5. Agarwal, S. C., Bhaskar, A. and Seshadri, T. R. (1973) *Indian J. Chem.* **11**, 9.
6. Bhaskar, A. and Seshadri, T R. (1973) *Indian J. Chem.* **11**, 404.
7. Siddiqui, S. (1937) *J. Indian Chem. Soc.* **14**, 703.
8. The plant material used in this investigation was obtained from the United Chemicals and Allied products, 10 Clive Row, Calcutta-1, where a voucher specimen is preserved.
9. Venkataraman, K. (1962) In *The Chemistry of Flavonoid Compounds* (Geissman, T. A. ed.) p. 75 Pergamon Press, Oxford.
10. Lee, H. H. and Tan, C. H. (1965) *J. Chem. Soc.* 2743.
11. Farkas, L., Nogradi, M., Sudarsanam, V. and Herz, W. (1966) *J. Org. Chem* **31**, 3228.

Phytochemistry, 1978, Vol 17, pp 588–589 Pergamon Press Printed in England

A NEW FLAVONE GLYCOSIDE FROM THE LEAVES OF *PITYRODIA COERULEA*

J. B. HARBORNE* and C. I. STACEY†

*Phytochemical Unit, Department of Botany, The University of Reading, RG6 2AS, England; †Chemistry Department, Western Australian Institute of Technology, Bentley, Western Australia, 6102

(*Received* 13 *October* 1977)

Key Word Index—*Pityrodia coerulea*, Verbenaceae; flavone; 6-hydroxyluteolin; 7-rhamnosylxyloside.

6-Hydroxyluteolin and its derivatives have rarely been found in the Verbenaceae [1]. There are two reports of it and its 6- and 3′-monomethyl ethers in *Lippia nodiflora* [2, 3]; and of the 6-glucoside of 6-hydroxylutcolin 7,3′-dimethyl ether in *Citharexylum subserratum* [4]. Both these plants are of Asian origin. In the course of a current survey of the flavonoids of the Western Australian Verbenaceae, we have isolated a new glycoside of 6-hydroxyluteolin which forms the major leaf flavonoid of *Pityrodia coerulea* Ewart & J. White. It appears to be a taxonomic marker for *Pityrodia coerulea* since it has not been found in any other species of the genus so far investigated. A number of other *Pityrodia* appear to have 6-hydroxyflavones or flavonols but these seem to occur with methylation rather than with sugar attachment.

The flavone glycoside was isolated as a yellow solid from the 70% ethanolic extraction of the dried leaves, and on acid hydrolysis yielded an aglycone and an equimolecular mixture of rhamnose and xylose (PC). The aglycone was identified as 6-hydroxyluteolin (NMR, MS, UV and co-chromatography). Spectral data suggested that the sugar molecules were attached as a disaccharide to the 7-position of the aglycone and this was confirmed by methylation of the glycoside with dimethyl sulphate followed by acid hydrolysis to give 7-hydroxy-3′,4′,5,6-tetramethoxyflavone. The partially methylated sugars obtained were 2,3,4-tri-*O*-methyl-L-rhamnose and 2,3-di-*O*-methyl-D-xylose (PC). On the basis of these results, the glycoside was identified as 6-hydroxyluteolin 7-*O*-L-rhamnosyl-(1 → 4)-D-xyloside. Such a sugar combination does not appear to have been reported before in the flavone series [5], though a related flavonol, quercetin 3-rhamnosylxyloside (linkage unspecified) was found in *Tilia argentea* flowers by Hörhammer *et al.* [6].

EXPERIMENTAL

Isolation of the glycoside. The dried leaves were extracted with boiling 70% EtOH. The extract was concd and chromatographed Whatman 3MM paper using BAW. The major band (R_f 0.23) was yellow and was eluted with 80% MeOH The eluate was concd and chromatographed using 15% HOAc The major band (R_f 0.27) eluted with 80% MeOH and concd gave a yellow compound, mp 253–255° (decomp.). PC R_f values were 0.23 in BAW, 0.27 in 15% HOAc, 0.45 in BEW, 0.80 in Forestal and 0.50 in PhOH. UV max (nm) in MeOH were 260*sh*, 275, 302*sh*, 344 and spectral shifts with NaOH (band I, $\Delta\lambda$ +47), NaOAc (band II, +2), NaOAc + H_3BO_3 (band I, +32), $AlCl_3$ (band I, +96), $AlCl_3$ + HCl (band I, + 16) were observed In the MS the compound showed the presence of a parent ion at 302 ($C_{15}H_{10}O_7$ requires MW 302). The NMR spectrum (run in $CDCl_3$ as the acetate) gave signals centred at δ 7.58 (2′, 6′-H), 7.3 (5′-H), 6.94 (8-H), 6.53 (3-H), 3.92, 5.19 (sugars), 2.47, 2 36, 2.16, 2.02 (9 acetoxyl's), 1.17 (rhamnosyl Me).

Acid hydrolysis of glycoside. The glycoside in MeOH was hydrolysed with an equal vol. 2M HCl and the aglycone extracted with EtOAc. The aglycone was found to be 6-hydroxyluteolin (UV, NMR of acetate, co-chromatography) and the aq. residue was found to contain equimolecular amounts of rhamnose and xylose (co-chromatography) Hydrolysis carried out for periods up to 30 s resulted in the same products with no intermediate monoglycoside being found

Methylation of glycoside and hydrolysis of methylated product. The glycoside was methylated with Me_2SO_4–K_2CO_3 in Me_2CO for 36 hr and the methyl ether was hydrolysed with 2M HCl and the aglycone extracted with EtOAc. The aglycone was found to be 7-hydroxy-3′,4′,5,6-tetramethoxyflavone UV (max) in MeOH were 271, 328 and the spectral shift with NaOAc (band II, +10) was observed. The MS showed a parent ion at 358 ($C_{19}H_{18}O_7$ requires MW 358) and a major peak at 343 (—Me) which is characteristic of a methoxyl in the 6-position [7]. The partially methylated sugars were found to be 2,3,4-tri-*O*-methyl-L-rhamnose and 2,3-di-*O*-methyl-D-xylose (PC) [8].

Acknowledgements—We wish to thank the staff of the W.A. Herbarium (where a voucher specimen is deposited) for identification of the plant CIS wishes to thank the WAIT for financial support for this project.

REFERENCES

1. Harborne, J. B. and Williams, C. A. (1971) *Phytochemistry* **10**, 367.

2. Barau, A. K., Chakraborti, P. and Sanal, P. K. (1969) *J. Indian Chem. Soc.* **46**, 271.
3. Nair, A. G. R., Ramach, P., Nagarajan, S. and Subramanian, S. S. (1973) *Indian J. Chem.* **12**, 1316.
4. Mathuram, S., Purushathaman, K. K., Sarada, A. and Connolly, J. D. (1976) *Phytochemistry* **15**, 838.
5. Harborne, J. B. and Williams, C. A. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H. eds) pp. 376–441. Chapman & Hall, London.
6. Hörhammer, L., Stich, L. and Wagner, H. (1961) *Arch. Pharm.* **294**, 685.
7. Spiteller, G. (1971) *Physical Methods in Heterocyclic Chemistry* (Katritzky, A. R. ed.) Vol. III, p. 267. Academic Press, New York.
8. Percheron, F. (1966) *Chromatography* (Heftmann, E. ed.) p. 578. Reinhold, New York.

Phytochemistry, 1978, Vol 17, pp. 589–591 Pergamon Press. Printed in England.

ON THE NATURAL OCCURRENCE OF GOSSYPETIN 7- AND 8-MONOMETHYL ETHERS

JEFFREY B. HARBORNE*, NABIEL A. M. SALEH* and DALE M. SMITH†

* Phytochemical Unit, Plant Science Labs., University, Reading RG6 2AS, England;
† Dept. of Biological Sciences, University of California, Santa Barbara, CA93106, U.S.A.

(*Received* 20 *October* 1977)

Key Word Index—*Eriogonum nudum*; Polygonaceae; *Lotus corniculatus*; Leguminosae; *Geraea canescens*; Compositae; yellow flower pigments; gossypetin 7-methyl ether; gossypetin 8-methyl ether.

Abstract—The 7-methyl ether of gossypetin occurs, as a mixture of 4 glycosides, in the yellow inflorescence of *Eriogonum nudum*. In contrast to previous reports, however, it does not occur in *Lotus corniculatus* flowers, nor is it present in leaves of *Medicago sativa*. The 8-methyl ether, which is present in *Lotus* flowers, has been found for the first time in the Compositae, in flowers of *Geraea canescens*.

INTRODUCTION

Although gossypetin (8-hydroxyquercetin) is well known as a relatively common yellow pigment in plants [1], its monomethyl ethers have rarely been recorded [2]. The 8-methyl ether was first reported in flowers of *Lotus corniculatus* [3], while a yellow pigment which appeared to be different and hence was assigned the 7-methyl ether structure was also reported from the same source [4]. Gossypetin 7-methyl ether was also described as occurring in *Ranunculus* flowers [5] and in *Medicago sativa* leaves [6]. There were difficulties in identification since the 7-methyl ether had not been synthesized and spectral and chromatographic properties of authentic material were not known. However, this situation has recently been rectified by Wagner *et al.* [7] who have synthesized both isomers, together with the 4′-methyl ether, and at the same time have shown that the pigment from *Ranunculus repens* flowers is the 8- and not the 7-methyl ether.

In our continuing studies of the contribution of yellow flavonoids to flower colour in the angiosperms, we have discovered that the 7-methyl ether is the major yellow pigment of flowers of *Eriogonum nudum*. In reporting this, we wish to correct the earlier misidentification of the

RESULTS

Eriogonum is a Western North American genus of some 205 spp., the flowers of which are gathered in a showy involucre, but which are generally pink or white. Flowers of *Eriogonum nudum* ssp. *saxicola* are unusual in the genus in having a distinctive yellow colour, reminiscent in shade of the flower colour of those members of *Primula* and *Rhododendron* which are pigmented by gossypetin [1] rather than by the much more common carotenoids. Hydrolysis of the flower extract gave a gossypetin-like aglycone, which had slightly higher R_fs in all solvents when compared with gossypetin. It was clearly a monomethyl ether, and gave gossypetin on demethylation. It was readily identified as the 7-methyl ether by direct comparison (Table 1) with a synthetic specimen, being clearly distinguished in R_f and spectral properties from the 7-methyl ether.

Gossypetin 7-methyl ether is thus the major yellow colouring matter of these flowers, since carotenoids are essentially absent. It occurs in glycosidic form and four glycosides were identified: the 8-glucoside, the 3-arabinoside, the 3-galactoside and the 3-galactoside-8-glucoside. Small amounts of an isomeric aglycone were also detected during identification of these glycosides and this was identified as the 8-methyl ether by direct comparison with authentic material from *Lotus* (see below). *Eriogonum nudum* is thus the first plant in which both the 7- and 8-monomethyl ethers of gossypetin have been detected. Analyses of the other flavonoids in the flowers showed the presence of six common flavonol glycosides: the 3-galactoside, 3-glucuronide, 3-arabinoside and 3-rutinoside of quercetin and the 3-galactoside and 3-glucuronide of myricetin.