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6-HYDROXYLUTEOLIN 7-*O*-APIOSIDE FROM *LEPIDAGATHIS CRISTATA*

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Key Word Index—*Lepidagathis cristata*; Acanthaceae; flavonoids; 6-hydroxyluteolin and its 7-*O*-apioside.

We wish to report a new glycoside, 6-hydroxyluteolin 7-*O*-apioside from *Lepidagathis cristata*. This discovery represents the first report of 6-hydroxyluteolin from the Acanthaceae.

EXPERIMENTAL

Fresh leaves of *Lepidagathis cristata* Willd. syn. *L. shuteri* T. Anders [1, 2] (voucher specimen No. 1/79 deposited at the Autonomous PG Centre) collected from the PG Centre Campus, Tiruchirapalli (S. India) during March, were extracted with hot 80% EtOH under reflux and the residue fractionated using petrol 60–80°, Et_2O and EtOAc. The petrol fraction did not yield any crystalline material. The residue from the Et_2O extract on cryst. (EtOH) afforded yellow plates, mp 282–284°. The compound appeared intense black under UV and dark brown with NH_3 under UV, olive green with Fe^{3+} and had λ_{max} nm: 256 (sh.), 282, 346 (MeOH); 280 (sh.), 320, 336 (sh.), 392 (dec.) (NaOMe); 268 (sh.), 303 (sh.), 416 ($AlCl_3$); 260 (sh.), 294, 372 ($AlCl_3$/HCl); 272 (sh.), 386 (NaOAc); 280, 312 (sh.), 382 (H_3BO_3) and R_f: (×100, PC, ascending, 30 ± 2°) 6 (15% HOAc); 12 (30% HOAc); 46 (60% HOAc); 60 (BAW); 55 (PhOH); 50 (Forestal) and 57 (TBA). Its pentaacetate melted at 211–213°. On methylation, it gave pale yellow prisms, mp 174–176°, which on demethylation gave 6-hydroxyluteolin (mmp and co-PC). From these data, the flavone was identified as 6-hydroxyluteolin [3] and the identity was further confirmed by direct comparison with the compound obtained from *Stereospermum suaveolens* [4].

The residue from the EtOAc extract was dissolved in a minimum amount of Me_2CO and left in an ice-chest for a few days. A pale yellow solid separated, which on cryst. (MeOH) gave dull yellow crystals not melting up to 280° but with sintering around 210° (yield 0.2%). It appeared purple under UV with and without NH_3, olive brown with Fe^{3+}, gave a positive Molisch's test, and R_f: (×100, PC) 2 (H_2O); 3 (5% HOAc); 8 (15% HOAc); 24 (30% HOAc); 55 (60% HOAc); 41 (BAW); 62 (PhOH); 44 (TBA) and 52 (Forestal). It had λ_{max} nm: 255 (sh.) 284, 346 (MeOH); 259, 386 (dec.) (NaOMe); 273, 302, 340 (sh.), 428 ($AlCl_3$); 260 (sh.), 296, 372 ($AlCl_3$–HCl); 270, 394 (NaOAc); 260, 284, 356 (H_3BO_3) and IR (Nujol) bands at 3330 (br.), 2870 (br.), 1620, 1560, 1420 (s), 1360 (s), 1280 (br.), 1025, 965 (br.), 860, 810 (br.) and 710 cm^{-1}. The ^1H NMR data for the TMSi ether and the ^{13}C NMR [5] data for the compound supported a 6-hydroxyluteolin structure (Table). It was completely hydrolysed (2 N H_2SO_4, 50% MeOH, 100°, 2 hr) to 6-hydroxyluteolin and D-apiose. The identity of the sugar as D-apoise was confirmed by direct TLC comparison (cellulose, pyridine–EtOAc–HOAc–H_2O, 36:36:7:21) with an authentic sample. The glycoside on methylation (Me_2SO_4 + anhydr. K_2CO_3–Me_2CO, 40 hr) followed by hydrolysis (as above) gave pale yellow needles (MeOH), mp 218–220° which was identical with the mp of 7-hydroxy-5,6,3′,4′-tetramethoxyflavone as reported earlier [6]. The UV data and the diagnostic shifts with various reagents [7, 8] are indicative of the presence of 5,6,7,3′,4′-pentahydroxyflavone with glycosylation at C-7. From the above data, the new glycoside is identified as 6-hydroxyluteolin 7-*O*-apioside.

Table 1. ^1H and ^{13}C NMR data for 6-hydroxyluteolin 7-*O*-apioside*

C and H No.	^1H (δ)	^{13}C (δ)
2		164.2
3	6.30 (*s*)	102.4
4		182.3
5		149.0†
6		130.7
7		151.5
8	6.77 (*s*)	94.1
9		146.8†
10		105.5
1′		121.6
2′	7.25 (*d*, J = 2.5)	113.4
3′		145.8†
4′		149.7†
5′	6.84 (*d*, J = 8)	116.2
6′	7.41 (*dd*, $J_{2',6'}$ = 2.5, $J_{5',6'}$ = 8)	119.1
1″	5.48 (*d*, J = 3.5)	107.8
2″	4.49 (*d*, J = 3.5)	76.1
3″		78.8
4″	4.15 (*d*, J = 9), 3.80 (*d*, J = 9)	74.7
5″	3.61 (*d*, J = 10), 3.43 (*d*, J = 10)	62.4

* The ^1H NMR spectrum was measured for the TMSi ether in CCl_4 at 100 MHz, with TMS as an internal standard. The ^{13}C NMR spectrum was recorded in DMSO-d_6 at 22.6 MHz, also with TMS as an internal standard.

† May be interchanged.

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