

REASSESSMENT OF THE STRUCTURE OF A FLAVONOL GLYCOSIDE FROM *RUDBECKIA BICOLOR*

SURAJ B. KALIDHAR

Department of Chemistry and Biochemistry, Haryana Agricultural University, Hisar 125 004, India

ABSTRACT.—The structure 5,4'-dihydroxy-6,7-dimethoxyflavone 3-O-rhamnoside for a flavonol glycoside previously isolated from *Rudbeckia bicolor* is shown to be doubtful by use of ¹H-nmr glycosyloxylation shifts. The revised structure is 3,4'-dihydroxy-6,7-dimethoxy-5-rhamnosyloxyflavone [4].

¹H-nmr glycosyloxylation shifts have been shown to be useful for the location of a sugar in naturally occurring flavones (1,2). The method involves a comparison of the ¹H-nmr spectra of the aglycone peracetate and the glycoside peracetate. Larger changes in chemical shifts have been observed for aromatic protons which are ortho and para to the site bearing the sugar. Using ¹H-nmr glycosyloxylation shifts, this paper reassesses the structure of a flavonol glycoside from *Rudbeckia bicolor* Nutt. (Compositae) (3).

In 1979, the flavonol glycoside was proposed (3) to be 5,4'-dihydroxy-7,8-dimethoxyflavone 3-O-rhamnoside [1]. In 1988, its aglycone was proposed (4) to be 3,5,4'-trihydroxy-6,7-dimethoxyflavone [2], i.e., its oxygenation pattern in the A ring was shown to be 5,6,7 (and not 5,7,8). When these two reports (3,4) are considered together, the flavonol glycoside is concluded to be 5,4'-dihydroxy-6,7-dimethoxyflavone 3-O-rhamnoside [3].

The reported ¹H nmr (3,4) for the 3,5,4'-trihydroxy-6,7-dimethoxyflavone

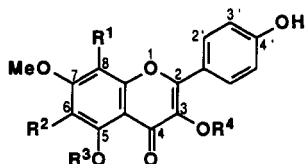
[2] peracetate shows (δ , CDCl₃) 7.80 (H-2' and H-6'), 7.20 (H-3' and H-5'), and 7.03 (H-8). The ¹H nmr (3,4) for the 5,4'-dihydroxy-6,7-dimethoxyflavone 3-O-rhamnoside [3] peracetate shows (δ , CCl₄) 7.73 (H-2' and H-6'), 7.12 (H-3' and H-5'), and 6.64 (H-8). The glycosyloxylation shifts from 2 to 3 (peracetates) are $\Delta H-2' = +0.07$, $\Delta H-6' = +0.07$, $\Delta H-3' = 0.08$, $\Delta H-5' = +0.08$, and $\Delta H-8 = +0.39$. These shifts (ΔH) clearly show that the peracetates of 2 and 3 differ at C-5 and not at C-3. If there had been glycosyloxylation at C-3, $\Delta H-2'$ and $\Delta H-6'$ would have been negative and numerically larger (1,2). There is glycosyloxylation at C-5, and H-8, which is para to the site of difference in 2 and 3 peracetates, has undergone a larger change in chemical shift. The corrected structure for the flavonol glycoside is, therefore, concluded to be 3,4'-dihydroxy-6,7-dimethoxy-5-rhamnosyloxyflavone [4].

EXPERIMENTAL

¹H-NMR DATA.—The data utilized in this paper were previously published (3,4) for 4, but interpreted incorrectly.

LITERATURE CITED

1. S.B. Kalidhar, *J. Chem. Res., Synop.*, 311 (1989).
2. S.B. Kalidhar, *J. Chem. Res., Miniprint*, 2416 (1989).
3. P.K. Jauhari, S.C. Sharma, J.S. Tandon, and M.M. Dhar, *Phytochemistry*, **18**, 359 (1979).
4. T. Horie, Y.M. Tsukayama, Y. Kawamura, and S. Yamamoto, *Phytochemistry*, **27**, 1491 (1988).



- 1 R¹=OMe, R²=R³=H, R⁴=Rha
- 2 R¹=R³=R⁴=H, R²=OMe
- 3 R¹=R³=H, R²=OMe, R⁴=Rha
- 4 R¹=R⁴=H, R²=OMe, R³=Rha

Rha=rhamnosyl

Received 19 January 1990