A New C₁₃ Glycoside from Gentiana pneumonanthe

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Gentiana pneumonanthe L. (Gentianaceae) has been reported for its anticonvulsive and antirabic properties in Russian popular medicine (1). The plant was collected at Lavour (Ain-France). A voucher specimen was deposited at the laboratory of pharmacognosy.

Previous studies on G. pneumonanthe (2) chloroformic leaves extract, permitted the characterization of a C_{13} glycoside named pneumonanthoside (1), and the known secoiridoids sweroside and swertiamarin. We report now on a second C_{13} glycoside isolated from the same extract.

The dried and powdered leaves (300 g) of the title species were extracted as described elsewhere (2). The chloroformic extract (9 g) was fractionated on polyamide column (C_6H_6 -MeOH, 95:5). The middle fractions were then subjected to a silica gel column (CHCl₃,MeOH, 95:5) to afford 1 (17 mg) and 2 (12 mg) after purification on Sephadex LH-20 column (CHCl₃-MeOH, 30:70).

1 R = arabinosyl

2 R = H

Compound 2 exhibited an identical UV spectrum (λ nm MeOH = 230) to that of 1, but its R_f value (TLC on silica gel CHCl₃-MeOH 85:15), was higher than that of 1, indicating 2 to be less polar than 1. This applarity was due to the lack of the arabinosyl moiety, as shown by FAB+MS [m/z = 371(M + H)⁺], ¹H- and ¹³C-NMR data (see Table 1), which also demonstrated that 1 and 2 have identical aglycones. The sugar unit of 2 was identified as glucose (3) after acid hydrolysis (2N HCl, 100 °C for 1 hour). The $\beta\text{-configuration}$ of the glucose was determined by the ¹H coupling constant $J_{1',2'} = 8$ Hz, and the chemical shifts values of anomeric proton and carbon [δ = 4.30 ppm (H-1'), $\delta = 100.9$ ppm (C-1')]. The other NMR data (see Table 1) were also characteristic of a pyranosyl form for this glucosyl moiety. From the above findings and in accordance with literature data (4, 5), 2 was identified as the new compound dearabinosyl pneumonanthoside.

Table 1 ¹H-NMR and ¹³C-NMR chemical shifts of 2 (CD₃OD, 300/75 MHz).

Atom H/C	¹H-NMR δ (ppm)	J(Hz)	¹³ C-NMR δ (ppm)
1 2A 2B 3 4 5 6 7 8 9 10 (3H) 11 (3H) 12 (3H)	2.45 d 2.05 d — 5.90 dq — 2.66 d 5.70 dd 5.60 dd 4.45 dq 1.24 d 1.04 s 0.99 s	(16.5) (16.5) (1.5) (9) (16-9) (16-7) (7-6) (6)	36.9 48.1 177.0 126.0 165.0 56.6 131.0 136.0 74.7 22.1 28.0
13 (3H) 1' 2', 3', 4', 5' 6'A 6'B	1.98 d 4.30 d 3.20 – 3.60 3.85 dd 3.67 dd	(1) (8) (11.5-2.5) (11.5-5.5)	23.8 100.9 74.5–77.5–71.4–78.1 62.6

^{*, **} Values with the same exponent may be reversed.

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Errata

de Pascual Teresa, J., Anaya, J., Caballero, E., Cruz Caballero, M^a., Navarro, J. J. (1989) Planta Med. 55, 406

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Parts of the above two Letters were inadvertently exchanged in the August 1989 issue of Planta Medica. These two Letters are published again in this issue on pages 491 and 492, respectively, in their correct forms.