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ISORHAMNETIN 3,7-DISULPHATE FROM *FLAVERIA BIDENTIS*

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Key Word Index—*Flaveria bidentis* var. *angustifolia* O.K.; Compositae; isorhamnetin 3,7-disulphate.

EXPERIMENTAL

Plant source. Flaveria bidentis var. *angustifolia* O.K. was collected in the area of the Mar Chiquita Lake (Córdoba Province, Argentine) during the February March period and identified by Prof. Ing. Agr. A. T. Huntziker (Botanical Museum, National University of Córdoba).

Isolation. 250 g of flowers were dried, ground and extracted at low temp. with petrol and then with CH_2Cl_2 and finally with EtOH–H_2O (1:1). This last extract was concn and a crystalline solid was obtained (200 mg), recrystallized in H_2O and chromatographed in PC (Whatman 3MM). R_f's (× 100) were 78 in H_2O, 12 in TBA, 72 in 15% HOAc and 47 in BAW. Mp (hot stage) 240° (dec.). UV spectral max. in MeOH at 253 (log ε 4.35) and 353 nm (log ε 4.28) with bathochromic shift in the presence of NaOMe (+ 63 nm) and $AlCl_3$ (+ 48 nm). IR (KBr), ν_{max} cm^{-1}: 3350 (HO), 1640 (CO), 1250 and 1040 (SO). NMR (D_2O, 60 MHz) δ 3.6 (3H, *s*, OMe, C3'); 6.5 (2H, *d*, $J_{6,8-8,6} = 2.5$ Hz, C6-C8; 6.7 (1H, *d*, $J_{5'-6'} = 10$ Hz, C5'); 7.20 (1H, *d*, $J_{2',6'} = 2.5$ Hz, C6') and 7.30 (1H, *d*, $J_{6',2'} \simeq 2$ Hz, C2'). Analysis: Found: S: 11.59%, Calc. for $C_{16}H_{10}O_{13}S_2K_2$, S: 11.60%.

Acid hydrolysis gave isorhamnetin, identified by its spectral properties in UV, IR and chromatography against an authentic sample. The hydrolysate also gave a white ppt. with $BaCl_2$. Test for carbohydrates were negative. On demethylation [3] the reaction product gave quercetin, identified by usual techniques. 60 mg of 3,7-disulphate were methylated [1], the product hydrolyzed and its observed UV properties were those of quercetin 5,3',4'-trimethyl ether. Alkaline degradation of this [4] gave veratric acid among other products.

Partial hydrolysis was carried out with 0.05 N HCl [5], the soln being chromatographed in water. Four spots were detected eluted and analyzed by UV. The first R_f 0.00 was identified as isorhamnetin; the second at 0.12 was identified as isorhamnetin-7-sulphate [6], the third with R_f 0.65 was identical to persicarin [7], and the fourth at R_f 0.78 was unchanged 3,7-disulphate.

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ANTHOCYANINS OF *FUCHSIA* (ONAGRACEAE)

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Key Word Index—*Fuchsia*; Onagraceae; anthocyanins; distribution; genetics.

Abstract—3-Glucosides and 3,5-diglucosides of pelargonidin, cyanidin, peonidin, delphinidin, petunidin and malvidin have been identified as flower pigments in *Fuchsia* species. These pigments in varying admixture appear to be solely responsible for different flower colours in this genus. Their production and inheritance seems to be under a complex system of genetic control.

In spite of the considerable ornamental value of the genus *Fuchsia*, little work has been devoted to the identification of the pigments responsible for the wide range of flower colours present. Only three pigments

Table 1. Anthocyanins of *Fuschia*

		3,5-Diglucosides						3-Glucosides						Acylated		relative
		Pg 1	Cy 2	Pn 3	Dp 4	Pt 5	Mv 6	Pg 7	Cy 8	Pn 9	Dp 10	Pt 11	Mv 12	Cy 13	Pn 14	pigment concentration
(a) *Species*																
F. triphylla L.	Fl	+						+								1 > 7
F. fulgens Moc. & Sesse	P	+						+	+							7 > 1 > 8
	S	+	+					+	+							7 > 8 > 1 > 2
F. serratifolia Hook.	P	+		t												1 > 3
	S	t	+	+												3 > 2 > 1
F. arborescens Sims	Fl	t	+	+			+									3 > 6, 2 > 1
F. procumbens Cunn.	Fl		+	+	+		+									3 > 6, 2, 4
F. boliviana Carr. cv *luxurians* Johnston	Fl		+	+	t		t									3 > 2 > 6 > 4
F. boliviana f. *puberulenta* Munz	Fl		+	+												3 > 2
F. microphylla var *aprica*	Fl		t	+					+	+						3 > 8, 9. 2
F. excorticata L.	Fl		+	+	+	+	+		+	t	+	+	+			12 > 11 > 6 > others
	A								+		+	+	+			11 > 12 > 8 > 10
F. magellanica Lam. var. *molinae* Espinosa*	Fl			+			t									3 > 6
F. splendens Zucc.	Fl		+	+					+					+	+	8 > 2 > 3 > 13, 14
(b) *Cultivars*																
"Fanfare"	P	+		+												1 > 3
	S	t	+	+												3 > 2 > 1
"White Phenomenal"	P		+	+												3 > 2
	S		+	+												3 > 2
"Queen Mary"	P	+		+			+									3 > 1 > 6
	S		+	+					t							3 > 2 > 8
"Tennessee Waltz"	P			+			+									3 > 6
	S		+	+												3 > 2
"Mission Bells"	P			+			+									6 > 3
	S		+	+					t							3 > 2 > 8
"Phryne"	P	+	+	+			+									6 > 3 > 1 > 2
	S		+	+												3 > 2
"Lord Byron"	P			+			+									6 > 3
	S		+	+												3 > 2
(c) *Hybrids*																
F. boliviana x *F. triphylla*	P	+	+	+												3 > 1 > 2
	S		+	+												3 > 2
F. triphylla x *F. procumbens*	P		t	+	t		+									6 > 3 > 2, 4
	S		+	+	+		+									6 > 3 > 2, 4
F. magellanica x *F. excorticata*	Fl			t	+		+		+		+					6 > 10 > 4, 8, 3
F. magellanica x *F. fulgens*	P	+		+			+									3 > 6 > 1
(3x)	S	+	+	+			t									3 > 2 > 1 > 6
F. magellanica x *F. fulgens* (6x)	P	+	t	+			+		+	+			+			6 = 3 > 1 > 12 > others
	S		+	+					+	+				+		3 > 2 > 8 > 9 > 13
(6x) hybrid x *F. magellanica* (back-cross) (5x)	P			+			+		+				+			6 > 3 > 8 > 12
	S		+	+	+				+	+	+			+	+	3 > 2 > 8 > others
F. magellanica x *F. splendens*	P			+			+		+	+			+			8 > 3 > 6 > 9, 12
	S								+	+				+	+	8 > 9 > 13, 14
F. splendens x *F. fulgens*	P	+	+					+	+							7 > 1 > 8 > 2
	S	+	+	+				+	+							2 > 3 > 1 > 8 > 7
(*F. splendens* x *F. fulgens*)? = *F. speciosa*"?	Fl		t	+					+	+						8 > 9 > 3 > 2

Key: Pg, pelargonidin; Cy, cyanidin; Pn, peonidin; Dp, delphinidin; Pt, petunidin; Mv, malvidin; Fl, flowers; S, sepals; P, petals; A, anthers.

**F. magellanica* used is a variety with pale pink flowers, without the red sepals and blue petals of the typical species; it has been derived directly from the type species.

have been identified and these in garden forms: the 3,5-diglucosides of pelargonidin, malvidin and cyanidin [1, 2]. A detailed study is now presented of the anthocyanins present in ten of the approximately 50 known species [3], in various species hybrids and in horticultural cultivars (Table 1). Among the species included in the survey are *F. magellanica* and *F. fulgens*, from which garden forms are thought to have originated. Two series of pigments are represented, the 3-glucosides and 3,5-diglucosides, of all six common anthocyanidins. These pigments occur in varying degrees of admixture in the different plants. Two minor pigments (**13** and **14**) were incompletely identified, but appear to be acylated anthocyanins. In addition it was observed that purple fruits (e.g. of *F. boliviana. F. arborescens*, etc.), are rich in Pt 3,5-diglucoside and may be used as a reference source of this compound.

Flower colour in *Fuchsia* appears to be almost wholly determined by anthocyanins. Orange shades (*F. triphylla, F. fulgens, F. serratifolia* and hybrids) relate to a predominance of Pg derivatives. Red colouration (particularly in the sepaloid structures) is largely due to Cy and Pn pigments, whilst the tendency to blueness in the central petaloid cone can be correlated with a gradient in Mv concentration (thus note the series represented by the horticultural varieties, White Phenomenal → Queen Mary → Tennessee Waltz → Mission Bells → Phryne → Lord Byron, Table 1b). There was no evidence from the present study to support the suggestion that 'blueness' is related to flavone co-pigmentation [2]. The flavone content in most flowers examined was negligible.

Examination of progeny from a number of artificial hybrids (Table 1c) suggests that there are present in *Fuchsia* several Mendelian genes controlling hydroxylation, methylation and glucosylation of the anthocyanins. From the limited data available, it is not possible to relate specific genes to these biochemical processes. However, the inheritance of anthocyanin hydroxylation does not appear to be controlled, as in most plants studied [4], in such a way that production of delphinidin (Dp) is dominant to production of cyanidin (Cy) which in turn, is dominant to production of pelargonidin (Pg). The situation in *Fuchsia* seems to be highly variable. Thus, inheritance of hydroxylation pattern is apparently additive in (a) the cross of *magellanica* (Cy/Dp) with *fulgens* (Pg/Cy) where the hybrid contains all three types. and (b) in the cross of *splendens* (Cy) with *fulgens* (Pg/Cy) where the hybrid contains both Cy and Pg. On the other hand, pelargonidin formation is dominant in the cross of *boliviana* (Cy/Dp) and *triphylla* (Pg) since the hybrid lacks Dp. Conversely, delphinidin is apparently dominant in the cross *triphylla* (Pg) x *procumbens* (Cy/Dp) since in this case Pg is lacking. The complex dominance-recessive relationships thus revealed in the control of hydroxylation pattern in *Fuchsia* may, in part, be due to the fact that most of these species are bird-pollinated, so that natural selection for a dominant scarlet (Pg) corolla colour would be favoured.

While the corollas and sepals of *Fuchsia* were low in co-occurring flavonols and flavones, the leaves contained considerable quantities of different glycosides of quercetin, kaempferol, luteolin and apigenin. Studies of two-dimensional chromatographic patterns of leaf extracts showed that, in general, additive inheritance occurred in the flavone and flavonol glycoside components. Studies of both flower and leaf flavonoids should thus be of value both in future breeding programmes, to produce new horticultural varieties, and in the determination of possible parentages of existing garden hybrids.

EXPERIMENTAL

Fresh plant material was collected from Shinfield Gardens, University of Reading. Extraction, purification and identification of anthocyanins was carried out as previously described [5].

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GLYZARIN, A NEW ISOFLAVONE FROM *GLYCYRRHIZA GLABRA*

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Key Word Index—*Glycyrrhiza glabra*; Leguminose; glyzarin, 2-methyl-7-hydroxy-8-acetylisoflavone.

Plant: *Glycyrrhiza glabra L., Source.* Dr. S. C. Sankhyadhar, experimental gardens of Govt. Ayurvedic College, Jammu (India). *Uses.* Medicinal [1].

Present work. We earlier reported the occurrence of three 2-methylisoflavones, some other polyphenols [2] and liqcoumarin [3] from indigenous *G. glabra* roots. In the present communication, we report the isolation of a new 2-methylisoflavone, herein named glyzarin.

An EtOH extract of air-dried roots (1.2 kg) was concentrated and the solvent-free residue exhaustively extracted with Et_2O. The Et_2O soluble fraction was chromatographed on Si gel. The C_6H_6-EtOAc (3:1)