

## SHORT COMMUNICATION

### 4'-O-METHYLQUERCETIN 3-GLUCOSIDE FROM *ASTRAGALUS MISER* VAR. *OBLONGIFOLIUS*

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**Abstract**—4'-O-Methylquercetin 3- $\beta$ -glucoside was isolated from the title plant.

## INTRODUCTION

THE TITLE plant is a poisonous vetch found in the high mountain meadows of the Wasatch and Uinta mountains of northern Utah and Colorado, U.S.A. The poisonous principle of this plant has been extensively studied.<sup>1</sup> During the extraction of the poisonous principle, a flavonol glycoside was isolated and identified as 4'-O-methylquercetin 3- $\beta$ -glucoside.

## RESULTS

A flavonol glycoside having a melting point of 243–244° after several recrystallizations from ethanol, was isolated in 0.4 per cent yield from the title plant. The flavonol glycoside (0.06 g) was hydrolyzed in 2 N HCl to yield 0.03 g of a flavonol with a melting point of 254–255° and a carbohydrate moiety. Thin-layer and gas chromatography (of the trimethylsilyl ether) indicated the carbohydrate moiety was glucose. Ultra violet and NMR data indicated the aglycone was a quercetin derivative and the carbohydrate moiety was connected to the 3-position of quercetin via a  $\beta$ -linkage. That the 4'-oxygen was substituted was suggested by the u.v. data. The NMR data of the aglycone indicated one O-methyl group in the molecule. That the aglycone was 4'-O-methylquercetin (tamarixetin) was confirmed by mixed m.p. with an authentic sample (courtesy of L. Jurd). For a detailed analysis of the u.v. data see Ref. 2, for a detailed analysis of the NMR data see Ref. 3.

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<sup>1</sup> M. C. WILLIAMS and W. BINNS, *Weeds* **15**, 359 (1967); M. C. WILLIAMS and F. A. NORRIS, *Weeds* **17**, 236 (1969); M. C. WILLIAMS, K. R. VANKAMPEN and F. A. NORRIS, *Am. J. Vet. Res.* (in press); M. C. WILLIAMS, F. A. NORRIS and K. R. VANKAMPEN, *Am. J. Vet. Res.* (in press); F. R. STERMITZ, F. A. NORRIS and M. C. WILLIAMS, *J. Am. Chem. Soc.* **91**, 4599 (1969).

<sup>2</sup> L. JURD, in *The Chemistry of Flavonoid Compounds* (edited by T. A. GEISSMAN), MacMillan, N.Y. (1962).

<sup>3</sup> T. J. MABRY, J. KAGAN and H. RÖSLER, *Phytochem.* **4**, 177 (1965).

## DISCUSSION

This is the second time that a 4'-*O*-methylquercetin 3-glucoside has been reported in nature. Gupta and Seshadri<sup>4</sup> reported the isolation and identification of tamarixin (from *Tamarix troupi*, Tamaricaceae) as 4'-*O*-methylquercetin 3-glucoside. However, the Gupta and Seshadri compound melted at a much higher temperature, 315–316°. No work has been reported which determined the configuration of the carbohydrate–aglycone linkage of tamarixin. Melting points of flavonol glycosides are not reliable enough to ascertain whether the compound reported here is, or is not, tamarixin. No tamarixin was available for direct comparison.

## EXPERIMENTAL

*Materials*

*Astragalus miser* Dougl. var. *oblongifolius* (Rydb.) Cron. (Leguminosae) was supplied by M. Coburn Williams. A voucher sample has been placed with the Intermountain Herbarium, Utah State University, Logan, Utah, under voucher number 123412.

*Extraction and Purification*

The dried and ground material was extracted with 95% ethanol in a Soxhlet. The ethanol extract was cooled, filtered and the solvent removed. The residue was triturated with water; the aqueous solution was washed first with  $\text{CHCl}_3$ , then with 1-butanol. The butanol extract contained the flavonoid. The butanol was removed and the flavonoid recrystallized from ethanol.

*Hydrolysis*

The flavonol glycoside was hydrolyzed with 2 N HCl by refluxing the solution for 4 hr. After the solution cooled, the aglycone was removed by filtration leaving the carbohydrate moiety in the aqueous solution.

*Trimethylsilylation*

The glycoside, the aglycone and the sugar moiety were silylated by the method of Mabry *et al.*<sup>3</sup> The oily residue was taken up in dry  $\text{CCl}_4$  for NMR analysis and/or gas chromatography.

*Chromatography*

TLC was performed using commercially prepared silica gel F plates (Brinkmann Instruments). The solvent systems were *n*-BuOH–HOAc– $\text{H}_2\text{O}$  (6:1:2) and 20% HOAc. Diphenylamine was used as the visualization agent. Gas chromatography was performed on an Aerograph Hy-Fi model 600 D with a hydrogen detector using a SE-30 microcolumn (5 ft  $\times$   $\frac{1}{8}$  in.) at 100°. The carrier gas was nitrogen at 20 lb/in<sup>2</sup> and 25 ml/min.

*Spectral Data*

U.v. spectrum of the glycoside:  $\lambda_{\text{max}}$  (EtOH) 255, 262 sh, 352; ( $\text{AlCl}_3$ /EtOH) 265, 352, 395; ( $\text{NaOAc}$ /EtOH) 270, 370; ( $\text{NaOAc}$ /EtOH) 260, 355 nm. U.v. spectrum of aglycone:  $\lambda_{\text{max}}$  (EtOH) 255, 370; ( $\text{AlCl}_3$ /EtOH) 260, 425; ( $\text{NaOAc}$ /EtOH) 270, 395; ( $\text{NaOAc}$ / $\text{B}_2\text{O}_3$ /EtOH) 260, 370; ( $\text{NaOEt}$ /EtOH) 275, 420 nm (stable). NMR spectrum of the trimethylsilyl ether of the glycoside measured in  $\text{CCl}_4$  (tetramethyl silane external standard): 2.55 $\tau$  (shoulder), 2.65 $\tau$  (singlet, 2H), 3.25 $\tau$  (singlet, 1H), 3.4 $\tau$  (small singlet), 3.7 $\tau$  (doublet,  $J=2.5$  cps, 1H), 4.05 $\tau$  (doublet,  $J=2.5$  cps, 1H), 4.3 $\tau$  (doublet,  $J=7$  cps, 1H) (The 2–5 $\tau$  region appears almost exactly like that of rutin shown in Ref. 3.) 6.3 $\tau$  (large broad band) 6.6 $\tau$  (large broad band). NMR spectrum of the trimethylsilyl ether of the aglycone was virtually the same except no bands at 4.3 $\tau$  and a 3-proton singlet at 6.4 $\tau$ .

<sup>4</sup> S. R. GUPTA and T. R. SESHADE, *J. Chem. Soc.* 3063 (1954).