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NEW FLAVANONGLYCOSIDE FROM *Glycyrrhiza glabra*

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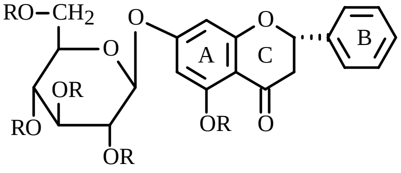
A new flavanonglycoside pinocembroside, 2(S)-7-O-β-D-glucopyranosyl-5-hydroxyflavanone, was isolated from the aerial part of Glycyrrhiza glabra *L. Its structure was determined using chemical transformations and spectral data.*

Key words: *Glycyrrhiza glabra,* 2(S)-7-O-*β*-D-glucopyranosyl-5-hydroxyflavanone.

We isolated 7-O-methylglabranin, 6-C-prenylpinocembrin, glabranin, pinocembrin, galangin, and the new isoflavonoid glabrisoflavone from the aerial part of *Glycyrrhiza glabra* L. [1]. In continuation of the research, we obtained a new compound **1** from the $CHCl_3$ fraction of the alcohol extract. The UV spectrum of **1** (λ_{max}, nm, 286, 351) is characteristic of flavanone derivatives [2]. This is confirmed by the PMR spectrum, which contains signals for H-2 as a doublet of doublets with spin—spin coupling constants (SSCC) 4.0 and 11.5 Hz and for 2H-3 as two binary doublets [2]. Furthermore, the spectrum exhibits signals for seven aromatic protons, an anomeric proton, and other protons of the carbohydrate in addition to a bonded hydroxyl (see Experimental). Therefore, the compound is a glycoside.

Acetylation of **1** produced the pentaacetyl derivative **2**, the mass spectrum of which has a weak peak for the molecular ion with *m/z* 628 and strong peaks for fragments of the tetraacetylhexose with *m/z* 331, 169, and 109 [3].

Acid hydrolysis of **1** afforded pinocembrine [4] and D-glucose.



1: R = H;
2: R = $COCH_3$

The site of carbohydrate attachment was established by comparing the UV spectra of **1** and its aglycone. The absorption maxima in the spectrum of **1**, in contrast with those of the aglycone, do not experience a bathochromic shift upon addition of NaOAc. This indicates that the 7-OH of the flavanone was glycosylated [2].

The PMR spectrum of **1** has the resonance of the anomeric proton of D-glucose at 5.63 ppm as a doublet with SSCC 6.5 Hz. This is consistent with a *β*-glycosidic bond of the carbohydrate to the aglycone [2]. Therefore, pinocembroside is 2(S)-7-O-*β*-D-glucopyranosyl-5-hydroxyflavanone (**1**) and is a new natural compound.

EXPERIMENTAL

We used solvent systems $CHCl_3$—CH_3OH (97:3) (1) and *n*-butanol—pyridine—water (6:4:3) (2).

Column chromatography used KSK 100/160 μm silica gel. TLC was performed on Silufol UV-254 plates. Compounds on TLC were visualized using UV light and ammonia vapor. Sugar on paper chromatography (Filtrak No. 12) was developed by spraying with acidic anilinium phthalate with subsequent heating for 3-5 min at 90-100°C.

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PMR spectra were recorded on a Tesla BS-567A 100 MHz instrument (δ, ppm, 0 = HMDS). Mass spectra were obtained on an MX-1310 instrument with 50 eV ionization potential. IR spectra were recorded on a Perkin—Elmer System 2000 FT-IR Fourier spectrometer in KBr pellets; UV spectra, on a Perkin—Elmer Lambda 16 spectrometer.

Isolation of Pinocembroside (1). Further elution of the $CHCl_3$ fraction [1] on a column using system 1 isolated from fractions 179-186 compound **1** (0.25 g), $C_{21}H_{22}O_9$, mp 139-141°C. UV spectrum (EtOH, λ_{max}, nm): 286, 351; CH_3CO_2Na: 285, 353. IR spectrum (KBr, ν_{max}, cm^{-1}): 3570-3340 (OH), 1660 (C═O of γ-pyrone), 1615, 1568, 1517 (aromatic C═C), 1100-1005 (C–O of glycosides).

PMR spectrum (δ, ppm, J/Hz, C_5D_5N): 2.74 (1H, dd, J = 4.0, J = 17.5, H-3 eq), 3.07 (1H, dd, J = 11.5, J = 17.5, H-3ax), 3.82-4.55 (carbohydrate protons), 5.33 (1H, dd, J = 4.0, J = 11.5, H-2ax), 5.63 (1H, d, J = 6.5, H-1″), 6.48 (2H, br.s, H-6,8), 6.95-7.44 (m, 5H-Ar ring B), 11.93 (1H, br.s, 5-OH).

Pinocembroside Pentaacetate (2). Glycoside **1** (20 mg) was dissolved in pyridine (1 mL) and acetic anhydride (3 mL) and worked up as usual after 4 h to prepare the pentaacetate of **2** (12 mg), mp 93-95°C, $C_{31}H_{32}O_4$. Mass spectrum, *m/z*: M^+ 628, 585 [M - 43], 542, 511, 471, 381, 369, 365, 351, 331, 293, 271, 256, 211, 179, 169, 127, 109.

Acid Hydrolysis of Pinocembroside. Glycoside **1** (25 mg) was hydrolyzed in HCl (15 mL, 5%) for 4 h on a boiling-water bath. The precipitated aglycone was filtered off and recrystallized from $CHCl_3$—hexane. Yield of pinocembrin (5,7-dihydroxyflavanone) 9 mg, mp 194-196°C, $C_{15}H_{12}O_4$ (M^+ 256) [4]. The hydrolysate contained D-glucose according to PC in system 2.

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