon which corresponds to C-2 of an isoflavone and excluded the isomeric flavone structure [4]. Moreover, the H-2 chemical shift value of δ8.15 substantiated its isoflavone nature.

The glycosidic nature of **1** and its sugar moiety was proved by hydrolysis followed by paper chromatography. The aglycone was identified as prunetin and the sugar as glucose (see Experimental). The presence of a distinct bathochromic shift (12 nm) on addition of $AlCl_3$–HCl to its aglycone and its absence in the UV spectrum of the respective glycoside **1** indicated that the sugar was attached to C-5–OH. The ^1H and ^{13}C chemical shifts as well as ^1H–^1H coupling constants confirmed that the sugar was glucose and it has the β-configuration [$J_{1'',2''} \approx 7.6$ Hz].

The sites of linkages of the two substituents, Me and β-D-glucosyl, were ascertained by two NOE difference experiments. On irradiation of the anomeric proton (H-1″, δ4.91) signal enhancements are observed for one aromatic proton only (H-6) proving that the sugar is attached to C-5–OH. The appearance of H-3″/5″ responses provides a further argument for the β-configuration of the glucosyl grouping. Irradiation of the methoxy protons, however, induces NOE of both the H-6 and H-8 signals; thus, this substituent is positioned between them, i.e. at C-7–OH. The NOE on H-6 is clearly smaller than that on H-8. Therefore, the methyl group is directed preferably towards the H-8 atom due to its steric interference with the bulky sugar moiety.

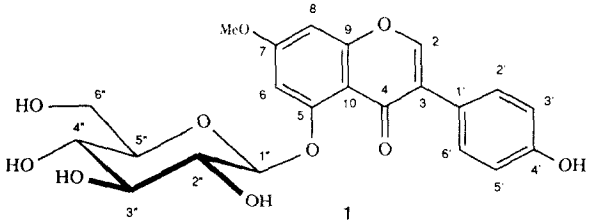
EXPERIMENTAL

The Me_2CO extract of the peduncle was concd under red. pres. and the resulting semi-solid (50 g) was chromatographed over a polyamide column (580 g; MN polyamide SC6) yielding six fractions containing mainly genistin [5]. The mother liquor was further chromatographed over polyamide. The 40% MeOH elute provided a crude prutinoside which was further subjected to Sephadex LH 20 to yield pure **1** (28.1 mg) as crystalline colourless plates (mp 237–239°). UV λ_{max} (MeOH) nm: 259; (+$AlCl_3$) 259; (+$AlCl_3$–HCl) 259; (+NaOAc) 259; (+NaOAc–H_3BO_3) 259; (+NaOMe) 280.

Hydrolysis. Compound **1** (10 mg) was dissolved in 6% aq. HCl (0.5 ml) and heated at 100° for 45 min. The mixture was worked-up according to standard methods to give a pale yellow solid which yielded silky needles on crystallization. UV λ_{max}^{MeOH} nm: 263, 327 (sh); (+$AlCl_3$) 275, 310 (sh); (+$AlCl_3$/HCl) 275, 310 (sh); (+NaOMe) 275, 325 (sh). It was identified as prunetin (mmp, co-TLC). In the aqueous filtrate glucose was identified by PC.

All NMR spectra were recorded at 400.1 MHz ^1H and 100.6 MHz in a 1:1 mixture of deuterated methanol and DMSO. The MeOH peaks were used as internal reference: $\delta(^1H) = 3.30$ and $\delta(^{13}C) = 49.0$.

NMR spectral data. ^1H chemical shifts (δ) 8.15 (H-2, *s*), 7.38 (H-2′/6′, *m*), 6.99 (H-6, *d*), 6.87 (H-3′/5′, *m*), 6.85 (H-8, *d*), 4.91 (H-



1″, *d*), 3.95 (OMe, *s*), 3.92 (H-6″, *dd*), 3.70 (H-6″, *dd*), 3.56 (H-2″, *dd*), 3.51 (H-5″, *m*), 3.48 (H-3″, *dd*), 3.38 (H-4″, *dd*); ^1H–^1H coupling constants (Hz) J (6, 8) = 2.4, J (1″, 2″) = 7.6, J (2″, 3″) = 9.0, J (3″, 4″) = 9.0, J (4″, 5″) = 9.5, J (5″, 6″) = 2.4 and 6.2, J (6‴,6″) = 12.0; ^{13}C chemical shifts: 153.3 (C-2), 126.9 (C-3), 177.6 (C-4), 160.6/160.3 (C-5/C-9), 97.2 (C-6), 165.6 (C-7), 105.2 (C-8), 111.3 (C-10), 124.0 (C-1′), 131.8 (C-2′/6′), 116.2 (C-3′/5′), 158.7 (C-4′), 104.1 (C-1″), 74.8 (C-2″), 77.2 (C-3″), 71.3 (C-4″), 78.9 (C-5″), 62.5 (C-6″), 56.9 (OMe).

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DELBIDINE, AN ALKALOID FROM A HYBRID POPULATION OF *DELPHINIUM OCCIDENTALE* AND *DELPHINIUM BARBEYI*

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Key Word Index—*Delphinium occidentale/barbeyi*; Ranunculaceae; C_{20}-diterpenoid alkaloid, delbidine.

Abstract—A new C_{20}-diterpenoid alkaloid delbidine has been isolated from a hybrid population of *Delphinium occidentale* (S. Wats.) S. Wats. and *Delphinium barbeyi* (Huth) Huth and its structure elucidated by spectroscopic methods. The structure was confirmed by its correlation with geyeridine.

INTRODUCTION

The diterpenoid alkaloids occur mostly in several of the *Aconitum* and *Delphinium* species which belong to the Ranunculaceae. These alkaloids have long been of interest because of their usefulness in medicine and intensely poisonous property. *Delphinium barbeyi* Huth is a herbaceous perennial plant native to the Rocky Mountain region of the United States. It grows above 7000 ft in the mountains of Utah, Wyoming and Colorado [1].

The occurrence of the C_{19}-diterpenoid alkaloids anthranoyllycoctonine [2], delpheline [3], deltaline [3] and lycoctonine [2, 3] from *D. barbeyi* Huth (*D. glaucum* S. Wats) has been recorded by earlier investigators. Recently from a hybrid population of *Delphinium occidentale* (S. Wats.) S. Wats. and *Delphinium barbeyi* (Huth) Huth delcosine [4], deltamine [4] and dictyocarpine [4] have been reported. The isolation of an unusual alkaloid barbeline containing a C(19) = N azomethine group in the C_{19}-diterpenoid alkaloid skeleton has also been reported [5] from this hybrid population. In the present note we wish to report the isolation and structure elucidation of a new C_{20}-diterpenoid alkaloid from this hybrid population.

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RESULTS AND DISCUSSION

Ethanol extraction and subsequent isolation of the basic fraction of the *Delphinium* hybrid gave a crude alkaloid which was found by TLC to be a mixture of a number of alkaloids. The mixture was purified by vacuum liquid chromatography [6] on alumina and a polar fraction was collected by elution with acetone–25% methanol. From this fraction, delbidine (**3**) was obtained