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Short Communications

Chemical Studies on Bryophytes. 23. ^{13}C NMR Analysis of a Biflavone from *Dicranum scoparium*

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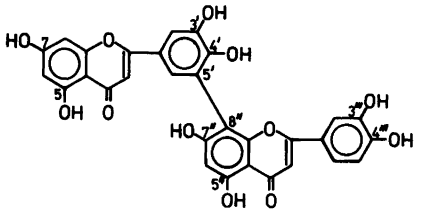
The isolation and identification of 5′,8″-biluteolin (*1*) from the moss *D. scoparium* has been reported earlier.[1] Most of the naturally occurring biflavonoids have carbon–carbon interflavonoid linkages. Their structures are difficult to determine, especially whether C–6 or C–8 is involved in the carbon–carbon linkage. In most cases, synthesis is necessary to confirm the structures.



^{13}C NMR spectroscopy has proved to be a superior method for the structure determination of biflavonoids.[2–5] The ^{13}C chemical shift values of the natural product 5′,8″-biluteolin (*1*), three synthetic biluteolin octamethyl ethers and two other related compounds are given in Tables 1 and 2.

The chemical shifts in Table 1 were assigned on the basis of proton noise-decoupled and off-resonance decoupled spectra and by comparison with the data published earlier for luteolin and carbon–carbon linked biflavonoids.[2–6] The presence of two signals at 181.9 and 182.3 ppm due to two flavone carbonyl carbon atoms, C–4 and C–4″, in the ^{13}C NMR spectrum of *1*, and the similarity of the remaining signals to the signals of luteolin indicated that *1* must be a dimer of luteolin.

In ^{13}C NMR spectra of 5,7-dihydroxyflavonoids, the signals for C–6 and C–8 are always found between 90 and 100 ppm, with the signal for C–6 found downfield from C–8.[2–8] Thus, the signal at 99.3 ppm is assigned to C–6 and C–6″, and that at 94.3 ppm to C–8. The absence of a signal in the range 90 to 96 ppm indicates that C–8″ is substituted. The C-arylation of C–6 or C–8 in 5,7-dihydroxyflavonoids shifts the signal of the corresponding aglycone carbon downfield by 4 to 10 ppm and does not markedly affect the signal of the other carbon.[2–5] Thus, the intense signal at 104.2 ppm, which is not split in the off-resonance decoupled spectrum, is assigned to C–8″. By comparison with luteolin, the signal at 104.2 ppm also represents the C–4a and C–4a″ carbons. The two signals at 103.5 and 103.0 ppm are assigned to C–3 and C–3″.

There are eight signals in the range 112.7 to 122.7 ppm. Five of these, at 112.7, 114.1, 116.1, 119.1 and 122.7 ppm, are split into doublets in the off-resonance decoupled spectrum, and are assigned to C–2′, C–2‴, C–5‴, C–6′ and C–6‴, respectively. Among the remaining three intense signals, at 120.6, 121.4 and 122.4 ppm, the lowfield signals are due to C–1′ and C–1‴. The signal at 120.6 ppm is assigned to the C–5′ carbon, which is shifted downfield by 4.5 ppm due to the substitution effect of the interflavonoid linkage.

The lowfield signals between 145.9 and 164.4 ppm due to oxygenated carbons have been assigned (see Table 1) by comparison with the signals in the spectrum of luteolin.

Permethylated *1* showed a more complicated spectrum than 5′,5‴- and 8,8″-biluteolin octamethyl ether, which both have very simple spectra owing to high symmetry. In the spectrum of 5′,5‴-biluteolin octamethyl ether the signal for C–5′ and C–5‴ has moved downfield to 132.2 ppm. Compared with that of luteolin 5,7,3′,4′-tetramethyl ether, this shift of 20.7 ppm is much larger than the corresponding shift of 5.9 ppm in 8,8″-biluteolin octamethyl ether and those reported previously in C–C linked biflavonoids [2–5]

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Table 1. ^{13}C NMR chemical shifts of biflavones and related compounds (ppm, TMS=0).

Compound	C-2 C-2″	C-3 C-3″	C-4 C-4″	C-5 C-5″	C-6 C-6″	C-7 C-7″	C-8 C-8″	C-8a C-8a″	C-4a C-4a″	C-1′ C-1‴	C-2′ C-2‴	C-3′ C-3‴	C-4′ C-4‴	C-5′ C-5‴	C-6′ C-6‴
Luteolin[6]	165.1	103.9	182.6	161.6	99.9	164.3	94.9	158.2	104.8	123.1	114.4	146.0	149.8	117.1	120.1
5′,8″-Biluteolin (*1*)	164.4	103.5[a]	182.3[b]	161.8[c]	99.3	164.4	94.3	157.7	104.2	121.4[d]	112.7	145.9	148.6	120.6[d]	119.1
	164.4	103.0[a]	181.9[b]	161.0	99.3	162.1[c]	104.2	155.0	104.2	122.4[d]	114.1	146.2	149.8	116.1	122.7
Luteolin 5,7,3′,4′-tetramethyl ether	160.1	107.0	175.6	159.6	93.3	163.5	96.1	159.1	108.2	123.0	109.1	148.9	151.5	111.5	119.2
5′,5‴-Biluteolin octamethyl ether	160.6	108.5	177.3	160.0	92.7	163.8	96.2	159.6	109.0	126.5	109.3	149.3	152.8	132.2	120.9
8,8″-Biluteolin octamethyl ether	161.0	106.8	177.7	161.6	91.6	164.8	102.0	160.4	107.7	123.4	107.7	148.8	151.4	111.0	118.9
5′,8″-Biluteolin	160.7[a]	108.1	177.3	160.1	92.8	163.9	96.2	159.6	109.1	–[e]	109.1	149.4	152.9	–[e]	122.4
octamethyl ether	160.9[a]	106.9	177.3	160.9[a]	91.6	164.6	–[e]	160.7[a]	107.7	–[e]	107.7	148.8	151.4	111.0	119.2

[a,b,c,d] Assignments bearing the same superscript in any spectrum may be reversed. [e] Chemical shifts not assigned due to the small amount of sample available.

Table 2. ^{13}C NMR chemical shifts of the methoxyl carbons.

Compound	Chemical shifts (ppm)
Luteolin 5,7,3′,4′-tetramethyl ether	55.7, 55.9, 55.9 and 55.9
5′,5‴-Biluteolin octamethyl ether	55.8, 56.0, 56.3 and 60.9
8,8″-Biluteolin octamethyl ether	55.8, 56.0, 56.1 and 56.5
5′,8″-Biluteolin octamethyl ether	55.4, 55.8, 56.0, 56.0, 56.0, 56.5, 56.5 and 60.9

and might be explained by steric effects.

In the spectrum of permethylated *1* the chemical shifts for the C–5′ and C–8″ carbons could not be observed due to the small amount of sample available, but the absence of signals corresponding to unsubstituted C–5′ and C–8″ confirmed the carbon–carbon linkage between these carbons.

The chemical shifts of the methoxyl carbons of the permethylated biflavones are shown in Table 2. Most of the chemical shifts of methoxyl carbons in flavones usually occur between 55.5 to 56.0 ppm.[8] In some cases the signals are shifted downfield due to steric crowding when the methoxyl group is *ortho*-disubstituted with bulky substituents.[9–13] Thus, the signal at 60.9 ppm in 5′,5‴- and 5′,8″-biluteolin octamethyl ether are assigned to the methoxyl groups in the 4′- and 4‴-position. No individual assignment is possible for the remaining methoxyl carbons.

Experimental. ^{13}C NMR spectra were recorded as described earlier.[14] Chemical shifts were referred to external TMS on the basis of the chemical shifts of DMSO-d_6 and $CDCl_3$ (39.5 and 77.0 ppm, respectively). Both proton noise-decoupled and off-resonance decoupled spectra have been recorded. The methyl ethers were measured in $CDCl_3$ (23 °C), and *1* in DMSO-d_6 (50 °C).

Isolation of 5′,8″-biluteolin (*1*) from the moss *D. scoparium*, syntheses of luteolin 5,7,3′,4′-tetramethyl ether, 5′,5‴-biluteolin octamethyl ether, 8,8″-biluteolin octamethyl ether and 5′,8″-biluteolin octamethyl ether were described earlier.[1]

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