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OXEPINE DERIVATIVES FROM THE ROOTS OF *SMYRNIUM ROTUNDIFOLIUM*

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Key Word Index—*Smyrnium rotundifolium*; Umbelliferae; eudesmanolides; oxepine derivatives.

Abstract—Besides the known eudesmanolides and oxepine derivatives we have isolated two new oxepine type sesquiterpene lactones from the roots of *Smyrnium rotundifolium*. The new compounds were smyrnicordi-8-enolide and isosmyrnicordiolide, its stereochemistry at C-8 and C-10 could not be established.

INTRODUCTION

Previously we have isolated two eudesmanolides and two oxepine derivatives from the fruits of *Smyrnium cordifolium*. In this study in addition to above compounds two oxepine derivatives were obtained from the roots of *Smyrnium rotundifolium*. The structure of the new and known compounds were established by spectral methods.

RESULTS AND DISCUSSION

Ether–petrol extracts of the roots of *Smyrnium rotundifolium* afforded the known compounds 1β-acetoxy-8β-hydroxyeudesmen-4(15),7(11)-dien-8α,12-olide (**1**), smyrnicordiolide (**2**), 8β-hydroxysmyrnicordiolide (**3**) [1] as well as two new oxepine derivatives smyrnicord-8-enolide (**4**) and an isosmyrnicordiolide (**5**). The known compounds were identified by comparing their spectra to those of compounds as well as by TLC comparison with authentic samples.

The IR spectrum of compound **4** exhibited the presence of a γ-lactone (1770 cm^{-1}) and unsaturation (1650, 1670 cm^{-1}). The structure of compound **4** was established by ^1H NMR and mass spectrometry. Its ^1H NMR spectrum was very similar to that of smyrnicordiolide (**2**), except that while the peaks at δ2.345 *dd* (H-9), 1.055 *t* (H-9′) and 4.77 *br dd* (H-8) were lacking, there was an extra vinylic proton at 5.62. Together with the molecular ion peak at *m/z* 244 ($C_{15}H_{16}O_3$) these indicated the presence of another double bond in the molecule which could be only at C-9. The alternating position for the third double bond could be at C-5, in this case the H-9 and H-9′ and H-8 protons should be observed and its UV spectrum should exhibit a longer conjugation.

The IR spectrum of compound **5** showed a γ-lactone (1750 cm^{-1}) and unsaturation (1650, 1675 cm^{-1}). The mass spectrum exhibited a molecular ion peak at *m/z* 246 indicating that the molecular formula was $C_{15}H_{18}O_3$. The ^1H NMR spectrum of compound **5** was similar to that of smyrnicordiolide (**2**), however there were a few differences which helped to decide the structure of compound **5**. In compound **2** H-1 was at δ4.41 *dd*, *J* = 7, 2.5 Hz; H-8 at 4.77 *dd*, *J* = 12.5, 6 Hz and H-2 at 6.15 *d*, *J* = 7.5 Hz whereas in compound **5** these protons were at 4.29 *d*, *J* = 7 Hz, (H-1), 4.97 *tt* (H-8) and 5.92 *br d* (H-2). Due to the small amount of material available it was not possible to establish its stereochemistry at C-8 and C-10 although **5** may be an epimer of **2**.

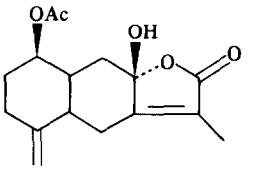
EXPERIMENTAL

Smrynium rotundifolium was collected from the western section of Turkey (Izmir). A voucher ISTE 19055 is deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul. Dried and powdered roots of *Smyrnium rotundifolium* (680 g) were extracted with Et_2O–petrol (1:2) and the extract was treated with MeOH to remove long chain saturated hydrocarbons, the

Table 1. ^1H NMR spectral data of compounds **2**, **4** and **5** (400 MHz, $CDCl_3$, TMS as internal standard)

H	2	4	5
1	4.41 *dd*	4.44 *dd*	4.294 *br d*
2	6.154 *d*	6.03 *d*	5.92 *br d*
3	6.195 *q*	6.22 *q*	6.195 *q*
5	1.80 *dddd*	2.24 *br d*	2.48 *m*
6	2.798 *dd*	2.79 *dd*	2.755 *m*
6′	2.59 *br d*	2.71 *ddd*	
8	4.77 *br d*	—	4.925 *tt*
9	2.345 *dd*	5.62 *s*	2.208 *dd*
9′	1.055 *t*	—	1.662 *dd*
13	1.817 *t*	1.88 *d*	1.78 *br s*
14	1.232 *s*	1.38 *s*	1.22 *s*
15	1.715 *d*	1.74 *d*	1.72 *d*

J (Hz). Compound **2**: 1, 2 = 8; 1, 8 = 1.2; 3, 15 = 1.5; 6, 6′ = 15; 5, 6 = 14; 5, 6′ = 4.5; 6, 8 = 1.5; 8, 9 = 6; 8, 9′ = 12.5. Compound **4**: 1, 2 = 7.5; 1, 9 = 2; 5, 6 = 12.5; 5, 6′ = 5; 6, 6′ = 18; 6, 13 = 1.5; 3, 15 = 1.5. Compound **5**: 1, 2 = 7.5; 3, 15 = 1.5; 8, 9 = 9.5; 8, 9′ = 7.5; 8, 14 = 1.5; 9, 9′ = 15.



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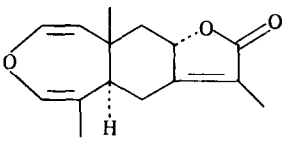

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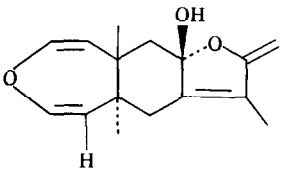

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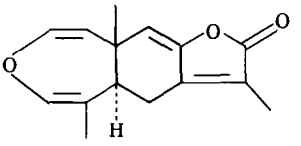

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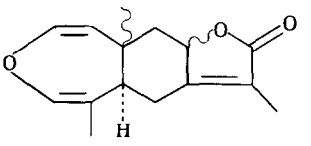

5

residue was roughly separated by CC (silica gel), then the fractions were further separated by TLC. Thus 4 mg **1**, 5 mg **2**, 94 mg **3**, 2 mg **4** and 1 mg **5** were obtained.

Spectra were recorded with the following instrument: IR, Perkin–Elmer 577; MS, Varian MAT 721, 70 eV; ^{1}H NMR, Bruker WM 400 MHz.

Compounds **1–3**. The spectral data were given in ref. [1].

Smyrnicordi-8-enolide (**4**). Amorphous, colourless compound. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2910, 2850, 1770, 1680, 1650, 1450, 1375, 1280, 1110, 1010, 865, 750. ^{1}H NMR (400 MHz, $CDCl_3$): see Table 1. MS *m/z* (rel. int.): 244.1089 $[M]^+$ ($C_{15}H_{16}O_3$) (67), 229 $[M-Me]^+$ (41), 162 (67), 149 $[C_{10}H_{13}O]^+$ (100).

Isosmyrnicordiolide (**5**). Amorphous, colourless compound. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2910, 2860, 1750, 1675, 1650, 1450, 1110, 1030, 750. ^{1}H NMR (400 MHz, $CDCl_3$): see Table 1. MS *m/z* (rel. int.): 246 $[M]^+$ ($C_{15}H_{18}O_3$) (24), 231 $[M-Me]^+$ (3), 135 $[C_9H_{11}O]^+$ (100), 95 $[C_6H_5O]^+$ (60).

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