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SESQUITERPENE LACTONES FROM THE FRUITS OF *SMYRNIUM CONNATUM*

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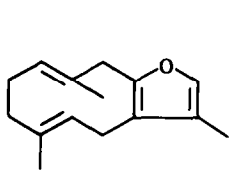
Key Word Index—*Smyrnium connatum*; umbelliferae; fruits; sesquiterpene lactones.

Abstract—A new sesquiterpene lactone, 1β,8-dihydroxyeremophila-3,7(11)dien-8,12-olide, was identified in the fruits of *Smyrnium Connatum*, along with five known lactones.

In a previous study with the aerial parts of *Smyrnium connatum* (Boiss.) Kotschy (Umbelliferae) an eremophilenolide, istanbulin C [1] was isolated. In a further study with the fruits of the same plant we have obtained furodiene (**1**) [2] and some known sesquiterpene lactones which have previously been obtained from other *Smyrnium* species, 1β-acetoxy-eudesma-4(15), 7(11)-dien-8α,12-olide (**2**) [3], 1β-acetoxy-8β-hydroxyeudesma-4 (15),7(11)-dien-8α,12-olide (**3**) [3], 1β,10α-epoxy-4-methoxyglechomanolide (**4**) [4] 1β,10α-epoxy-4-methoxy-8-hydroxyglechomanolide (**5**) [4] and istanbulin D (**6**) [5]. In addition we have isolated a new sesquiterpene lactone 1β,8-dihydroxyeremophila-3,7(11)dien-8,12-olide which was found to be an isomer of istanbulin D and was named istanbulin F (**7**). The identification of the known compounds was established by spectral data and by thin layer chromatographic comparison with authentic samples.

The IR spectrum of **7** showed the presence of hydroxyl group(s) (3400 cm^{-1}), an α,β-unsaturated-γ-lactone (1740 cm^{-1}) and unsaturation (1680 cm^{-1}). The ^1H NMR indicated the presence of three methyl groups at δ1.22 (*s*, H-14), 1.77 (*s*, H-15) and 1.74 (*s*, H-13). The chemical shift of H-14 is considered an evidence for *cis* annelation of rings A and B [6, 7]. A broad singlet at δ5.3 showed the vinylic hydrogen at C-3. The lack of a lactone



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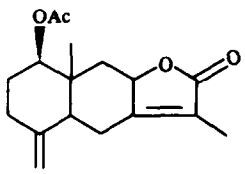

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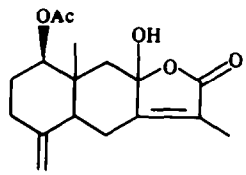

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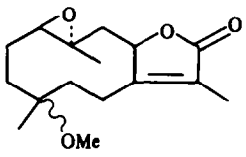

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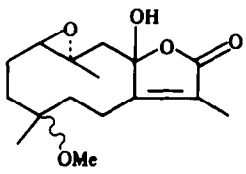

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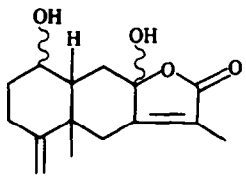

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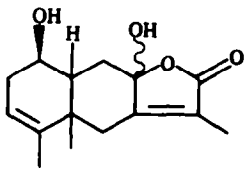

7

proton indicated a hydroxyl group at C-8. The double doublet at δ3.485 showed a second hydroxyl sited at C-1. The stereochemistry at C-1 was observed from coupling constants between H-1 and H-2, H-2' ($J_{1\alpha,2\alpha} = 11.5$ Hz, $J_{1\alpha,2e} = 4$ Hz, H-1α) and by studying a Dreiding model. In the mass spectrum the molecular ion peak at m/z 264 indicated the molecular formula $C_{15}H_{20}O_4$.

Istanbulin F (7). Colourless, amorphous. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 2980, 2850, 1740, 1680, 1450, 1380, 1100, 1050, 880. ^{1}H NMR (Bruker 400 MHz, $CDCl_3$) given in the text. MS (Varian MAT 311) 264 $[M]^+$ ($C_{15}H_{20}O_4$) (53), 246 $[M-H_2O]^+$ (75), 228 $[246-H_2O]^+$ (51), 213 $[228-Me]^+$ (54), 107 $[C_7H_7O]^+$ (40), 105 $[C_7H_5O]^+$ (68), 91 $[C_7H_7]^+$ (70), 43 (100).

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EXPERIMENTAL

The fruits of *Smyrnium connatum* were collected from Eğridir-Isparta (south western Turkey) in July 1985 by one of us (N.G) (a voucher is deposited in the Herbarium of Faculty of Pharmacy, University of Istanbul, ISTE 26209). Dried and powdered fruits of *S. connatum* (500 g) were extracted with Et_2O–petrol (1:2) at room temp. The extract was filtered and evapd under vacuum without heating. The residue was treated with hot MeOH and heated, the soln was cooled for 2 hr to ppt. the long chain saturated hydrocarbons. The MeOH filtrate was evaporated to dryness and roughly separated on a Si gel column, eluting with petrol, a gradient of Et_2O (to 100%) and MeOH (to 100%). The fractions were further separated and cleaned by prep. TLC; 20 mg **1**, 2 mg **2**, 3 mg **3**, 43.5 mg **4**, 18 mg **5**, 26 mg **6** and 25 mg **7** were obtained.

REFERENCES

1. Ulubelen, A., Ates, N. and Nishida, T. (1979) *Phytochemistry* **18**, 338.
2. Hikino, N., Agatsuma, K. and Takemodo, T. (1968) *Tetrahedron Letters* 931.
3. Ulubelen, A., Gören, N., Bohlmann, F., Jakupovic, J., Grenz, M. and Tanker, N. (1985) *Phytochemistry* **24**, 1305.
4. Gören, N., Ulubelen, A., Jakupovic, J., Bohlmann, F. and Grenz, M. (1984) *Phytochemistry* **23**, 2281.
5. Ulubelen, A. and Abdolmaleky, H. (1982) *Phytochemistry* **21**, 2128.
6. Samek, Z., Harmatha, J., Novotny, L. and Sorm, F. (1969) *Collect. Czech. Chem. Commun.* **34**, 2792.
7. Bohlmann, F., Förster, H. J. and Fisher, C. H. (1976) *Just. Liebigs Ann. Chem.* 1487.