was further purified by TLC using the following elutants: (i) $CHCl_3$–EtOH (19:1) (R_f 0.66), (ii) *n*-hexane–Me_2CO (2:1) (R_f 0.38), (iii) isopropyl ether–toluene (3:1) (plate run × 6). In each case the compound was recovered by eluting from the Si gel with redistilled EtOAc. The final product was TLC pure in all the above systems and GLC gave a single peak on two columns: (i) 3% OV 17 on 80–100 mesh gaschrom Q at 250°, (ii) 2% SE-30 on 80–100 mesh gaschrom Q at 215° (yield 10 mg).

Synthesis of 7,8-dimethoxyflavanone. 2-Hydroxy-3,4-dimethoxyacetophenone was prepared by partial methylation of 2,3,4-trihydroxyacetophenone with Me_2SO_4 [4]. 2′-Hydroxy-3′,4′-dimethoxychalcone was prepared by a base-catalysed Aldol condensation similar to that described by ref. [5]. 2-Hydroxy-3,4-dimethoxyacetophenone (2.0 g) and freshly distilled PhCHO (2.0 g) were successively added with stirring to a soln of NaOH (4.0 g) in H_2O–EtOH (1:1) (35 ml) under N_2, at a temp. below 20°. The chalcone so formed was not isolated, but cyclized directly by diluting with H_2O (8 ml), acidifying by the slow addition of conc HCl (17 ml) with stirring and refluxed for 3 hr. The mixture was extracted with Et_2O (3 × 100 ml) and the extract washed with aq. Na_2CO_3, and H_2O, before evaporation. The residue was recrystallized from 100 to 120° petrol giving white needles of 7,8-dimethoxyflavanone (yield 1.0 g (35%), mp 115–116°).

Acknowledgements—The authors thank Miss P. Rowell for technical assistance and Prof. R. L. Wain for his support for the work.

REFERENCES

1. Pederiva, R., Kavka, J. and D'Arcangelo, A. (1975) *An. Asoc. Quim. Argent.* **63**, 85 ((1975) *Chem. Abstr.* **83**, 203739j).
2. Markham, K. R. and Mabry, T. J. (1975) in *The Flavanoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds.) p. 68. Chapman & Hall, London.
3. Pelter, A., Stainton, P. and Barber, M. (1965) *J. Heterocycl. Chem.* **2**, 262.
4. Crabtree, H. and Robinson, R. (1922) *J. Chem. Soc. Trans.* **121**, 1033.
5. Browne, M. F. and Shriner, R. L. (1957) *J. Org. Chem.* **22**, 1320.

Phytochemistry, 1979, Vol. 18, pp. 1766–1767. © Pergamon Press Ltd. Printed in England. 0031-9422/79/1001-1766 $02.00/0

A NEW FLAVANONE GLYCOSIDE FROM THE STEM OF *HIBISCUS MUTABILIS*

JAGDISH S. CHAUHAN, T. J. VIDYAPATI and AWADHESH K. GUPTA
Chemical Laboratories, University of Allahabad, Allahabad, India

(*Received* 16 *October* 1978)

Key Word Index—*Hibiscus mutabilis*; Malvaceae; naringenin 5,7-dimethyl ether 4′-*O*-β-D-xylopyranosyl-β-D-arabinopyranoside.

Hibiscus mutabilis, commonly known as Guliajaib, has not been studied chemically but various parts of the plant are used medicinally [1, 2]. In the present study, a new flavanone glycoside, naringenin 5,7-dimethyl ether 4′-*O*-β-D-xylopyranosyl-β-D-arabinopyranoside, was identified from the stem tissue.

EXPERIMENTAL

The air-dried powdered stem of *Hibiscus mutabilis* was extd exhaustively with hot EtOH. The conc EtOH extract deposited a yellow ppt. after 2 days in the cold, which was retained for further study. The filtrate was diluted with H_2O, separated into 2 fractions and the H_2O sol. fraction extracted with increasingly polar organic solvents. The EtOAc extract gave the new flavanone glycoside which was crystallized from EtOAc–petrol and shown to be homogeneous by PC and TLC; mp 88–90°, $C_{27}H_{32}O_{13}$. (Found: C, 57.2; H, 5.17. Calc.: C, 57.44; H 5.67%). Acid hydrolysis of the glycoside (7% EtOH–H_2SO_4) gave naringenin 5,7-dimethyl ether, $C_{17}H_{16}O_5$. (Found: C, 67.72; H, 5.19. Calc.: C, 68.00; H, 5.33%). mp 140–1° (UV, IR, methoxyl) arabinose and xylose.

Alkaline degradation of the aglycone (50% EtOH–KOH) produced phloroglucinol dimethyl ether and *p*-hydroxybenzoic acid (mp, mmp and co-PC). The colour reactions, formation of phenyl hydrazone, negative Shinoda test, spectral data [UV λ_{max}^{MeOH} nm: 280, no shifts with various reagents, viz. NaOAc and NaOMe; IR ν_{max}^{KBr} cm^{-1}: 3350, 2850, 1685, 1600, 1510, 1460, 1360, 1280, 1170, 1120, 1020 and 825; NMR signals (in CCl_4 and TMS as an internal standard) (in ppm): δ 2.78 (H-3), 3.82 (5-OMe, 7-OMe), 5.15 (H-2), 5.87 (H-6), 6.0 (H-8), 6.82 (H-3′, H-5′) and δ7.12 (H-2′ and H-6′)] and the above chemical degradations of the glycoside indicated it to be a 5,7-dimethoxyflavanone glycoside.

The hydrolysability of the glycoside with almond emulsin (yielding both arabinose and xylose), the first appearance of xylose on partial acid hydrolysis (1% H_2SO_4), consumption of 3 mol periodate to produce 1 mol HCOOH per mol of glycoside, acid hydrolysis of the completely methylated glycoside (DMS/dry K_2CO_3) yielding 2,3-di-*O*-methyl arabinose (phenyl hydrazone and periodate oxdn.) and 2,3,4-tri-*O*-methyl xylose (mmp and co-chromatography with an authentic sample) indicated the sugar moiety to be β-D-xylopyranosyl-β-D-arabinopyranoside attached to the only 4′-free hydroxyl group present in the aglycone by a 1 → 4 linkage. Demethylation of the aglycone (50% HBr/HOAc) gave naringenin (UV, IR, R_f and co-PC). Hence the structure of the new flavanone glycoside has been assigned as naringenin 5,7-dimethyl ether 4′-*O*-β-D-xylopy-

ranosyl-β-D-arabinopyranoside (1 → 4 linkage).

Acknowledgements—T. J. V. thanks the C.S.I.R., New Delhi, for a research fellowship and Dr. Gowri Shanker, Head, Horticulture Department, Allahabad Agr. Inst., for providing the plant material.

REFERENCES

1. Kirtikar, K. R. and Basu, B. D. (1935) *Indian Medicinal Plants*, Vol. 1, p. 339. L. M. Basu, Allahabad.
2. Chopra, R. N., Nayar, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 133. C.S.I.R., New Delhi.

Phytochemistry, 1979, Vol. 18, pp. 1767–1768. © Pergamon Press Ltd. Printed in England.

PARALLELISM IN HILL ACTIVITY AND ANTHOCYANIDIN CONTENT IN *EUPHORBIA PULCHERRIMA*

D. BANERJI and V. SHARMA

Department of Botany, Institute of Advanced Studies, Meerut University, Meerut (U.P.), India

(*Received* 9 *March* 1979)

Key Word Index—*Euphorbia pulcherrima*; Euphobiaceae; Hill activity; anthocyanidin; chlorophyll.

Abstract—Pigment compositions and Hill activities of red-leafy bracts, red-green leaves and green leaves of *E. pulcherrima* were studied. Interestingly enough, the chloroplasts from anthocyanidin-containing leaves are intrinsically more active than those from green leaves.

The inflorescence of *Euphorbia pulcherrima* Willd. ex Klotzsch (poinsettia) has an involucre of bright red-leafy bracts and some red-green foliage below, besides the usual green leaves. It was of interest to find whether the red bracts contain chlorophylls besides the obvious anthocyanins and if so, whether they are photosynthetically active. Hence, comparative studies on Hill activities, anthocyanidins and chlorophyll compositions of three types of fully expanded foliage, i.e. the red-leafy bracts, red-green leaves and green leaves, were undertaken.

The comparative Hill activity and pigment compositions are shown in Table 1. It is remarkable that on the basis of Hill activity, the most active chloroplasts are those from the red bracts. Thus, the Hill activity of the green leaf is 132.6 μM DCPIP reduced/mg chl./hr and while the activity of the chloroplasts from red-green leaves is about 7% higher, that of red-leafy bracts is about 60% higher.

The red bracts contain maximal anthocyanidin, the red-green leaves lower amounts and in green leaves anthocyanidins could not be detected. In the red-leafy bracts and red-green leaves there are two anthocyanidins, cyanidin and pelargonidin, and the relative amount of cyanidin in both is about twice that of pelargonidin. The total chlorophyll content of the green leaves is 2.15 mg/g fr.wt and those of the red-green leaves and leafy bracts are much lower. The chlorophyll b/a ratio is *ca* 0.5 in the green and red-green leaves and in the leafy bract it is *ca* 0.3, indicating the existence of a proper pigment system. The association of higher anthocyanin content with higher Hill activity in leaves is noteworthy.

These results indicate that the red-leafy bracts, although completely pigmented like petals, are capable of photosynthesizing and fulfilling, at least partly, their nutrient requirement. Photosynthetic activity also in the red-purple coloured leaves of the 14 cultivars of *Coleus* has been reported [1]. Such work and the novel association of higher Hill activity with the occurrence of anthocyanins reported here and the reports of the presence of flavonoid glycosides in chloroplasts [2] show that such unconventional systems as anthocyanin-containing leaves can be used for photosynthetic studies. Such an approach will not only lead to a better understanding of the possible role of different pigments in the bio-utilization of solar energy, but also a better appraisal of the role of flavonoids customarily overlooked as secondary.

Table 1. Hill activity and pigment composition of the leafy-bract and different leaf types of *Euphorbia pulcherrima*

Leaf type	Hill activity μM DCPIP reduced/mg chlorophyll/hr	Chlorophylls (mg/g fr. wt) a	b	Total	Anthocyanidin Cyanidin *A* 535/g fr. wt	Pelargonidin *A* 520/g fr. wt	Total *A* 525/g fr. wt
Red-leafy bract	210.0	0.025	0.007	0.07	0.13	0.05	0.89
Red-green leaf	139.8	0.311	0.115	0.77	0.08	0.04	0.54
Green leaf	132.6	0.803	0.476	2.15	*	*	*

* Not detected in our method.

EXPERIMENTAL

Anthocyanidin extraction and chromatography were done by the method of ref. [3]. Total anthocyanidin estimations were made by measuring A_{525} in MeOH–HCl (99:1) with a final vol. of 20 ml/g fr. wt. The extract was concd to dryness, redissolved in 1 ml MeOH–HCl/g fr. wt and 0.1 ml subjected to PC in formic solvent (conc HCl–HCO_2H–H_2O, 2:5:3) and Forestal solvent (conc. HCl–HOAc–H_2O, 3:30:10). The fractionated anthocyanidins were eluted, made up to 10 ml with MeOH–HCl and quan-