

¹³C NMR Data of flavonol methyl ethers of *Solanum pubescens*

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Abstract. The ¹³C NMR data of flavonol-3-methyl ethers indicated that the methylation of one of the hydroxyl groups in the *o*-dihydroxy system causes an upfield shift in the unsubstituted *o*-carbon as usual but with the other hydroxylated *o*-carbon the shift is always downfield. The spectra of the acetates indicated that 5-OCOCH₃ and 5-OCOCH₃ resonated downfield compared to that of other acetoxy groups. The ¹³C NMR data of these compounds is being reported for the first time.

Keywords. Flavonol methyl ether; ¹³C NMR; *Solanum pubescens*; Solanaceae.

1. Introduction

The usefulness of ¹³C NMR data in the structural elucidation of flavonoids was demonstrated by many workers (Calvert *et al* 1979) and well-reviewed (Agarwal and Rastogi 1981). The study of the ¹³C NMR of kaempferol-3,7,4'-trimethyl ether (1), quercetin, 3,7,3',4'-tetramethyl ether (2), quercetin, 3,7,3'-trimethyl ether (3), quercetin-3,7,4'-trimethyl ether (4), quercetin-3,3'-dimethyl ether (5), myricetin-3,7,3'-trimethyl ether (6) isolated from *Solanum pubescens* Willd (Krishna Kumari *et al* 1984, 1985), and their acetates, was found to be useful in locating the 5-OH group and the position of the methoxyl group in *o*-dioxygenated systems.

2. Experimental

The natural abundance ¹³C NMR spectra were obtained in the pulse Fourier transform mode with a JEOL-FX 100 spectrometer operating at 25.14 MHz. The samples, ranging in quantity from 20 mg to 100 mg, were examined as solutions in spinning tubes at 27°C. TMS was used as the internal reference. A pulse width of 7-10 sec was used (45°) with repetition times ranging from 5-10 sec as necessary. The spectral width was 6024 Hz with 8k data points. The compounds 1-6 were isolated as mentioned at our earlier reports (Krishna Kumari *et al* 1984, 1985). The data are given in table 1.

3. Results and discussion

The 5-acetoxy group in 1 and 2 acetates gives signals at δ 169.4 (5-OCOCH₃) and at δ 21.1 (5-OCOCH₃) ppm (table 2). From a study of the spectra of the acetates of compounds 1 to 6 having different substitution patterns, it is seen that the

Table I. ^{13}C NMR data of flavonoid methyl ethers.

| Compound | Position | | | | | | | | | | | OMe | | | | |
|---------------------------------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|------------------------|--------------------------|------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------------------|
| | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 1' | 2' | | 3' | 4' | 5' | 6' |
| Kaempferol*7 ($\text{CDCl}_3 + \text{DMSO-}d_6$) | 146.8 154.6 (+7.8) | 135.6 137.5 (+1.9) | 175.9 177.3 (+1.4) | 160.7 160.5 (-1.5) | 98.2 96.7 (-1.5) | 163.9 164.2 (+0.3) | 93.5 90.9 (-2.6) | 156.2 155.5 (-0.7) | 103.1 104.7 (+1.6) | 121.7 121.4 (-0.3) | 129.5 128.9 (-0.6) | 115.4 113.0 (-2.4) | 159.2 160.5 (+1.3) | 115.4 113.0 (-2.4) | 115.4 113.0 (-2.4) | 129.5 128.9 58.8, 54.7 54.3 |
| Luteolin**8 | 164.5 | 103.3 | 182.2 | 162.1 | 99.2 | 164.7 | 94.2 | 157.9 | 104.2 | 122.1 | 113.8 | 146.2 | 150.2 | 116.4 | 119.3 | |
| Diosmetin***9 | 163.6 | 103.7 | 181.8 | 161.7 | 99.0 | 164.4 | 94.0 | 157.9 | 104.0 | 123.3 (+1.2) | 113.1 | 146.9 (+0.7) | 151.2 (+1.1) | 112.1 (-4.3) | 118.7 | 55.8 |
| Chrysoeriol***10 | 163.7 | 103.8 | 181.8 | 161.6 | 98.8 | 164.2 | 94.0 | 157.4 | 103.3 | 121.7 (-3.6) | 110.2 | 150.8 (+1.1) | 148.0 (+1.1) | 115.8 | 120.4 | 56.0 |
| Quercetin*11 ($\text{CDCl}_3 + ^2\text{DMSO-}d_6$) | 146.9 154.6 (+7.7) | 135.5 137.5 (+2.2) | 175.8 177.5 (+1.7) | 160.7 160.6 (-0.1) | 98.2 96.9 (-1.3) | 163.9 164.4 (+0.5) | 93.5 91.1 (-2.4) | 156.2 155.7 (-0.5) | 103.1 104.8 (+1.7) | 122.1 121.7 (-0.4) | 115.5 110.6 (-4.9) | 145.0 147.8 (+2.8) | 147.6 150.5 (+2.9) | 115.6 110.3 (-5.3) | 120.0 121.3 55.0 | 55.1 |
| 3 | 155.4 (+8.5) | 137.7 (+2.2) | 177.8 (+2.0) | 160.8 (+2.0) | 97.4 (-0.8) | 164.3 (+0.4) | 92.0 (-1.5) | 155.9 (-1.5) | 105.0 | 122.1 | 112.1 (-3.4) | 147.3 (+2.3) | 149.7 (+2.1) | 115.5 (-0.1) | 120.7 | 59.4, 55.7 |
| 4 | 155.3 (+8.4) | 138.0 (+2.5) | 177.8 (+2.0) | 160.8 (+2.0) | 97.5 (-0.7) | 164.9 (+1.0) | 91.9 (-1.6) | 156.0 (-1.6) | 105.0 | 120.2 | 115.0 (-3.4) | 146.2 (+2.3) | 150.1 (+2.5) | 111.7 (-3.9) | 121.1 | 59.5, 55.8 55.5 |
| 5 | 155.3 (+8.4) | 137.6 (+2.1) | 177.7 (+1.9) | 161.5 (+1.9) | 98.5 (+2.1) | 164.0 (+1.9) | 93.7 (+1.9) | 156.2 (+1.9) | 104.1 | 122.1 | 112.1 (-3.4) | 147.3 (+2.3) | 149.6 (+2.0) | 115.5 (+2.0) | 120.8 | 59.5, 55.7 |
| Isorhamnetin***12 | 147.1 | 136.1 | 176.3 | 161.2 | 98.6 | 164.4 | 93.9 | 156.8 | 103.5 | 122.6 | 112.7 (-2.8) | 149.4 (+2.3) | 147.9 (+2.0) | 116.0 | 122.2 | 56.2 |
| Myricetin**13 | 147.1 | 136.1 | 176.0 | 161.0 | 98.5 | 164.2 | 93.5 | 156.4 | 103.3 | 121.2 | 107.5 | 146.0 | 136.1 | 146.0 | 107.7 | |
| 6 | 155.8 (+8.7) | 138.0 (+1.9) | 177.9 (+1.9) | 160.9 (+1.9) | 97.6 (-0.9) | 165.1 (+0.9) | 92.2 (-1.3) | 156.2 (-1.3) | 104.5 | 119.6 | 105.1 (-2.4) | 148.1 (+2.1) | 138.1 (+2.0) | 145.6 (+2.0) | 109.8 | 59.6, 56.2 56.0 |
| Eriodictyol***14 Homoeiro- dictyol***15 | 78.4 | 42.2 | 196.0 | 163.6 | 95.9 | 166.7 | 95.1 | 162.9 | 102.0 | 129.7 | 114.5 | 145.3 | 145.7 | 115.6 | 117.9 | |
| Hesperetin***16 | 78.7 | 42.1 | 196.3 | 163.5 | 95.8 | 166.6 | 95.0 | 162.9 | 101.8 | 129.4 | 111.1 (-3.4) | 147.5 (+2.2) | 146.9 (+1.2) | 115.2 (+1.7) | 119.6 | 55.6 (+1.7) |

The solvent in all cases is $\text{DMSO-}d_6$, unless specified otherwise.

δ values in ppm from TMS at 25-14 MHz; figures in brackets are $\Delta\delta$ values.

*, ** assignments have to be interchanged;

* Markham et al 1978.

** Gaydoum and Bianchini 1977;

*** Markham et al 1982

Table 2. ¹³C NMR data of the acetates of flavonol methyl ethers.

| Compound | Position | | | | | | | | | | | OMe | OAc | | | | |
|--------------|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------------|--------------|
| | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 1' | 2' | | | 3' | 4' | 5' | 6' |
| <u>1</u> -Ac | 154.1 | 140.7 | 173.0 | 150.5 | 107.9 | 163.1 | 98.6 | 157.7 | 110.5 | 122.9 | 129.8 | 113.9 | 161.3 | 113.9 | 129.8 | 59.9, 55.9 | 169.4 |
| | | | | | | | | | | | | | | | | 55.3 | 21.13 |
| <u>2</u> -Ac | 153.8 | 140.6 | 173.2 | 151.2 | 108.0 | 163.2 | 98.6 | 157.7 | 111.0 | 123.1 | 111.0 | 148.8 | 150.5 | 111.4 | 121.9 | 60.0, 56.1 | 169.4 |
| | | | | | | | | | | | | | | | | 56.0 | 21.1 |
| <u>3</u> -Ac | 153.0 | 141.2 | 172.4 | 150.5 | 108.1 | 163.4 | 98.6 | 157.7 | 111.0 | 129.2 | 112.6 | 151.1 | 141.6 | 122.9 | 121.1 | 60.2, 56.0 | 169.4, 168.4 |
| | | | | | | | | | | | | | | | | 55.9 | 21.1, 20.6 |
| <u>4</u> -Ac | 152.9 | 140.9 | 172.9 | 150.7 | 108.0 | 163.2 | 98.5 | 157.5 | 111.1 | 122.7 | 123.0 | 139.5 | 152.7 | 112.0 | 127.4 | 59.8, 55.9 | 169.4, 168.6 |
| | | | | | | | | | | | | | | | | | 21.1, 20.6 |
| <u>5</u> -Ac | 153.7 | 141.7 | 173.0 | 150.1 | 113.2 | 156.4 | 108.8 | 158.3 | 113.2 | 128.8 | 112.4 | 151.0 | 143.5 | 122.9 | 121.2 | 60.2, 56.0 | 169.2, 168.5 |
| | | | | | | | | | | | | | | | | | 167.9, 21.0 |
| | | | | | | | | | | | | | | | | | 20.6 |
| <u>6</u> -Ac | 152.2 | 141.7 | 172.9 | 150.4 | 108.3 | 163.4 | 98.5 | 157.6 | 111.2 | 128.6 | 109.8 | 152.1 | 133.7 | 143.3 | 115.3 | 60.2, 56.2 | 169.4, 168.2 |
| | | | | | | | | | | | | | | | | 56.0 | 167.3, 21.1 |
| | | | | | | | | | | | | | | | | | 20.6, 20.2 |

δ values in ppm from TMS at 25-14 MHz; the acetates of the respective compounds have been studied; all spectra were taken in CDCl₃.

5-O \underline{C} OCH₃ and 5-OCO \underline{C} H₃ always resonate more downfield (δ 169.4 and 21.1 ppm respectively) than the other acetoxy carbonyl and methyl groups (δ 167.3–168.6 and 20.2–20.6 ppm respectively). Diacetates of compounds 3 and 4 show signals at δ 169.4, 168.4 and 169.4, 168.6 ppm for acetyl carbonyl carbons and at δ 21.1, 20.6 and 21.1, 20.6 ppm for acetyl methyl carbons, respectively. As both the compounds contain a 5-OCOCH₃ group in common along with the signals at δ 169.4 and 21.1 ppm, these signals are assigned to 5-O \underline{C} OCH₃ and 5-OCO \underline{C} H₃ respectively analogous to the signals of compounds 1 and 2 monoacetates. The other signals at δ 168.4 and 20.6 ppm in the compound-3-acetate are assigned to 4'-O \underline{C} OCH₃ and 4'-OCO \underline{C} H₃, respectively, as that is the only other acetoxy present. Similarly, signals at δ 168.6 and 20.6 of the compound-4-acetate are assigned to 3'-OCO \underline{C} H₃ and 3'-OCO \underline{C} H₃ respectively. Hence, the above values can be considered diagnostic for 5-acetoxy rendering support for the presence of 5-hydroxyl group in flavonol-3-methyl ethers. The deshielding can be attributed to the anisotropic effect of 4-carbonyl group (table 2).

A comparison of the spectra of compound-3-diacetate with that of compound-5-triacetate shows the 7-acetoxy carbonyl upfield (δ 167.9). One of the acetoxy groups in an *o*-diacetoxy system as in 6-acetate is also observed upfield (δ 167.3 ppm). Except for these three characteristic differences, all other acetoxy carbonyls appear between δ 168.4–168.6 ppm. However, no shift difference is observed for other -OCO \underline{C} H₃ groups and appears between δ 20.2–20.6 ppm except for 5-OCO \underline{C} H₃. Hence, the downfield carbonyl signals can be assigned to 5-O \underline{C} OCH₃ and the upfield signal to either 7-O \underline{C} OCH₃ or one acetoxy group in an *o*-diacetoxy system as the case may be.

The ¹³C NMR assignments of compounds 1 to 6 were made on the basis of earlier assignments (Pelter *et al* 1976; Markham *et al* 1978; Agarwal and Rastogi 1981). When a phenolic hydroxyl is methylated, the *o*-carbons are reported to move upfield and the *ipso*-carbon downfield (Agarwal and Rastogi 1981). But when one of the hydroxyls in an *o*-dihydroxy system in ring-B is methylated, only the unsubstituted *o*-carbon moves upfield, while the hydroxylated *o*-carbon moves downfield. The above observation was made by a comparison of the spectra of 3 and 4 with quercetin (11, Markham *et al* 1978) and 6 with myricetin (13, Gaydoun and Bianchini 1977, table 1). The signals for the 4'-carbon of homoeriodictyol (15) and the 3'-carbon of hesperetin (16) appear at δ 146.9 and δ 146.7 respectively showing downfield shifts ($\Delta\delta +1.2$ and $\Delta\delta +1.4$ ppm), respectively, when compared with 4' (δ 145.7) and 3' (δ 145.3) carbons of eriodictyol (14) (Markham *et al* 1982). Similarly the 3'-carbon of diosmetin (9) is observed more downfield (δ 146.9) than that of luteolin (8) (δ 146.2) supporting our observation (Markham *et al* 1982) (table 1).

The earlier assignments of chrysoeriol (10) and isorhamnetin (12) (Markham *et al* 1982) are to be interchanged [C-3' (δ 150.8 \rightarrow 148.0), C-4' (δ 148.0 \rightarrow 150.8) in 10 and C-3' (δ 149.4 \rightarrow 147.9), C-4' (δ 147.9 \rightarrow 149.4) in 12] (table 1), respectively, to account for the downfield shifts ($\Delta\delta$ 80.7 and $\Delta\delta$ 81.8) observed in other flavonoids for the *o*-hydroxylated carbon. The steric repulsion between the *o*-hydroxylated methoxyls can be expected to dominate over the mesomeric effect, causing this abnormality. The extent of the downfield shift varies from $\Delta\delta$ 80.7 to 2.1 ppm. It is possible to locate the position of a methoxyl group in the B-ring from this observation.

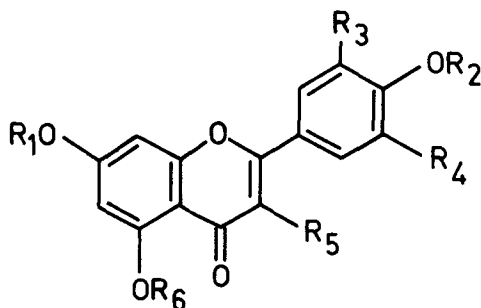


Chart 1.

1. $R_1 = R_2 = \text{Me}, R_3 = R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{H}$
- 1 Ac $R_1 = R_2 = \text{Me}, R_3 = R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{Ac}$
2. $R_1 = R_2 = \text{Me}, R_3 = \text{OMe}, R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{H}$
- 2 Ac $R_1 = R_2 = \text{Me}, R_3 = \text{OMe}, R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{Ac}$
3. $R_1 = \text{Me}, R_2 = \text{H}, R_3 = \text{OMe}, R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{H}$
- 3 DiAc $R_1 = \text{Me}, R_2 = \text{Ac}, R_3 = \text{OMe}, R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{Ac}$
4. $R_1 = R_2 = \text{Me}, R_3 = \text{OH}, R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{H}$
- 4 DiAc $R_1 = R_2 = \text{Me}, R_3 = \text{OAc}, R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{Ac}$
5. $R_1 = R_2 = \text{H}, R_3 = \text{OMe}, R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{H}$
- 5 TriAc $R_1 = R_2 = \text{Ac}, R_3 = \text{OMe}, R_4 = \text{H}, R_5 = \text{OMe}, R_6 = \text{Ac}$

6. $R_1 = \text{Me}, R_2 = \text{H}, R_3 = \text{OMe}, R_4 = \text{OH}, R_5 = \text{OMe}, R_6 = \text{H}$
- 6 TriAc $R_1 = \text{Me}, R_2 = \text{Ac}, R_3 = \text{OMe}, R_4 = \text{OAc}, R_5 = \text{OMe}, R_6 = \text{Ac}$
7. $R_1 = R_2 = R_3 = R_4 = \text{H}, R_5 = \text{OH}, R_6 = \text{H}$
8. $R_1 = R_2 = \text{H}, R_3 = \text{OH}, R_4 = R_5 = R_6 = \text{H}$
9. $R_1 = \text{H}, R_2 = \text{Me}, R_3 = \text{OH}, R_4 = R_5 = R_6 = \text{H}$
10. $R_1 = R_2 = \text{H}, R_3 = \text{OMe}, R_4 = R_5 = R_6 = \text{H}$
11. $R_1 = R_2 = \text{H}, R_3 = \text{OH}, R_4 = \text{H}, R_5 = \text{OH}, R_6 = \text{H}$
12. $R_1 = R_2 = \text{H}, R_3 = \text{OMe}, R_4 = \text{H}, R_5 = \text{OH}, R_6 = \text{H}$
13. $R_1 = R_2 = \text{H}, R_3 = R_4 = R_5 = \text{OH}, R_6 = \text{H}$

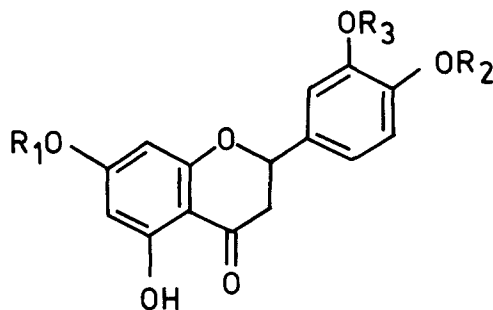


Chart 2.

14. $R_1 = R_2 = R_3 = \text{H}$
15. $R_1 = R_2 = \text{H}, R_3 = \text{Me}$
16. $R_1 = \text{H}, R_2 = \text{Me}, R_3 = \text{H}$

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