Decahydrorhodophytin **3**. (A) From *Z*-dihidrorodophytin **1**. Catalytic hydrogenation of **1** for 30 min gave the decahydro derivative **3** in 95% yield after chromatography (5% *n*-hexane–EtOAc), oil; $[\alpha] = +18°$ ($CHCl_3$; *c* 0.23). IR ν^{CHCl_3} 3000, 2965, 1460, 1340 and 1070 cm^{-1} ^1H NMR ($CDCl_3$) δ: 1.05 (3H, *t*, $J = 7.2$ Hz); 1.67 (*m*, 18H); 4.03 (*m*, 4H). MS: $[M]^+$ at *m/z* (rel. int.): 338, 340, 342 $[M]^+$ (2); 260, 262 $[M - Br]^+$ (7); 217, 219 $[M - C_3H_6Br]^+$ (4).

(B) From *trans*-dihydrorhodophytin **2**. Hydrogenation of **2** for 1 hr in the same manner as described above for **1** gave in 92% yield the octahydro derivative **3**: oil, $[\alpha] = +17.5°$ ($CHCl_3$; *c* 0.11). IR, NMR and MS were as described in (A) above.

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OXEPINE DERIVATIVES AND ANTHRAQUINONES FROM *ASPHODELINE TENUIOR* AND *A. TAURICA*

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Key Word Index—*Asphodeline tenuior*; *A. taurica*; Liliaceae; anthraquinones; eudesmanolide; oxepine derivatives.

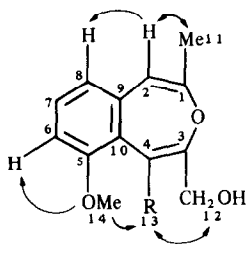
Abstract—From the chloroform extracts of *Asphodeline taurica* and *A. tenuior* anthraquinones chrysophanol, asphodeline and microcarpin as well as β-sitosterol, sitosteryl 3β-glucoside were isolated. In addition, *A. taurica* yielded an eudesmanolide 1β-acetoxy-8β-hydroxy-eudesman-4(15),7(11)-dien-8α,12-olide, while aleoemodin and two new oxepine derivatives, tenual and tenucarb, were obtained from *A. tenuior*.

In a continuation of our chemical studies with *Asphodeline* species [1, 2] we have now investigated *A. taurica* (Pallas) Kunth and *A. tenuior* (Fisher) Ledeb. subsp. *tenuiflora* (C. Koch) E. Tuzlacı var. *puberulenta* E. Tuzlacı. These two species are placed in different sections (Appendicigera E. Tuzlacı and Asphodeline respectively) which were recently described [3]. *A. tenuior* subsp. *tenuiflora* var. *puberulenta* is an endemic taxon in Turkey.

In our previous studies with *A. globifera*, *A. damascena* [1] and *A. anatolica* [2] (Sect. Appendicigera) we have obtained eudesmanolides in addition to anthraquinones. In the present study with *A. taurica* from the same section we have obtained a eudesmanolide 1β-acetoxy-8β-hydroxy-eudesman-4(15),7(11)-8α,12-olide in addition to anthraquinones chrysophanol, asphodeline and microcarpin as well as β-sitosterol and sitosteryl 3β-glucoside, while *A. tenuior* (Sect. Asphodeline) yielded aleoemodin and two new oxepine derivatives tenual and tenucarb in addition to the above compounds with the exception of the eudesmanolide.

The high resolution mass spectrum of tenual (**1**) gave a molecular ion peak at *m/z* 246.08921 indicating a molecular formula $C_{14}H_{14}O_4$. The UV spectrum of **1** at 336, 312, 298, 283, 259, 230 nm indicated a conjugated aromatic system which was correlated with the IR peaks at 3050, 1584, 1555, 1520 cm^{-1}. The presence of hydroxyl (3420 cm^{-1}) and aldehyde (1710 cm^{-1}) group were indicated by the same spectrum. ^1H NMR spectrum showed three adjacent aromatic proton peaks at δ7.38 (1H, *t*, $J = 8$ Hz, H-8), 6.79 (1H, *br d*, $J = 8$ Hz, H-6) and at δ7.12 (1H, *d*, $J = 8$ Hz, H-2). Other peaks showed the presence of an aldehyde group at δ9.96 (1H, s, CHO), a methoxyl group at δ4.09 (3H, *s*, OMe), an aromatic methyl at δ2.42 (3H, *d*, $J = 0.8$ Hz, Me) and a hydroxymethylene group at δ4.77 (2H, *br s*, CH_2OH) and at δ1.57 (1H, *br s*, OH) (D_2O exchange). The fourth oxygen function must be ether; this was correlated with its IR peaks at 1270, 1240, 1068 and 1035 cm^{-1}.

The positions of the functional groups were decided by NOE experiments and by the ^{13}C NMR spectrum. Since the ^1H NMR spectrum of **1** showed three adjacent aro-



R = CHO
R = COOMe[15]

matic protons, one of the substituents must be at C-5 in the aromatic ring. In the ^{13}C NMR spectrum there were four doublets, all in the lower field, only one was at δ104.4 indicating that it should be next to the methoxyl group [4]. Irradiation of the OMe caused NOE with H-6 (at δ6.79) confirming that the methoxyl group is at C-5. The same irradiation caused NOE also with the aldehyde group. Irradiation CHO caused NOE with the hydroxymethylene group indicating that the aldehyde group must be between the OMe and CH_2OH groups. Irradiation of the CH_2OH group caused NOE with the aldehyde group, therefore it must be situated at C-3 next to the ether function. Irradiation of the aromatic methyl caused NOE only with H-2 (at δ7.12), while irradiation of H-2 caused NOE both with Me (at δ2.42) and with H-8 (at δ7.31) indicating that Me must be at C-1. The shifts of ^{13}C NMR were in agreement with the suggested structure (Table 1).

The molecular ion peak of **2** at *m/z* 276, together with elemental analysis indicated a composition $C_{15}H_{16}O_5$. The UV and IR spectra of **2** were quite similar to those of **1** except the peak at 1720 cm^{-1} indicated the carboxymethyl group. The ^1H NMR spectrum showed three adjacent aromatic proton peaks at δ7.42 (1H, *dt*, $J = 8$ Hz and 1.5 Hz, H-7), 7.35 (1H, *dd*, $J = 8$, and 1.5 Hz, H-8), 6.80 (1H, *dd*, $J = 8$ and 1.5 Hz, H-6). At δ4.02 (3H, *s*, OMe), 6.92 (1H, *d*, $J = 0.8$ Hz, H-2), 2.38 (3H, *d*, $J = 0.8$ Hz, Me), at δ4.66 (2H, *br s*, CH_2OH) and at δ1.60 (1H, *br s*, CH_2OH) (D_2O exchange), at δ3.78 (3H, *s*, COOMe). ^{13}C NMR showed the carboxyl group at δ169.1 and the methyl of the carboxymethyl group at δ38.7; other peaks are in agreement with the suggested structure (Table 1).

EXPERIMENTAL

Asphodeline taurica and *A. tenuior* subsp. *teniflora* var. *puberulenta* were collected from eastern Turkey (Sivas) in July 1986. They were identified by one of us (Dr Ertan Tuzlacı) and voucher specimens were deposited in the Herbarium of the Faculty of Pharmacy, University of Marmara (Istanbul) (Mare 422 and 513) respectively. Dried and powdered whole plants *A. taurica* (1 kg) and *A. tenuior* (750 g) were extracted in Soxhlets with $CHCl_3$; 37 and 29 g residues were obtained respectively. The residues (20 g of each) were fractionated on silica gel columns (4 × 60 cm). The fractions were further separated and cleaned on prep. TLC plates (Merck). The main compounds of *A. taurica* were chrysophanol (350 mg) and microcarpin (150 mg), others were asphodeline (15 mg), eudesmanolide (4.5 mg). In *A. tenuior* chrysophanol (300 mg) and asphodeline (250 mg) were the main compounds, others were microcarpin (5 mg), aleoemodin (12 mg) and the new oxepine derivatives **1** (16 mg) and **2** (10 mg).

General ^1H NMR, 200–400 MHz; ^{13}C NMR, 50.323 MHz.

Table 1. ^{13}C NMR data of tenual (**1**) and tenucarb (**2**)

C	1	2
1	137.8	139.1
2	127.9	128.8
3	154.8	155.1
4	135.6	139.0
5	154.8	154.9
6	104.4	105.7
7	120.4	120.4
8	121.2	120.4
9	137.3	128.8
10	137.6	139.1
11	20.7	19.1
12	70.0	68.1
13	205.0	169.1
14	56.3	56.0
15	—	38.7

Tenual (**1**) UV λ_{max}^{ether} nm: 336 (log ε 3.6), 312 (log ε 3.5), 298 (log ε 3.7), 259 (log ε 4.2), 230 (log ε 4.7). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 3050, 2960, 1710, 1625, 1584, 1555, 1520, 1488, 1450, 1425, 1390, 1360, 1270, 1240, 1180, 1160, 1098, 1068, 1035, 975, 945, 840, 760. ^1H NMR ($CDCl_3$, TMS) given in the text. ^{13}C NMR given in Table 1. MS *m/z* (rel. int.): 246 $[M]^+$ ($C_{14}H_{14}O_4$) (11), 228 $[M-H_2O]^+$ (10), 215 $[M-CH_2OH]^+$ (100), 200 $[215-Me]^+$ (32), 172 $[200-CO]^+$ (6).

Tenucarb (**2**). UV λ_{max}^{ether} nm: 331 (log ε 3.4), 312 (log ε 3.4), 302 (log ε 3.7), 259 (log ε 4.2), 236 (log ε 4.8). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 3090, 1720, 1630, 1580, 1510, 1450, 1430, 1380, 1250, 1180, 1155, 1080, 1060, 1030, 975, 940, 850, 760. ^1H NMR ($CDCl_3$, TMS) given in the text. ^{13}C NMR given in Table 1. MS *m/z* (rel. int.): 276 $[M]^+$ ($C_{15}H_{16}O_5$) (14), 229 $[M-CH_2OH-CH_2]^+$ (100), 214 $[229-Me]^+$ (8), 186 (20). (Found: C, 65.24; H, 5.81. Calc. for $C_{15}H_{16}O_5$: C, 65.21; H, 5.79%).

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