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A NEW *C*-GLYCOSYLFLAVONE FROM *GENTIANA ASCLEPIADEA**

Michel Goetz, Kurt Hostettmann and André Jacot-Guillarmod
Institut de Chimie de l'Université, Neuchâtel, Switzerland

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Key Word Index—*Gentiana asclepiadea*; Gentianaceae; *C*-glycosylflavones; isoorientin; isovitexin; isovitexin 2″-*O*-glucoside; xanthones; mangiferin.

In the present investigation, a new *C*-glycosylflavone as well as five previously identified *C*-glycosylflavones and mangiferin were isolated from the methanol extract of the leaves of *Gentiana asclepiadea* L.

Successive column chromatography on polyamide, cellulose and Sephadex of the methanol extract afforded isoorientin, isovitexin, isoorientin 4′-*O*-glucoside, isoorientin 2″-*O*-glucoside, isovitexin 4′-*O*-glucoside, mangiferin and the new compound: isovitexin 2″-*O*-glucoside. Identification of the six known compounds was made by comparison with authentic samples previously isolated in this laboratory [2–4].

The new compound was identified as isovitexin 2″-*O*-glucoside on the basis of the following evidence. The UV spectrum and the shifts observed with diagnostic reagents [5] indicated the presence of 5-, 7- and 4′-hydroxyl groups in the flavone skeleton. Acidic hydrolysis gave glucose and isovitexin, which slowly isomerized to vitexin. Methylation (CH_2N_2) followed by acidic hydrolysis gave 5,7,4′-trimethylisovitexin (comparison with an authentic sample). The NMR spectrum of the decaacetate indicated the *O*-glucose to be in 2″ as a result of the absence of an acetyl signal between δ 1,70 and 1,83, typical of acetylated 6-*C*-glucosylflavones [6]. Furthermore, the large coupling constants ($J = 10$ Hz) of the anomeric protons indicated β configuration for both the *C*- and the *O*-glucopyranosyl moieties.

Isovitexin 2″-*O*-glucoside is encountered for the first time in nature; its 4′- and 7-isomers have been previously isolated [2,7]. Apart from isoorientin 2″-*O*-glucoside, which has only been found in *Gentiana verna* L. [3], the other compounds isolated here are fairly common to *Gentiana* species [2,4,8,9].

EXPERIMENTAL

Plant source. Gentiana asclepiadea was collected in the Gantrisch region, Bern, Switzerland, and identified by Prof. Cl. Favarger, University of Neuchâtel.

Isolation process. Dried powdered leaves were extracted with petrol, Et_2O, $CHCl_3$ and MeOH. MeOH extract was subjected to CC on polyamide and eluted with 50% MeOH with increasing proportions of MeOH. The various fractions obtained were further treated by CC on cellulose (5% HOAc) in the case of isovitexin, isovitexin 4′-*O*-glucoside, isovitexin 2″-*O*-glucoside and isoorientin 2″-*O*-glucoside, by CC on polyamide (80% MeOH for isoorientin 4′-*O*-glucoside and C_6H_6–MeOH–HOAc (45:32:16) for isoorientin) and by gel filtration on Sephadex LH20 for mangiferin.

Isovitexin 2″-O-glucoside. mp 208. R_f 0,62 (polyamide, 80% MeOH) R_f 0,78 (cellulose, 5% HOAc). UV data λ_{max} nm: MeOH 273, 334; $AlCl_3$ 264*sh*, 280, 304, 349, 378; $AlCl_3$ + HCl 264*sh*, 281, 303, 344, 378; NaOMe 280, 332, 397; NaOAc 280, 299*sh*, 387. *Decaacetate.* mp 142–144. (Found C, 56,10; H, 5,16. $C_{47}H_{50}O_{25}$ requires: C, 55,62; H, 4,96%). NMR (270 MHz, $CDCl_3$): δ 1,90, 1,91, 1,94, 1,99, 2,04, 2,08, 2,13 (3H each, *s*, aliphatic acetyl groups), 2,34, 2,39, 2,48 (3H each, *s*, aromatic acetyl groups), 3,54–5,28 (14H, m, aliphatic protons, including 3,98 (1H, *d*, $J = 10$ Hz, C-1″) and 4,82 (1H, *d*, $J = 10$ Hz, C-1‴), 6,57 (1H, *s*, C-3), 7,26 (2H, *d*, $J = 8{,}5$ Hz, C-3′ and C-5′), 7,37 (1H, *s*, C-8), 7,99 (2H. *d*, $J = 8{,}5$ Hz, C-2′ and C-6′).

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* Part 16 in the series "Contribution à la phytochimie du genre *Gentiana*". For part 15 see [1].