increasing polarity. The EtOAc eluate was found to contain a single entity which crystallized from EtOAc–petrol (3:1) mp 190°(*d*). UV $\lambda_{max}^{EtOH}$ nm: 220, 245, 250, 295; IR$\nu_{max}^{KBr}$ cm$^{-1}$: 3300, 1740, 1655, 1635, 1590, 1575, 1500, 1155, 1033, 1010 and 730–720. NMR (DMSO-$d_6$, 100 MHz) $\delta$ 6.55 (1H, *s*, C-8), 5.93 (1H, *br s*, C-3), 2.27 (3H, *br*, C–Me), 4.10 (2H, *s*, CO–$CH_2$–), 2.18 (2H, *s*, COMe), 3.55 (6H, *m*, glucosyl), 4.55 (1H, *d*, $J = 9$ Hz, H-1 of glucosyl).

*Oxidation of glycoside with ferric chloride.* The glycoside (50 mg), $FeCl_3$ (100 mg), conc HCl (4 ml) and conc $H_2SO_4$ (2 drops) were heated at 95° for 20 hr. A black solid was filtered from the soln, dried and extracted with boiling toluene. Removal of toluene yielded the aglycone, 5-acetonyl-7-hydroxy-2-methylchromone.

*Acknowledgements*—Thanks to the U.G.C. (India) for the award of a research associateship, CIBA Research Centre, Bombay (India) for the CH, IR, NMR and mass spectra and to Professor R. D. Tiwari, Head, Chemistry Department, University of Allahabad, India for valuable discussion.

## REFERENCES

1. Tiwari, R. D. and Singh, J. (1977) *Planta Med.* **34**, 319.
2. Tiwari, R. D. and Singh, J. (1979) *Phytochemistry* **19**, 2060.
3. Tiwari, R. D. and Singh, J. (1978) *Phytochemistry* **18**, 347.
4. Tiwari, R. D. and Singh, J. (1978) *Phytochemistry* **18**, 906.
5. Gupta, P. C. and Dubey, P. (1979) *Carbohydr. Res.* **72**, 151.
6. Sen, K. and Bagchi, P. (1959) *J. Org. Chem.* **24**, 316.
7. Wagner, H. (1964) *Methods of Polyphenol Chemistry*, p. 64. Pergamon Press, Oxford.
8. Prox, A. (1968) *Tetrahedron* **24**, 3697.

---

*Phytochemistry*, Vol. 21, No. 5, pp. 1179–1180, 1982.
Printed in Great Britain.

0031-9422/82/051179-02$03.00/0
Pergamon Press Ltd.

# 3, 5, 4'-TRIHYDROXY-6, 7-DIMETHOXYFLAVONE 3-GLUCOSIDE FROM *SESUVIUM PORTULACASTRUM*

Ravi K. Khajuria, Krishan A. Suri, Om P. Suri and Chand K. Atal

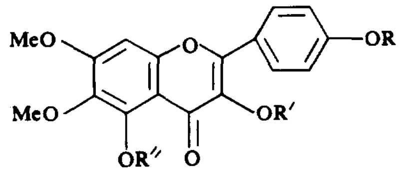
Regional Research Laboratory, Jammu-Tawi 180001, India

(*Revised received* 20 *October* 1981)

**Key Word Index**—*Sesuvium portulacastrum*; Aizoaceae; 3,5,4'-trihydroxy-6,7-dimethoxyflavone 3-*O*-glucoside; flavonol glycoside; eupalitin; eupalitin 3-*O*-glucoside.

**Abstract**—A new flavonol glycoside 3,5,4'-trihydroxy-6,7-dimethoxyflavone 3-*O*-glucoside has been characterized from *Sesuvium portulacastrum*, together with its aglycone, eupalitin.

Earlier workers have reported [1] the occurrence of eupalitin 3-*O*-rutinoside and $\alpha$- and $\beta$-ecdysones from *Sesuvium portulacastrum*. In the present investigation of the same plant a second glycoside (**1**) was isolated as yellow crystals, m.p. 223° and shown to be a flavonol with free hydroxyls at C-5 and C-4' and a substituted hydroxyl at C-7 from the UV data. The $^1H$ NMR spectrum (60 MHz) in DMSO-$d_6$ showed doublets ($J = 10$ Hz) at $\delta$ 6.8 and 8.0 representing $A_2B_2$ system in ring C. A singlet at $\delta$ 6.67 was assigned to *C*-8 proton. The presence of two methoxyls was inferred by signals at $\delta$ 3.8 and 3.85. Signals for free phenolic hydroxyls appear at $\delta$ 9.03 and 9.73. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1660, 1620, 1120, 1060. Strong absorption at 1060 and 1120 cm$^{-1}$ reflected the glycosidic nature of the compound [2]. The mass spectrum of the compound was similar to that of the aglycone eupalitin ($[M]^+$ 330) owing to the easy elimination of the sugar moiety from the glycoside [3]. The position of the sugar moiety in **1** was ascertained by methylation with dimethyl sulphate followed by hydrolysis (7% methanolic hydrochloric acid) which yielded 3-hydroxy-5, 6, 7, 4'-tetramethoxyflavone (**2**, mp 123°, yellow needles), whereas methylation with diazomethane and subsequent hydrolysis produced 3, 5-dihydroxy-6, 7, 4'-trimethoxyflavone (**3**, mikanin mp 222°). Hydrolysis of **1** (7% methanolic hydrochloric acid) yielded an aglycone which was identified as 3, 5, 4'-trihydroxy-6, 7-dimethoxyflavone (**4**, eupalitin) by UV data and $^1H$ NMR studies. The sugar moiety was determined as glucose by co-chromatography on paper with an authentic sample ($R_f$ 0.20, descending, *n*-BuOH–HOAc–$H_2O$, 4:1:5; aniline hydrogen phthalate spray). From these data **1** is characterized as the new glycoside 3, 5, 4'-trihydroxy-6, 7-dimethoxyflavone 3-*O*-glucoside. This structure was confirmed by synthesis of 3-glucosyloxy-5, 4'-dihydroxy-6, 7-dimethoxyflavone by treating the



**1** $R = R'' = H$, $R' = Glc$

**2** $R = R'' = Me$, $R' = H$

**3** $R = Me$, $R' = R'' = H$

**4** $R = R' = R'' = H$

aglycone with acetobromoglucose and potassium hydroxide in acetone [5]. The second constituent isolated from *S. portulacastrum* was established as eupalitin from its physical and spectral behaviour [4].

## EXPERIMENTAL

The plant material was identified by Miss Vir Bala Shah of Hoechst, Bombay and a voucher specimen has been deposited in the Herbarium of R. R. L. Jammu under accession No. 16091. A concd MeOH extract of dried whole plant material was successively triturated with petrol, $CHCl_3$, EtOAc and *n*-BuOH. The *n*-BuOH extract residue was charged on a Si gel column and graded elution with $CHCl_3$–MeOH mixtures yielded eupalitin (**4**) followed by the glycoside (**1**). The constituents were purified by crystallization from MeOH–EtOAc.

*UV data for* **1**, **4** *and* **2**. UV $\lambda_{max}^{MeOH}$ nm: **1** 265, 360, 380 sh; +$AlCl_3$ 270, 300 sh, 418; +$AlCl_3$–HCl 270, 300 sh, 418; +NaOMe 272, 415; +NaOAc 265, 360, 380 sh. **4** 265, 360; +$AlCl_3$ 270, 368 sh, 415; +$AlCl_3$–HCl 270, 368 sh, 415; +NaOMe 272, 415. **2** 252, 362; +$AlCl_3$ 262, 421; +$AlCl_3$–HCl 260, 420, +NaOMe 263, 400.

*Acknowledgement*—We thank Mr. Inderpaul Singh for technical assistance.

## REFERENCES

1. Banerji, A. and Chintalwar, G. J. (1971) *Indian J. Chem.* **9**, 1029.
2. Wagner, H. (1966) *Methods in Polyphenol Chemistry* p. 309. Academic Press, London.
3. Schmidt, R. D. (1972) *Tetrahedron* **28**, 3259.
4. Qui Jano, L., Malarico, F. and Rios Tirso (1970) *Tetrahedron* 2851.
5. Zemplen, G. and Farkas, L. (1943) *Chem. Ber.* **76**, 1110.

---

*Phytochemistry*, Vol. 21, No. 5, pp. 1180–1182, 1982.
Printed in Great Britain.
0031-9422/82/051180-03$03.00/0

# BERGENIN DERIVATIVES FROM *MALLOTUS JAPONICUS**

Takashi Yoshida, Kaoru Seno, Yukiko Takama and Takuo Okuda

Faculty of Pharmaceutical Sciences, Okayama University, Tsushima, Okayama 700, Japan

(*Received* 31 *July* 1981)

**Key Word Index**—*Mallotus japonicus*; Euphorbiaceae; polyphenols; 11-*O*-galloylbergenin; 4-*O*-galloylbergenin; 11-*O*-galloyldemethylbergenin; geraniin; methylellagic acid; $^{13}C$ NMR.

**Abstract**—Three new bergenin derivatives were isolated from the bark of *Mallotus japonicus* and determined to be 11-*O*-galloylbergenin, 4-*O*-galloylbergenin and 11-*O*-galloyldemethylbergenin. The $^{13}C$ resonances of bergenin were fully assigned.

The polyphenol-rich bark and leaf of *Mallotus japonicus* have been used in Japan as remedies for gastric ulcer. Although we isolated two new tannins, mallotusinic acid and mallotinic acid [1], along with geraniin [2], from the leaf extract, bergenin has been the only compound isolated from the bark of this tree [3, 4]. The present investigation on the aqueous acetone extract of bark afforded three new bergenin derivatives **1–3**. Five known polyphenols, 3,3′,4-tri-*O*-methylellagic acid, ellagic acid, geraniin, corilagin, and (−)-epigallocatechin gallate, in addition to bergenin (**4**), were also isolated.

Compounds **1** and **2** analysed as $C_{21}H_{20}O_{13}$ were shown to be monogalloyl esters of bergenin by their $^{1}H$, $^{13}C$ NMR and mass spectral data, and also by acid hydrolysis, which gave bergenin and gallic acid. The position of the galloyl group in **1** and **2** was elucidated by $^{13}C$ NMR. The carbon signals other than that of C-11 in the glucose moiety of bergenin, which have not been previously assigned [5], have now been assign-

---

*Part 2 in the series "Studies on Tannins and Polyphenols of *M. japonicus*". For Part 1 see ref. [1].