gum, UV λ_{max} 290 nm; NMR (60 MHz, $CDCl_3$) 7.72*d* and 6.50*d* (8, H-10 and H-11), 6.65 (H-1), 6.55 (H-4), 5.20*tbr* (7, H-2'), 4.90*t* (3.5, H-6a), 4.50*m* (2*p*, H-6), 3.81, 3.77 (OMe), 3.35*m* (2*p*, H-1'), 1.80 and 1.70 (3*p* each, H-4' and H-5'); MS (*m/z*) 412 (M^+), 394, 379, 338, 323, 300, 295, 265, 253, 225, 208 (base peak) 192, 179, 165, 149 (Calculated for $C_{23}H_{24}O_7$: MW 412.1520. Found: MW (MS) 412.1512). Methylation of 25 mg of **2b** with excess CH_2N_2 gave the monomethyl ether as a gum (25 mg); NMR (270 MHz, $CDCl_3$), 7.81*d* and 6.61*d* (8, H-11 and H-10), 6.53 and 6.48 (H-1 and H-4), 5.10*tbr* (6.5, H-2'), 4.59*m* (3*p*-deceptively simple looking ABC system of H-6a, H-6ax and H-6eq), 4.50*br* (-OH), 3.87, 3.81, 3.71 (OMe), 3.28*m* (2*p*, H-1'), 1.77 and 1.65 (3*p* each, vinyl Me): MS (*m/z*) 426 (M^+), 408, 379, 365, 341, 328, 314, 292, 290, 279, 256, 236, 219, 208 (base peak), 192.

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FLAVONOL AND DIHYDROFLAVONOL GLYCOSIDES OF *ECHINOCEREUS TRIGLOCHIDIATUS* VAR. *GURNEYI**

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Key Word Index—*Echinocereus triglochidiatus* var. *gurneyi*; Cactaceae; floral flavonoids; dihydroflavonols; flavonols; chemotaxonomy.

Abstract—Perianth parts, in particular, tepals of *Echinocereus triglochidiatus* var. *gurneyi* yielded a complex mixture of dihydroflavonols and dihydroflavonol 7-*O*-glucosides. Dihydroquercetin and its 7-*O*-glucoside were the predominant compounds while dihydrokaempferol and dihydromyricetin and their 7-*O*-glycosides were present in lesser amounts. Quercetin 7-*O*-glucoside was the principal flavonol glycoside: others present were quercetin and kaempferol 3-*O*-glucosides and 3-*O*-rhamnosylglucosides. The epidermis and spines yielded only traces of presumed flavonols as determined by two-dimensional TLC. No flavonoids were detected in the cortex tissue. This is the first report of dihydroflavonol derivatives from the Cactaceae and constitutes the first record of flavonoids from *Echinocereus*.

INTRODUCTION

Echinocereus triglochidiatus Engelmann is a morphologically variable cactus species that occurs over a wide range in south-western North America and parts of Mexico [1]. Several varieties have been described [1,2]. Populations referable to the variety in question here, *E. triglochidiatus* var. *gurneyi* Benson, occur on mountainsides and outwash plains in the northern Chihuahuan Desert and adjacent regions of New Mexico and Trans-Pecos Texas [1]. This is one of the more variable of the claret-cup cacti in terms of stem and flower size.

The distribution of flavonoids among species of Cactaceae is known only cursorily [3,4] although common flavonols; kaempferol, quercetin, and isorhamnetin, have been reported [5–9]. Here we report

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our observations on the flavonoids of *E. triglochidiatus* var. *gurneyi*; a first report of flavonoids from this genus and also the first report of dihydroflavonol derivatives from the Cactaceae.

RESULTS AND DISCUSSION

Analysis of floral tissue (tepals) of *E. triglochidiatus* var. *gurneyi* yielded a mixture of dihydrokaempferol, dihydroquercetin, dihydromyricetin, their corresponding 7-*O*-glucosides; quercetin 7-*O*-glucoside, and kaempferol and quercetin 3-*O*-glucosides and 3-*O*-rhamnosylglucosides (probably the rutinosides). No myricetin glycosides were found. An epidermal and spine extract possessed only traces of presumed flavonols as visualized by TLC screening. No flavonoids were found in cortex tissue.

Bate-Smith [5] reported traces of kaempferol and quercetin in hydrolysed extracts of one species each of *Opuntia* and *Epiphyllum*. Flavonol 3-*O*-glycosides have been reported in several species of *Opuntia* by Rösler *et al.* [6] and by Clark *et al.* [7,8, and refs. cited therein], while Richardson [9] reported kaempferol, quercetin, and isorhamnetin, in various combinations, in hydrolysed extracts of species of *Pereskesia*, *Opuntia*, *Pereskesiopsis*, *Quiabentia*, *Echinopsis*, *Epiphyllum*, and *Mammillaria*.

Our observations of tepal-occurring dihydroflavonols and their 7-*O*-glucosides in *Echinocereus triglochidiatus* var. *gurneyi* represents a possibly useful taxonomic marker. Studies are underway to establish the extent of distribution of these compounds and their biosynthetically related flavonol *O*-glycosides in the genus. It is impossible to assess the significance of the occurrence of quercetin 7-*O*-glucoside, which represents a first report of flavonol 7-*O*-glycosylation in the family, since some earlier studies employed acid hydrolysis before chromatographic analysis [5,9]. A further problem plaguing comparisons at this point is that our work and the several papers on *Opuntia* glycosides [6–8] involved floral tissue, whereas Richardson [9] examined leaf flavonoids. A difficulty in interpreting his meaning arises since, as stated by Benson [2], "Small, fleshy, ephemeral leaves appear on the new joints of the stems of chollas and prickly pears, and well-developed persistent leaves are to be found in the primitive tropical cacti of the genus *Pereskesia*, but most cacti do not have discernable leaves, or leaves are developed only on juvenile stems or at the growing point of the stem and they soon fall away." In dealing with members of Cactaceae it is essential to state clearly the tissue under investigation.

EXPERIMENTAL

Floral tissue was taken from a single plant collected 27 km south of Marathon, Brewster County, Texas (A. M. Powell 3616). Half of the stem was prepared for study of epidermal and spine flavonoids; the other half was pretreated with fluoroacetic acid and dried. The voucher specimen has been deposited in SRSC.

Flavonoids were isolated by means of gel filtration CC on Sephadex LH-20 using MeOH–H_2O. Final purifications were accomplished by prep. polyamide TLC using media and solvent systems described by Wilkins and Bohm [10]. UV data were obtained using the standardized procedures of Mabry *et al.* [11]. Total and partial hydrolyses of the glycosides was done with trifluoroacetic acid at 95 and 20°, respectively. The existence of dihydroflavonols was inferred from the UV spectra, which were characteristic of flavonoids having the reduced heterocyclic ring [11]. Strongly positive tests with magnesium and HCl confirmed this [12]. Boiling the suspected dihydroflavonols with satd aq. Na_2SO_3 for 1–2 hr converted them to the corresponding flavonol derivatives [13] whose identities were established by means of colour reaction with a diphenylboric acid–ethanolamine complex, UV spectral behaviour, and comparison with known compounds. Further confirmation of the structure of dihydromyricetin came from ^1H NMR studies. The ^1H NMR spectrum was identical with that of known dihydromyricetin isolated from *Leptarrhena pyrolifolia* [14].

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