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IDENTIFICATION OF 6″-*O*-ACETYL-8-*C*-GALACTOSYLAPIGENIN IN *BRIZA MEDIA*

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While studying flavonoid variation in the grass genus *Briza*, 8-*C*-galactosylapigenin (**1**) [1] together with an unidentified acylated derivative (**2**) [2] was isolated as the two major leaf constituents in diploid plants of *Briza media*. The two compounds are of biological interest since their synthesis is repressed by increasing ploidy level in this species; the corresponding autotetraploid plants contain mainly what are apparently the analogous luteolin derivatives [2, 3]. The acylated derivative **2** is of further interest phytogeographically, since it occurs regularly and exclusively in Eurasian species of *Briza*, being absent from South American taxa [3].

Earlier failures to identify by chromatographic means the acyl constituent in **2**, after alkaline hydrolysis, suggested that the acyl group might be derived from a volatile organic acid. Following ^{13}C NMR analysis the substituent has now been identified as acetyl. Two new carbon signals not present in the spectrum of the parent 8-galactosylapigenin were observed at 20.7 ppm (methyl of acetyl) and at 170.3 ppm (carbonyl of acetyl). Furthermore, ^{13}C NMR spectral comparison of the acetyl derivative **2** with **1** (Table 1) showed that the acetyl group is specifically located at the 6″-position of the galactose moiety. Thus, there is the expected downfield shift [4, 5] of 3.5 ppm of the C-6″ resonance in **2** compared with **1**, with a concomitant upfield shift of 3.8 ppm of the C-5″ signal. The complete assignment of the signals for the *C*-glucosyl unit in glucoflavones has been reported recently [6]. These results and published ^{13}C chemical shift data [7] for 1,5-anhydrogalactitol aided the assignment of the signals of the carbon atoms of the *C*-galactosyl moiety in **1**. The ^{13}C NMR data also provide useful confirmation of the earlier identification, based on MS analysis [1] and comparison with synthetic material [8], of the galactose unit, instead of the more common glucose unit, in the *Briza*

Table 1. Carbon chemical shift comparison (in ppm) between 8-galactosylapigenin and its 6″-*O*-acetate

	Carbon atom No.	1,5-Anhydro-galactitol*	8-Galactosyl-apigenin (**1**)	6″-Acetyl-8-galactosylapigenin (**2**)
	2		163.8	164.1
	3		101.8	101.8
	4		181.8	182.1
	5		160.2	160.5
	6		98.0	98.2
	7		162.5	162.6
	8		103.9	104.2
	9		155.9	156.1
Flavone	10		104.5	104.2
carbons	1′		120.9	121.0
	2′		129.5	129.5
	3′		115.5	115.9
	4′		160.9	161.1
	5′		115.5	115.9
	6′		129.5	129.5
Sugar	1″	70.0	73.9	73.8
carbons	2″	67.3	68.5	68.2
	3″	75.0	75.4	75.0
	4″	70.0	69.1	69.4
	5″	80.3	80.5	76.7
	6″	62.2	61.3	64.8

* These values were taken from ref. [7] and converted using $\delta_{CS_2}-\delta_{TMS} = 193.5$ ppm.

glycoflavones. 8-Galactosylapigenin, reported then for the first time from *Briza*, has subsequently been detected in *Polygonatum multiflorum* (Liliaceae) [9].

Although several acetylated derivatives of flavonol and flavone glycosides are known [10, 11], such compounds in the glycoflavone series are still rare. This identification of the 6″-*O*-acetate **2** in *Briza* represents the first report in nature of an acetyl derivative of an 8-galactosylflavone.

EXPERIMENTAL

The 8-galactosylapigenin and its acylated derivative were isolated and purified from *Briza media* leaves, as previously described [2, 3]. ^{13}C NMR analyses were carried out in DMSO-d_6 soln on a Jeol FS 100 NMR spectrometer.

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