

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*; Leguminosae; 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 Et₂O. The Et₂O soluble fraction was chromatographed on Si gel. The C₆H₆-EtOAc (3:1)

eluate on repeated preparative-TLC purification using C_6H_6 -EtOAc (1:1) gave three 2-methylisoflavones [2] and another fraction now identified as a new 2-methylisoflavone, glyzarin.

Glyzarin (50 mg), light yellow needles from EtOH, mp 207–8°, $C_{18}H_{14}O_4$ (M^+ 294; Found: C, 73.7; H, 4.3; required C, 73.4; H, 4.7%). It gave –ve Mg–HCl, –ve Zn–HCl but +ve Na–Hg/HCl tests and had λ_{max}^{MeOH} (log ϵ) 250 (4.13), 295 (3.74); +NaOAc 273, 317 nm; ν_{max}^{KBr} 3450, 1740, 1680 cm^{-1} . The colour reactions and UV spectrum indicated the possibility of glyzarin being an isoflavone. MS: m/e (rel. intensity) 294 (M^+) (100), 252 (98), 137 (33), 136 (28), 116 (55), and 77 (58). It gave an acetate (Ac_2O -Py) as colourless needles from aq. EtOH, mp 198–9°. PMR spectrum of glyzarin acetate (δ , $CDCl_3$; TMS internal standard): 2.35, 2.40 (6H, s, –OCOMe, C–Me), 3.00 (3H, s, –COMe), 7.20 (1H, d, $J_o = 8$ Hz, 6-H), 7.55 (5H, m, side phenyl protons), 8.10 (1H, d, $J_o = 8$ Hz, 5-H). The spectral data showed C–Me, C–acetyl and O–acetyl substituents and an unsubstituted side phenyl ring. The latter was also confirmed by the identification of phenylacetic acid after alkaline hydrolysis of glyzarin and its UV spectrum showed bathochromic shifts with NaOAc characteristic of a C–7 OH [4]. In addition a brown ferric reaction indicated the possibility of this OH being chelated with C–acetyl

which could be thus considered at C-6 or C-7. In the PMR the signals at δ 7.20 and 8.10 were assigned to the two *ortho*-coupled aromatic protons present at C-6 and C-5 respectively and the C–acetyl was thus placed at C-8. Since the signal due to the H at C-2 in isoflavones in the region of δ 7.60–7.88 [4] was absent, the remaining C–Me was fixed at C-2. Thus glyzarin was assigned the structure 2-methyl-7-hydroxy-8-acetylisoflavone which was confirmed by comparison with a synthetic sample obtained by heating 2-methyl-7-acetoxyisoflavone [6] with $AlCl_3$ under the conditions of Fries migration (mp, mmp, Co–TLC and superimposable IR).

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ISOLATION AND CONSTITUTION OF CORYLIDIN: A NEW COUMESTROL FROM THE FRUITS OF *PSORALEA CORYLIFOLIA*

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Previous work has been reported on the fruits of *Psoralea corylifolia* [1–4], and related species *P. drupaceae* [5–10], *P. plicata* [11] and *P. acaulis* [12].

The ether extract (800 g) of the whole dried seeds of *P. corylifolia* (5 g) was separated into individual constituents by repeated column chromatography over Si gel.

Elution with petrol (40–60°) afforded triacontane $C_{30}H_{62}$ mp 63–4°, mmp undepressed, TLC and Co–TLC, identical in all respects with the authentic sample.

The C_6H_6 -Et₂O (1:3) eluate yielded corylidin (1) as white crystalline needles (from EtOH–Me₂CO) (60 mg), mp 349–51°. It gives no ferric chloride reaction but a

yellow colouration was obtained with aq. NaOH. The compound analysed for $C_{20}H_{16}O_7$, M^+ 368.0867 ($C_{20}H_{16}O_7$ req. M^+ 368.0894) λ_{max}^{EtOH} nm (log ϵ) 210 (4.61), 220 (sh 4.38), 245 (4.26), 298 (sh 4.08), 312 (3.92), (4.40) and 365 (sh 4.35) which remained unaffected on the addition of NaOAc or $AlCl_3$, but shifted to λ_{max}^{275} nm on the addition of ethanolic KOH. IR ν_{max}^{KBr} cm^{-1} : 3360, 3210, 3100, 2980, 1701, 1635, 1610; 1575, 1495, 1450, and 870. NMR (100 MHz, d_6 -DMSO): two sharp singlets at δ 1.13 and 1.17 (3H each, $(Me)_2C<$), a one proton doublet at 4.27 ($J_{5'',4''} = 4.5$ Hz, C-5'' proton). There was a broad signal at 5.29 due to the C-4'' proton which changed to a sharp doublet ($J_{4'',5''} = 4.5$ Hz) on D₂O exchange, a double doublet at 6.89 ($J = 8.1$ and 2.1 Hz, 1H; C-5'), a singlet at 6.99 (1H, C-8), a doublet at 7.12 ($J = 2.1$ Hz, 1H C-7'), a proton doublet at 7.65 ($J = 8.1$ Hz, 1H C-4') and a singlet at 7.86 (1H, C-5).

The MS showed prominent peaks at m/e (rel. int.) 368 (M^+ , 100%), (24.4), 355 (96.51), (75.6), 308 (24.4), 296 (98.8), 293 (98.8), 292 (95.3), 281 (12.8), 69 (43.2), 59 (100) 43 (100), which was consistent with the structure proposed. The $CHCl_3$ -MeOH (9:1) eluate afforded

