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FLOWER FLAVONOIDS OF *OPUNTIA* SERIES *OPUNTIAE*

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Key Word Index—*Opuntia*; Cactaceae; prickly-pear; quercetin; isorhamnetin; kaempferol; 3-glycosides.

As part of an investigation into the possible hybrid origin of the tetraploid prickly-pear, *Opuntia curvospina* Griffiths, we undertook the identification of the flavonoids from this species and its potential parent species. *Opuntia chlorotica* Engelmann & Bigelow and *O. phaeacantha* Englemann var. *major* Englemann have been suggested as the putative diploid and hexaploid parents, respectively, of *O. curvospina* [1]. Additional closely related taxa in series *Opuntiae* were also examined. These included the tetraploid *O. littoralis* (Englemann) Cockerell var. *martiniana* (L. Benson) L. Benson, and the hexaploids *O. phaeacantha* var. *discata* (Griffiths) L. Benson & Walkington and *O. littoralis* var. *littoralis.* All taxa were investigated for their flower flavonoids. Prior to this report, studies of *Opuntia* flavonoids have been few and mostly incomplete [2–8].

RESULTS AND DISCUSSION

The flowers of all 6 taxa of *Opuntia* series *Opuntiae* examined produce the same flavonoids. These are quercetin and isorhamnetin 3-glucosides and 3-rutinosides, isorhamnetin 3-rhamnosylgalactoside, and kaempferol 3-galactoside. These flavonoid profiles suggest close relationships among all 6 taxa. The chemical data indicate a slight divergence between *O. lindheimeri* Englemann and these taxa. *Opuntia lindheimeri* produces two flavonoids found in the group (isorhamnetin 3-rutinoside and 3-rhamnosylgalactoside) and two that are not (quercetin and isorhamnetin 3-galactosides) [6]. This species, which is also included in series *Opuntiae* (Pinkava, D. J., personal communication), is the only other member of the genus whose flavonoid profile has been completely determined. At this time the available data can only indicate the potential usefulness of chemotaxonomic studies of *Optunia* species. The lack of qualitative differences in flavonoids among the taxa reported here lends no support nor does it contradict the hypothesis that *O. curvospina* arose from the hybridization of *O. phaeacantha* var. *major* and *O. chlorotica.*

EXPERIMENTAL

Vouchers of all plant material are deposited in ASU. Flavonoids were isolated from 85% aq. MeOH extracts by Polyclar AT and Sephadex LH-20 column chromatography using the methods of Mabry *et al.* [9]. Individual compounds were characterized by standard UV–visible spectral analyses [9]. Monosaccharides were obtained using standard acid hydrolytic procedures [9] and disaccharides were recovered after H_2O_2 oxidation of the flavonoid moieties [10]. Sugars were identified by co-retention with standards using HPLC [11].

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DERRONE, A NEW PYRANOISOFLAVONE FROM *DERRIS ROBUSTA* SEEDS

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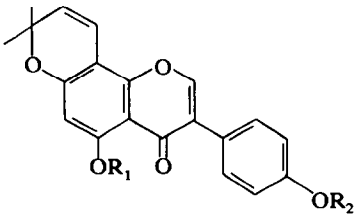
Key Word Index—*Derris robusta*; Leguminosae; derrone; 5,4'-dihydroxy-2",2"-dimethylpyrano(5",6":7,8)-isoflavone.

In continuation [1] of our work on the seeds of *Derris robusta* we wish to report the isolation of a new pyranoisoflavone, derrone, from the combined ethyl acetate and methanol extracts. It analysed for $C_{20}H_{16}O_5$ (M^+ 336). That derrone is an isoflavone containing a chelated hydroxyl was shown by absorption at 3400 and 1647 cm^{-1} in the IR spectrum, λ_{max}^{MeOH} 280 nm in the UV spectrum and by sharp singlets at δ13.80 (chelated hydroxyl) and 7.73 (H-2 of the isoflavones). Location of a chelated hydroxyl at position-5 is shown by a bathochromic shift of 9 nm with $AlCl_3$ in UV. Absence of a shift [2] with NaOAc in the UV spectrum indicated the absence of a free hydroxyl at position-7. The presence of two hydroxyls in derrone was shown by the NMR of its acetate which exhibited two singlets at δ2.44 and 2.30, each integrating for three protons. NMR of the compound showed a six-proton singlet at δ1.42, assignable to a gem-dimethyl group and two doublets (J = 10 Hz) at 6.68 and 5.56, integrating for one proton each, corresponding to vinylic protons (H-4" and H-3", respectively) suggesting the presence of a 2,2-dimethylchromen residue [3]. Two doublets (J = 9 Hz) at δ7.29 and 6.77, each integrating for two protons, characteristic of A_2B_2 pattern, in the NMR of the compound were attributed to the 2',6'- and 3',5'-protons respectively. The other hydroxyl is, therefore,



1 $R_1 = R_2 = H$
2 $R_1 = H$, $R_2 = Me$
3 $R_1 = R_2 = Ac$

assigned to the 4'-position which is evidenced by peaks at *m/e* 203(5%) and 118(3%) (arising from retro-Diels–Alder fission of the M − 15 ion) in the MS [4] of the compound. That the 2,2-dimethylchromen residue is at the 7,8-position in derrone was established by a negative Gibb's test and by comparing the chemical and spectral data of its monomethyl ether with that reported in literature [5]. Therefore, a sharp singlet at δ 6.27 was assigned to H-6. Hence derrone is 5,4'-dihydroxy-2",2"-dimethylpyrano(5",6":7,8)isoflavone (**1**).