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SESQUITERPENE LACTONES, FLAVONOIDS AND ANTHRAQUINONES FROM *ASPHODELINE GLOBIFERA* AND *ASPHODELINE DAMASCENA*

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Key Word Index—*Asphodeline globifera*; *Asphodeline damascena*; Liliaceae; acetoxyeudesmanolides; flavonoids; anthraquinones.

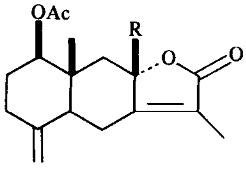
Abstract—The known compounds chrysoeriol, apigenin, luteolin, acacetin, scutellarein, 6-methoxyluteolin, apigenin 7-glucoside, luteolin 7-glucoside, esculetin, chrysophanol, asphodeline, mircocarpin, sitosterol, 1-β-acetoxyeudesman-4(15),7(11)-dien-2α,12-olide and 1-β-acetoxy-8β-hydroxyeudesman-4(15),7(11)-dien-8α,12-olide were isolated from *Asphodeline globifera* and *A. damascena*. A new sesquiterpene lactone 1-β-acetoxy-8β-ethoxyeudesman-4(15),7(11)-dien-8α,12-olide was also characterized. These are the first reports of sesquiterpene lactones in *Asphodeline* and in the Liliaceae.

INTRODUCTION

The genus *Asphodeline* Reichb. (Liliaceae) is represented by 14 species distributed in the Mediterranean area, five of which are endemic to Turkey [1, 2]. From the ethanolic extracts of the aerial parts of *Asphodeline globifera* J. Gay ex Baker and *A. damascena* (Boiss) Baker subsp. *damascena* we have obtained flavonoids, anthraquinones and sesquiterpene lactones. Previously anthraquinones [3–5], triterpenes and steroids [6] were reported from other *Asphodeline* species. This is the first chemical investigation of these two species.

RESULTS AND DISCUSSION

We have isolated two known and a new sesquiterpene lactone 1β-acetoxy-eudesman-4(15),7(11)-dien-8α,12-olide (**1**), 1β-acetoxy-8β-hydroxy-eudesman-4(15),7(11)-dien-8α,12-olide (**2**) [7] and 1β-acetoxy-8β-ethoxy-eudesman-4(15),7(11)-dien-8α,12-olide (**3**) from the ethanolic extracts of *A. globifera* and *A. damascena*. Both species also yielded sitosterol, chrysophanol, esculetin, apigenin, luteolin and chrysoeriol. In addition *A. globifera* yielded apigenin 7-glucoside, luteolin 7-glucoside, 6-methoxyluteolin, scutellarein and acacetin while *A. damascena* yielded two dimeric anthraquinones asphodeline and microcarpin. The known and new compounds were identified by spectral methods, by hydrolysis and, except for **3**, by direct comparison with authentic samples.



1 R = H
2 R = OH
3 R = OEt

The new compound (**3**) was assigned the composition $C_{19}H_{26}O_5$ on the basis of mass spectrometry ($[M]^+$, *m/z* 334, 50%). Its IR spectrum showed the lactone band at 1760 cm^{-1}, acetyl bands at 1730, 1235 cm^{-1} and unsaturation at 1690, 1645 cm^{-1}; no hydroxyl band was present. Its ^1H NMR spectrum confirmed the presence of an acetyl group at δ2.05 (3H, *s*) and showed an ethoxyl group methyl signal at 1.19 (3H, *t*, $J = 7$ Hz) and methylene proton signals at 3.25 (1H, *ddd*, $J = 9$, 7 and 2 Hz) and at 3.50 (1H, *dd*, $J = 7$, 11 Hz). Spin decoupling experiments showed the interrelation between methyl and methylene protons of the ethoxyl group. All other peaks were similar to those of **2** [7]. The MS of **3** exhibited the splitting peaks of ethoxyl (*m/z* 288) and acetoxyl (*m/z* 274) groups among other peaks. The new compound may be an artifact, probably formed during extraction of the plant material with ethanol.

EXPERIMENTAL

Asphodeline globifera was collected from Kayseri (Central Turkey) and *A. damascena* from Ankara; they were identified by one of us (E.T.) and voucher specimens ISTE 37682 and ISTE 45555 are deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul.

Isolation and characteriztion of the compounds. Air dried and powdered leaves and fruits of *Asphodeline globifera* (250 g) and *A. damascena* (160 g) were extracted separately with EtOH at room temp. After filtration, the extracts were concd *in vacuo* and subjected to CC over Polyclar (4 × 50 cm) column, eluting with $CHCl_3$–EtOH (2:1). The first fractions which contained anthraquinones were re-fractionated over a silica gel column (4 × 50 cm). Flavonoids were obtained from the later fractions of Polyclar column and were cleaned upon Sephadex LH-20. While separating anthraquinones, sesquiterpene lactones and sitosterol were also isolated. Compounds **1**–**3** were further purified on prep. TLC plates; anthraquinones were crystallized from EtOH. The spectral data including ^{13}C NMR for **1** and **2** are given in ref. [7]. Compound **3**: Yield 7 mg and 6 mg respectively, amorphous. UV λ_{max}^{EtOH}: 220 nm (log ε4.30); IR ν_{max}^{KBr} cm^{-1}: 2920, 1760, 1730, 1690, 1645, 1620, 1435, 1370, 1235, 1175, 1080, 1030, 960.

^{1}H NMR ($CDCl_3$): δ4.9 (1H, *br s*, H-15), 4.68 (1H, *br s*, H-15′), 4.62 (1H, *dd*, $J = 5$ and 11 Hz, H-1), 3.5 (1H, *dd*, $J = 7$ and 11 Hz, –O–$\underline{H}$CH–Me), 3.25 (1H, *ddd*, $J = 2$, 7 and 9 Hz, –O–HC$\underline{H}$–Me), 2.67 (1H, *dd*, $J = 3$ and 11 Hz, H-6), 2.53 (1H, *d*, $J = 15$ Hz, H-9), 2.35 (1H, *dd*, $J = 10$ and 12 Hz, H-6′), 1.40 (1H, *d*, $J = 15$ Hz, H-9′), 2.05 (3H, *s*, OAc), 1.86 (3H, *d*, $J = 2$ Hz, H-13), 1.19 (3H, *t*, $J = 7$ Hz, $OCH_2C\underline{H}_3$). MS (probe) 70 eV, *m/z* (rel. int.): 334 $[M]^+$ (50), 288 $[M - EtOH]^+$ (4), 274 $[M - AcOH]^+$ (5), 246 $[M - AcOH - C_2H_4]^+$ (57), 229 $[M - AcOH - OC_2H_5]^+$ (20), 201 $[229 - CO]^+$ (38), 173 $[201 - CO]^+$ (50).

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