2000 $\mu$ 20 × 20 cm silica gel plate. A band at $R_f$ zero (3:2, benzene–methanol) was extracted and yielded berberine. A band at $R_f$ 0·35 yielded allocryptopine and a wide orange band at $R_f$ 0·90 yielded sanguinarine. At the bottom of the orange band was a yellow band which yielded chelerythrine. All the alkaloids were identified by comparing the i.r., NMR, and mass spectra with those of authentic samples.* The amount of protopine present was estimated from the amount isolated and the relative amounts of the remaining alkaloids were estimated visually from analytical TLC (iodoplatinic acid visualization) of the residues.

* We are indebted to R. H. F. Manske for the authentic sample of chelerythrine.

---

Phytochemistry, 1971, Vol. 10, pp. 677 to 679. Pergamon Press. Printed in England.

## POLEMONIACEAE

# NEW *C*-GLYCOSYLFLAVONES FROM *PHLOX DRUMMONDII*

T. J. MABRY, H. YOSHIOKA, SHARON SUTHERLAND and SUSAN WOODLAND

The Cell Research Institute and Department of Botany, University of Texas at Austin, Austin, Texas 78712 U.S.A.

and

W. RAHMAN, MOHD. ILYAS, J. N. USMANI and NAJAMA HAMEED

Department of Chemistry, Aligarh Muslim University, Aligarh, India

and

JEAN CHOPIN and M. L. BOUILLANT

Laboratoire de Chimie Biologique, Faculte des Sciences de L'Universite de Lyon, France

(*Received* 20 *July* 1970)

**Abstract**—*O*-Rhamnosyl-6-*C*-Xylosyl derivatives of apigenin and luteolin were found to be the two major flavonoids of the flowers of *Phlox drummondii*.

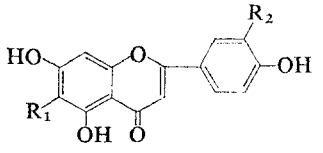
WE REPORT the isolation and structure determination of *O*-rhamnosyl-6-*C*-xylosylapigenin and *O*-rhamnosyl-6-*C*-xylosylluteolin, major flavonoids in the flowers of *Phlox drummondii* Hook. When the water-soluble portion of the residue obtained from the ethanol extract of flowers of *P. drummondii* was chromatographed over polyamide,[1] two major flavonoids, I, m.p. 198° and III, m.p. 210°, were obtained pure. Both substances yielded rhamnose upon acid hydrolysis.

*O-Rhamnosyl*-6-C-*xylosylapigenin* (*III*). Acid hydrolysis of compound III, the higher melting natural product, gave, in addition to rhamnose, a substance (IV), m.p. 228°, which

[1] T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, *The Systematic Identification of Flavonoids*, Springer-Verlag, New York (1970).

corresponded by co-chromatography in TBA and HOAc, m.p. and i.r. spectrum to synthetic 6-*C*-xylosylapigenin.[2] The presence of free hydroxyl groups at positions 5, 7, and 4′ in IV was confirmed by u.v. spectral analysis.* Since all six u.v. spectra for the rhamnoside (III) were essentially identical to those observed for IV, the rhamnose must be attached to the *C*-xylosyl moiety; the exact position of attachment has not yet been established. The u.v. spectra for both III and IV were almost identical with those previously recorded[1] for apigenin and isovitexin and are therefore not reported here. The NMR spectra of the trimethylsilyl ethers[1] of both III and IV and the acetate of III were in complete accord with the structure assignments.

*O-Rhamnosyl-6-C-Xylosylluteolin* (*I*). Acid hydrolysis of the major flavonoid isolated from the flowers of *P. drummondii* gave, in addition to rhamnose, a substance (II), m.p. 260°, which was shown to be identical with synthetic 6-*C*-xylosylluteolin[2] by co-chromatography, i.r. and mass spectra. The u.v. spectra for both I and II were the same as those previously obtained for both luteolin and isoorientin; therefore, the rhamnose must be attached to the *C*-xylosyl moiety.† Structures I and II were further supported by NMR analysis of their trimethylsilyl ethers and the acetate of I.




I, $R_1$=*O*-rhamnosyl-*C*-xylosyl, $R_2$=OH
II, $R_1$=*C*-xylosyl, $R_2$=OH
III, $R_1$=*O*-rhamnosyl-*C*-xylosyl, $R_2$=H
IV, $R_1$=*C*-xylosyl, $R_2$=H

## EXPERIMENTAL

The *Phlox drummondii* plant material‡ used in the present investigation was collected on the campus of the Aligarh Muslim University. All the two-dimensional chromatograms were on Whatman 3MM paper and were developed first in TBA (*t*-BuOH–HOAC–$H_2O$, 3:1:1) and then in 15% aq. HOAc. The NMR spectra were recorded using tetramethylsilane as an internal standard. The acid hydrolyses and preparations of acetates and trimethylsilyl ethers were carried out by standard procedures.[1]

*Extraction and isolation of I and III.* Dried and coarsely powdered white flowers of *Phlox drummondii* were extracted exhaustively with ethanol. Removal of the solvent left a brown gummy mass, which was taken up in water and filtered. The insoluble residue gave no test for flavonoids and was therefore discarded. The butanol extract of the aqueous solution was resolved into three components by paper chromatography on Whatman No. 3 filter paper using *n*-BuOH–HOAc–$H_2O$ (6:1:2). The components were further purified by passing them over a column of polyamide (Woelm). The homogeneity of each fraction was established by TLC on polyamide plates using a number of solvent systems.[1,3]

The two major components, I, m.p. 198°, and III, m.p. 210°, on acid hydrolysis gave II, m.p. 260° and IV, m.p. 228°, respectively. The hydrolysate in each case was identified as rhamnose by paper chromatography.[1]

*Properties of O-rhamnosyl-6-C-xylosylluteolin* (*I*). $R_f$(TBA). 0·29; $R_f$(HOAc): 0·52; 6-*C*-xylosylluteolin:‡ $R_f$(TBA) 0·29; $R_f$(HOAc): 0·23. NMR of TMS ether of I in $CCl_4$(ppm): H-2′6′, 7·3(m); H-5′, 6·8(d, $J$ = 8·5); H-8, 6·35(s); H-3, 6·22(s); rhamnose-H-1, centred at 4·6; sugar signals, 2·9–4·4; rhamnose-$CH_3$, 0·75(d, $J$ = 7). NMR acetate of I in $CDCl_3$: H-2′6′, 7·7(m); H-8, 7·35(s); H-5′, 7·25(d, $J$ = 8·5); H-3, 6·6 (s); sugar range, 4·0–5·8; aromatic acetyl range 2·2–2·6; sugar acetyl range 1·8–2·1; rhamnose-$CH_3$ 0·6(d, $J$ = 7).

* A set of six u.v. spectra[1] was recorded for each compound described here.

† An X-ray analysis of I is presently underway in collaboration with Dr. K. R. Markham in order to establish the exact position and nature of the rhamnose linkage to the 6-*C*-xylosyl group.

‡ *Phlox drummondii* is not native to India; the taxon examined was a cultivated variety.

[2] J. CHOPIN and M. L. BOUILLANT, *C.r. Acad. Sci., Paris* **270**, C, 331 (1970).

[3] P. R. BHANDARI, *J. Chromatog.* **16**, 130 (1964).

*Properties of O-rhamnosyl-6-C-xylosylapigenin** (*III*). NMR of TMS ether of III in $CDCl_3$(ppm): H-2′6′, 7·65(d, $J = 8·5$); H-3′5′, 6·8(d, $J = 8·5$); H-8, 6·35(s); H-3, 6·25(s); H-1 rhamnose, 4·9(br.s); H-1 xylose, centred at 4·6; sugar signals, 2·8–4·0; rhamnose-$CH_3$, 0·85 (d, $J = 9$). NMR of acetate of III in $CDCl_3$ (ppm): H-2′6′, 7·8(d, $J = 8·5$); H-3′5′, 7·2(d, $J = 8·5$); H-8, 7·25(s); H-3, 6·56(s); sugar signals 3·3–5·5; 4′,5′,7-aromatic acetyls, 2·56, 2·4, 2·3; sugar acetyls, 2·08, 2·01 (two), 1·9, 1·86; rhamnose-$CH_3$, 0·6(d, $J = 7$).

*Acknowledgements*—We wish to thank the Robert A. Welch Foundation (Grant F-130), the National Science Foundation (Grant 5548X), and the National Institutes of Health (Grant HD 04488) for financial support and Dr. Wazahat Hussain, Department of Botany, Aligarh Muslim University for assistance.

* The $R_f$s of 6- and 8-*C*-xylosides are quite different in 15% HOAc:

| | 6-*C*-Xyloside | 8-*C*-Xyloside |
|---|---|---|
| Apigenin | 0·37 | 0·26 |
| Luteolin | 0·23 | 0·12 |

Phytochemistry, 1971, Vol. 10, pp. 679 to 682. Pergamon Press. Printed in England.

## PRIMULACEAE

# UN NOUVEL EXEMPLE DE DÉRIVÉ NITRÉ D'ORIGINE NATURELLE: LE NITRO-3 MÉTHYL-5 GENTISATE DE MÉTHYLE, EXTRAIT DES RACINES DE *PRIMULA ACAULIS*

A. GORIS, P. FRIGOT, D. MOLHO, J. AKNIN, P. MULLER et M. CIBAULT

Laboratoire de Matière médicale et Botanique,
Faculté mixte de Médecine et de Pharmacie, 80-Amiens et Laboratoire de Chimie
(associé au C.N.R.S.), Muséum National d'Histoire Naturelle, Paris, France

(*Received* 30 *April* 1970, *in revised form* 19 *June* 1970)

**Résumé**—Présence dans les essences d'organes souterrains de la Primevère des jardins (*Primula acaulis* Jacq.) du nitro-3 méthyl-5 gentisate de méthyle.

**Abstract**—5-Methyl-3-nitrogentisic acid methyl ester was identified in the roots of *Primula acaulis* Jacq.

## INTRODUCTION

DANS un travail antérieur, deux d'entre nous[1] ont montré qu'une essence obtenue à partir de rhizomes d'une variété cultivée de *Primula acaulis*, après macération et hydrolyse enzymatique, renfermait en majorité de l'hydroxy-2 méthoxy-5 benzoate de méthyle (ou méthyl-5 gentisate de méthyle) puis, en quantités moindres, de l'hydroxy-2 méthoxy-4 benzoate de méthyle, du salicylate de méthyle, de l'hydroxy-2 méthoxy-4 acétophénone, de l'hydroxy-2 méthoxy-5 acétophénone et enfin des traces d'un produit coloré en jaune.

Nous avons pu obtenir, à partir d'un lot important de racines de *Primula*, des quantités suffisantes (0,5 g) de ce composé jaune (I) pour en déterminer la structure, objet du présent travail.

[1] P. FRIGOT et A. GORIS, *Ann. Pharm. Franc.* **26**, 287 (1968).