Acid hydrolysis of 1 with 6% HCl at 100° for 2 hr gave yellow crystals of an aglycone (2), mp 236°. When analysed for $C_{17}H_{12}O_{16}$, $[M]^+ = 314$ it was identical with authentic luteolin 7,6'-dimethyl ether (mp, MS, UV and IR). The acetate of 2, mp 185°, was also identical (MS and NMR) with authentic sample [3]. Compound 1 was also methylated and then hydrolysed with 6% HCl to give 5,7,4'-trimethoxy luteolin, mp 220°, UV λ_{max}^{MeOH} nm: 285, 335; + $AlCl_3$: 287, 335; + $AlCl_3$/HCl 287, 335; + NaOAc 285, 335; + NaOAc/H_3BO_3 285, 335; + NaOMe 290, 335. The identity of the sugar was confirmed as glucose by Co-PC with an authentic marker in *n*-butanol–HOAc–H_2O using aniline hydrogen phthalate as detection reagent.

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FLAVONOID AGLYCONES FROM *XANTHOCEPHALUM GYMNOSPERMOIDES* VAR. *GYMNOSPERMOIDES*

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Key Word Index—*Xanthocephalum gymnospermoides* var. *gymnospermoides*; Compositae; Astereae; 5,7,4'-trihydroxy-3,3',5'-trimethoxyflavone.

Abstract—Six known flavonoid aglycones and the newly described 5,7,4'-trihydroxy-3,3',5'-trimethoxyflavone were isolated from *Xanthocephalum gymnospermnoides* var. *gymnospermnoides*.

INTRODUCTION

In 1961, Solbrig recognised eight species for *Xanthocephalum* [1], while Lane (1980) treated the genus as having five species with other taxa being transferred to *Gutierrezia* [2]. As part of our continuing chemical systematics investigation of the '*Gutierrezia–Xanthocephalum* complex' [3–9], we report here the isolation of seven flavonoids from the aerial parts of *Xanthocephalum gymnospermoides* (Gray) B. and H. var. *gymnospermoides*.

RESULTS AND DISCUSSION

Column chromatography and preparative paper chromatography of the material from the dichloromethane and ethyl acetate extracts of a concentrated aqueous methanol extract of the aerial parts of *X. gymnospermoides* var *gymnospermoides* afforded flavonoids 1–7 including one new compound. The new substance is 5,7,4'-trihydroxy-3,3',5'-trimethoxyflavone (1) and the six known compounds are 5,3',5'-trihydroxy-3,7,4'-trimethoxyflavone (2), 5,7,4'-trihydroxy-3',5'-dimethoxyflavone (3), 5,7,4'-trihydroxy-3,3'-dimethoxyflavone (4), 5,3',4'-trihydroxy-3,7-dimethoxyflavone (5), 3,5,7,3',4'-pentahydroxyflavone (6) and 5,7,4'-trihydroxy-3-methoxyflavone (7). The flavonoid chemistry of this taxon is different from that of woody species of *Gutierrezia* [3–6] and the related monotypic *Gymnosperma glutinosum* [9]; these latter taxa produce large quantities of flavonoids with 6,8-oxygenation as well as flavonol 3-methyl ethers with rare 2'-oxygenation. In contrast, the flavonoids isolated from *Xanthocephalum gymnospermoides* var. *gymnospermoides* are similar to those of two herbaceous species of *Gutierrezia*, *G. wrightii* [8] and *G. alamanii* var. *megalocephala* [7], two taxa formerly placed in *Xanthocephalum* [2]. The species investigated here and the latter two species all yielded only a few flavonoids, which all lacked 6,8-oxygenation and 2'-oxygenation. Detailed data are presented only for compound 1.

^{1}H NMR spectrum in carbon tetrachloride of the TMSi ether of 1 showed one two-proton singlet which was assigned to protons at 2' and 6' (δ7.30 ppm) in a symmetrically substituted B-ring and two one-proton doublets at δ6.15 (J = 2.5 Hz) and 6.48 (J = 2.5 Hz) characteristic of H-6 and H-8, respectively [10]. The remaining signals in

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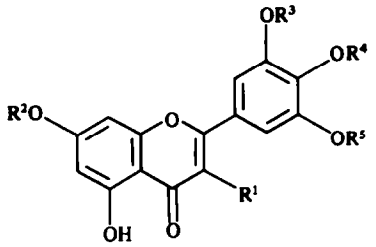
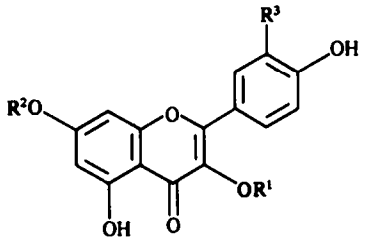


	R^1	R^2	R^3	R^4	R^5
1	OMe	H	Me	H	Me
2	OMe	Me	H	Me	H
3	H	H	Me	H	Me



	R^1	R^2	R^3
4	Me	H	OMe
5	Me	Me	OH
6	H	H	OH
7	Me	H	H

the ^{1}H NMR spectrum were in accord with three methoxyl groups: namely, one six-proton singlet (δ3.88) and one three-proton singlet (δ3.86). Thus, the ^{1}H NMR spectrum established that **1** has a 3,5,7,3',4',5'-oxygenation pattern. The MS of **1** exhibited a molecular ion peak at *m/z* 360 (100%) in accord with an aglycone containing three hydroxyl and three methoxyl groups. Compound **1** appeared as a purple fluorescent spot on paper under UV light and changed to yellow with ammonia, suggesting the presence of free 5 and 4'-hydroxyl groups. With the establishment of the 3,5,7,3',4',5'-oxygenation pattern and to accommodate the symmetrical substituted B-ring, the third hydroxyl group must be at the 7 position, a conclusion supported by UV spectra ($\Delta\lambda$ Band II NaOMe/MeOH relative to Band II MeOH: + 15 nm and the presence of Band III at 322 nm in MeOH + NaOMe and at 325 nm in MeOH + NaOAc). The ^{1}H NMR for the benzene-induced shifts of the methoxyl proton signals of the TMSi ether of **1** supported the methoxyl groups at C-3' and 5': one six-proton singlet at δ3.88 in carbon tetrachloride shifted to one six-proton singlet at δ3.49 in C_6D_6. Thus, the structure of **1** is 5,7,4'-trihydroxy-3,3',4'-trimethoxyflavone.

EXPERIMENTAL

Plant material. Xanthocephalum gymnospermoides (Gray) B. and H. var. *gymnospermoides* was collected on 7 September 1984 from Brewster country, Texas by F. R. Barrie and M. Leidig. Voucher specimens are on deposit in the Plant Resources Center at the University of Texas at Austin (F. Barrie and M. Leidig No. 972).

Isolation of flavonoids. Air-dried aerial parts of *X. gymnospermoides* var. *gymnospermoides* (1.4 kg) were exhaustively extracted in aq. MeOH, first in 85% concn (4 l × 3) followed by 50% concn (4 l × 2). The extracts were combined and evapd under red. pres. until only H_2O remained. The aq. layer was partitioned with CH_2Cl_2 and EtOAc. The CH_2Cl_2 fractions were evaporated to dryness *in vacuo* (yield 93.4 g, dry wt). The material was transferred to a column bearing 600 g of cellulose powder (Merck) and the column was eluted successively with 25% aq. HOAc and 35% aq. HOAc until all the material except the chlorophylls had eluted; the elution was continued until the chlorophylls had moved close to the stopcock of the column. All eluates were combined and evaporated to dryness and the resultant material was chromatographed over a Polyclar AT (GAF Corp) column packed in toluene–MeOH (95:5). Elution of the column was initiated with toluene–MeOH (95:5) gradually increasing in 10% increments to 100% MeOH and finally with Me_2CO–H_2O (1:1). The material in each band (the bands were monitored on the column with UV light) was collected and finally separated by PC, using 15% aq. HOAc or 25% aq. HOAc on Whatman 3 MM paper. The CH_2Cl_2 fraction afforded compounds **1**–**5** and **7**. The EtOAc fraction (24.2 g, dry wt), separated by the same procedure as that used for the CH_2Cl_2 fraction, afforded **6**. Final purification of each compound for spectral analysis was by standard procedures [10] using 75% or 100% aq. MeOH over Sephadex LH-20 columns. Chromatography and spectral analyses were made using standard procedures [10].

Trimethylsilylation. This was done as described in ref. [10].

Data for compound **1**. Colour: UV purple; UV/NH_3 yellow; NA (Naturstoffreagenz A in MeOH) yellow. TLC R_f (on cellulose plates): 0.88 TBA (*t*-BuOH–HOAc–H_2O, 3:1:1), 0.08 15% aq. HOAc. UV λ_{max}^{MeOH} nm: 358, 305sh, 270sh, 253; + NaOMe: 421, 325, 265; + $AlCl_3$: 405, 366sh, 310sh, 280sh, 257; + $AlCl_3$ + HCl: 400, 360, 315sh, 280sh, 255; + NaOAc: 415, 325, 280sh, 268; + NaOAc + H_3BO_3: 361, 305sh, 270sh, 250. MS: *m/z* (rel. int.): 360 $[M]^+$ (100%), 345 $[M-15]^+$ (68%), 317 $[M-43]^+$ (59%), 181 $[B_2]^+$ (5%), 153 $[A_1+1]^+$ (11%). ^{1}H NMR (90 MHz, as TMSi ether in CCl_4, TMS): δ6.15 (1H, *d*, H-6), 6.48 (1H, *d*, H-8), 7.30 (2H, s, H-2' and H-6'), 3.86 (3H, *s*, 3-OMe) and 3.88 (6H, *s*, 3'- and 5'-OMe); ^{1}H NMR (90 MHz, as TMSi ether in C_6D_6, TMS): δ6.50 (1H, *d*, H-6), 6.65 (1H, *d*, H-8), 7.38 (2H, *s*, H-2' and 6'), 3.80 (3H, *s*, 3-OMe) and 3.49 (6H, *s*, 3'- and 5'-OMe); ^{1}H NMR (90 MHz, acetone-d_6, TMS): δ6.26 (1H, *d*, 6-H), 6.50 (1H, *d*, 8-H), 7.50 (2H, *s*, H-2' and 6'), 3.89 (3H, s, 3-OMe) and 3.94 (6H, *s*, 3'- and 5'-OMe).

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SESQUITERPENE ALKALOIDS FROM THE CELASTRACEAE

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Key Word Index—*Orthosphenia mexicana*; *Rzedowskia tolantonguensis*; Celastraceae; sesquiterpene alkaloids; dihydro-β-agarofuran derivative.

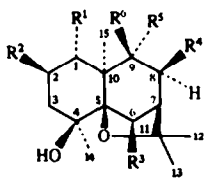
Abstract—The new sesquiterpene alkaloids 1α-benzoyloxy-6β-nicotinoyloxy-9β-acetoxy-4β-hydroxydihydro-β-agarofuran, 1α-cinnamoyloxy-6β-nicotinoyloxy-9β-acetoxy-2β,4β-dihydroxydihydro-β-agarofuran, 1α-benzoyloxy-6β-nicotinoyloxy-8β,9α-diacetoxy-4β-hydroxydihydro-β-agarofuran and 1α-benzoyloxy-6β-nicotinoyloxy-9α-acetoxy-8β,4β-dihydroxydihydro-β-agarofuran were isolated from the aerial part of *Orthosphenia mexicana* and from the root bark of *Rzedowskia tolantonguensis* and their structures determined by spectroscopic and chemical studies.

INTRODUCTION

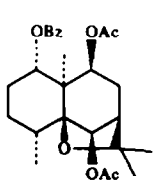
The Celastraceae frequently yield polyester dihydro-β-agarofuran sesquiterpenes [1] and when the ester formation is due to nicotinic acid or its derivatives, these sesquiterpenes are termed Celastraceae alkaloids [2]. From the American Celastraceae, sesquiterpenes [3], diterpenes [3], triterpenes [4] and triterpene quinone methides [5] have been isolated. The alkaloid-containing fractions of *Orthosphenia mexicana* [6] and *Rzedowskia tolantonguensis* [7], plants endemic to north-eastern Mexico, have now been analysed.

RESULTS

Compound 1 was assigned the structure 1α-benzoyloxy-6β-nicotinoyloxy-9β-acetoxy-4β-hydroxydihydro-β-agarofuran based on the following data. It was isolated as a crystalline solid, mp 139–141°, molecular formula $C_{30}H_{35}O_8N$. The IR spectrum showed hydroxyl and ester group bands; the alcohol grouping was tertiary since it could not be acetylated under normal conditions. The mass spectrum suggested the presence of a nicotinate with fragments at *m/z* 124 and 106, a benzoate fragment at *m/z* 105 and an acetate fragment at *m/z* 42 [8]. The ^{1}H NMR spectrum showed signals corresponding to the protons of a nicotinate with the geminal proton at δ 5.66 as a singlet, a benzoate with the geminal proton centred at 5.35 as a double doublet (J = 4.0, 12.0 Hz) an acetate methyl at 1.62 with the geminal proton at 5.08 as a doublet (J = 6.5 Hz) and four angular methyls as singlets at 1.34, 1.41, 1.50 and 1.51. Analysis of the above data character-



	R¹	R²	R³	R⁴	R⁵	R⁶
1	OBz	H	ONic	H	H	OAc
2	OCinn	OH	ONic	H	H	OAc
3	OCinn	OAc	ONic	H	H	OAc
4	OBz	H	ONic	OAc	OAc	H
5	OBz	H	ONic	OH	OAc	H
6	OBz	H	OH	OH	OAc	H
7	OH	H	OH	OH	OH	H
8	OAc	H	OH	OAc	OH	H
10	OCinn	OH	OAc	H	H	OAc



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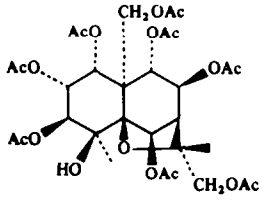

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