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FLAVONOIDS FROM *DALEA SCANDENS* VAR. *PAUCIFOLIA* AND *DALEA THYRSIFLORA**

X. A. Domínguez†, R. Franco†, A. Zamudio†, Dulce María Barradas D.†, W. H. Watson‡, V. Zabel‡ and A. Merijanian§

† Departmento de Química I.T.E.S.M., Monterrey, N. L., México; ‡ FASTBIOS Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, U.S.A.; § Department of Chemistry, William Patterson College, Wayne, NJ 07470, U.S.A.

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Key Word Index—*Dalea scandens* var. *paucifolia*; *D. thyrsiflora*: Fabaceae; flavonoids; louisfieserone; isolouisfieserone; aurentiacin A; alpinetin; mannitol.

INTRODUCTION

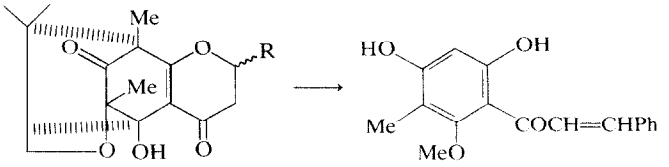
Dalea is a member of the tribe Daleae (Fabaceae) and contains perhaps 250–300 species distributed in the warmer areas of the Americas [1, 2]. Only three species have been studied chemically. *D. emoryi* contains coumarin, 5-methoxycoumarin, dalrubone and methoxydalrubone, while *D. polyadenia* contains 2*S*-demethoxymatteucinol along with the first three compounds [3]. *D. tinctoria* has the same chemical composition as *D. emoryi* [4].

D. scandens var. *paucifolia* and *D. thyrsiflora* are native to Mexico and are reputed to be of medicinal value [5]. Both plants contain essential oils which are rich in mono- and sesquiterpenes. These terpenes will be described elsewhere.

RESULTS AND DISCUSSION

The petrol extract of *D. scandens* var. *paucifolia* was refluxed for 30 min with 20 times its weight of MeOH, and the fractions were separated. Purification of the MeOH-soluble fraction by Si gel chromatograph led to the isolation of sitosterol, the rare isoprenylflavanone louisfieserone [6, 7] (**1a**), mp 217°, $[\alpha]_{589}$ +384.3° and its 2*R*-stereoisomer isolouisfieserone (**1b**). The difference in configuration was established by X-ray diffraction techniques (Watson, W. H. and Zabel, V., unpublished work). Also isolated were the chalcone aurentiacin A (**2**) and alpinetin (**3**). The chalcone gave a negative Shinoda test and a positive $FeCl_3$ test. From the appearance and behavior of the UV spectrum in various media [8] and from the IR spectrum, it was inferred that **2** was a 1,3-dihydroxychalcone with the B-ring unsubstituted. In support of this assignment, the ^{1}H NMR spectrum (δ $CDCl_3$) exhibited two doublet 1H signals at 6.97 and 7.45 (J = 16 Hz each), which were assigned to the *trans* protons of the unsaturated carbon–carbon chain of the chalcone. The remainder of the spectrum exhibited a 5H multiplet at 7.39–7.55, a 1H singlet at 6.65, and two 3H singlets at 3.78 (OMe) and 2.36 (ArMe). Acetylation of **2** yielded a compound whose ^{1}H NMR spectrum showed additional methyl signals at 1.94 and 2.19. The MS spectrum of **2** gave ions at 284 (M^+), 207 ($M-C_6H_5$), 181 ($M-CC{=}CHC_6H_5$), and 131 ($M-OCCH{=}CH{-}C_6H_5$). On the basis of chemical and spectral data and on biogenetic grounds, the compound was assigned structure **2**. This is identical to the structure proposed for aurentiacin A isolated from *Didymocarpus aurentiaca* (Gesneriaceae) [9].

A compound with M^+ = 270 ($C_{16}H_{14}O_4$), colorless needles, mp 216°, exhibited IR, ^{1}H NMR and color reactions identical to alpinetin (5-methoxy-7-hydroxyflavanone). Mass fragmentation patterns, mmp and co-TLC with an authentic sample confirmed the identification.



1a R = α-Ph
1b R = β-Ph

2

The petrol extract of *D. thyrsiflora* afforded louisfieserone, isolouisfieserone and sitosterol. Mannitol was isolated from the methanol extracts of both *Dalea* species.

* Part XXXVIII in the series "Mexican Medicinal Plants". For Part XXXVII see Dominguez, S. A., Franco, R. O., Cano, G. O., Gonzalez, A. G., Pugliese, O. C., Domínguez, M. A. and Aldofo Sanchez, G. (1979). *Rev. Latinoam. Quim.* **10**, 94.

EXPERIMENTAL

^{1}H NMR: δ values, TMS as int. standard; mps uncorr.; optical rotation: $CHCl_3$; MS: DuPont 490, 70 eV. Elemental analyses were performed in the laboratory of Dr. H. Mallissa, Mulheim, Germany. Flowering plants of *D. scandens* var. *paucifolia* were collected in December 1977, in Tlalexcoyan, Ver., voucher specimen 7609. *D. thyrsiflora* was collected in May 1978, around Monterrey, N.L., voucher specimen 7253B. Dried, coarsely milled plants of *D. scandens* var. *paucifolia* (860 g) and *D. thyrsiflora* (732 g) were separately Soxhlet-extracted with petrol followed by MeOH. The petrol extract was refluxed for 30 min with 20 times its weight of MeOH. The MeOH layer was separated and the MeOH was evapd. The residue was subjected to CC and the fractions subjected to prep. TLC. Louisfieserone (**1a**), sitosterol and alpinetin were identified by their IR, ^{1}H NMR, MS spectra and comparison with authentic samples (TLC, mp, mmp, co-TLC and by prepn of derivatives). The petrol extract (60 g) from *D. scandens* yielded 123 mg louisfeiserone (**1a**), 43 mg sitosterol and 60 mg isolouisfieserone (**1b**). $C_{22}H_{24}O_5$, mp 178°, IR(KBr) cm^{-1}: 3389 (OH), 1720 (carbonyl), 1618 (C=C—CO), 1379, 1365. UV (EtOH) nm: 213 (ε 29 100), 285 (24 300), 330 (1000). MS *m/e* (%): 368 (M^+, 12) 340 (M − CO, 29), 325 (M − CO—Me, 27), 221 (67), 203 (29), 98 (100), 77 (15).

$$[\alpha]_{28}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436}{+213 \quad +230 \quad +291 \quad +1015} (c = 2.0).$$

Anal. Calc. for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.60; H, 6.39%. The residue from the MeOH extract (60.36 g) was partitioned in $CHCl_3$–H_2O and the $CHCl_3$ portion was evapd to yield 37.3 g of residue. The residue, (3 g), placed on a Si gel column using mixtures of C_6H_6–Me_2CO as eluents, yielded 15 mg aurentiacin A, 30 mg alpinetin and 35 mg mannitol.

Aurentiacin A (**2**). Yellowish-orange needles, mp 202°, IR (KBr) cm $^{-1}$: 3125 (OH), 3016, 2941, 1666 (C=O), 1639 (C=COO), 1538, 1123, 869, 800. MS: *m/e* (%): 284 (M^+, 52), 207 (M − Ph), 181 (M − PhCHCH, 40), 130 (60). Anal. Calc. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.67; H, 5.53%. Aurentiacin A diacetate, mp 138°. ^{1}H NMR: 1.94 (*s*, 3H), 2.19 (*s*, 3H), 2,36 (*s*, 3H), 3.78 (*s*, 3H), 6.65 (*s*, 1H), 6.97 (*d*, *J* = 16, 1H), 7.45 (*d*, *J* = 16, 1H), 7.39–7.55 (*m*, 5H).

Alpinetin. Solid, mp 216°, $C_{16}H_{14}O_4$. IR (KBr) cm^{-1}: 3508 (OH), 1652 (ArCO), 1612, 1183, 843, 775. UV (MeOH) nm: 227 (ε 9850), 285 (9920). ^{1}H NMR: 2.69 (*q*, 1H), 2.97 (*q*, 1H), 3.81 (*s*, OMe), 5.42 (*q*, 1H), 6.06 (*q*, 1H), 7.4 (*m*, 5H). MS *m/e* (%): 270 (M^+, 100) 193 (30), 166 (98), 138 (30). From the H_2O-soluble portion of the MeOH extract, 35 mg mannitol, mp 167°, were isolated. The optical rotation, mmp, co-TLC, IR and MS were in agreement with an authentic sample. *D. thyrsiflora* was extracted by the same procedure as *D. scandens*. From 3 g of the MeOH-soluble portion of the petrol extract, 225 mg louisfieserone, 118 mg isolouisfieserone and 85 mg sitosterol were isolated. The MeOH extract yielded 825 mg mannitol.

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