

ADDITIONAL SESQUITERPENOIDS FROM THE FRUITS OF  
*SMYRNIUM GALATICUM*

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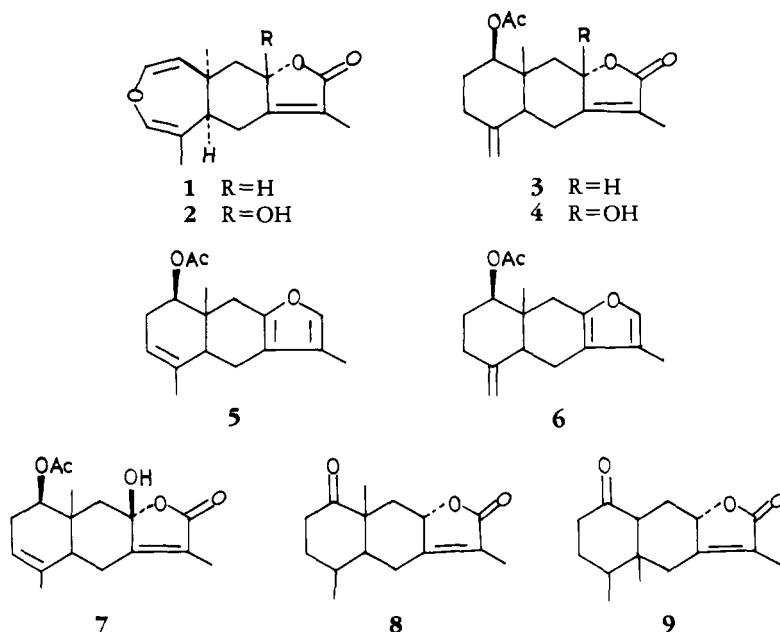
In a previous study of the roots and fruits of *Smyrniium galaticum* Czeczott (Umbelliferae) (1) we isolated two oxepine and two eudesmane-type sesquiterpene lactones: smyrnicordiolid (1), 8-hydroxysmyrnicordiolid (2), 1 $\beta$ -acetoxyeudesma-4(15),7-dien-8,12-olide (3), and 1 $\beta$ -acetoxy-8 $\beta$ -hydroxyeudesma-4(15),7-dien-8,12-olide (4), as well as steroidal and aromatic compounds. In a recent investigation of the fruits of the same plant material we isolated three new eudesmane-type compounds, one of which was a furanoeudesmane and the other two were lactones. All three compounds were the isomers of previously obtained sesquiterpenoids. 1 $\beta$ -Acetoxyeudesma-3,7,11-trien (5) is the isomer of 1 $\beta$ -acetoxyeudesma-4(15),7,11-trien (6) (2); 1 $\beta$ -acetoxy-8-hydroxyeudesma-3,7-dien-8,12-olide (7) is the isomer of (4), and 1-oxoeudesm-7(11)-en-8,12-olide (8) is the isomer of istanbulin B (9) (3,4). During the course of this study we observed the facile oxidation of 5 to 7.

The mass spectrum of 1 $\beta$ -acetoxyeudesma-3,7,11-trien (5) indicated a molecular formula C<sub>17</sub>H<sub>22</sub>O<sub>3</sub> (M<sup>+</sup>, m/z 274). The ir spectrum showed the acetyl peak at 1725 cm<sup>-1</sup>, unsaturation at 1650 cm<sup>-1</sup>, and furan at 880 cm<sup>-1</sup> but no hydroxyl or lactone peaks. The <sup>1</sup>H-nmr spectrum showed two methyl singlets at  $\delta$  1.34 (H-14) and 1.70 (H-15), one methyl doublet at  $\delta$  1.94 ( $J=1$  Hz) (H-13), and the acetyl peak at  $\delta$  2.14. The furan ring proton was observed at  $\delta$  7.08 (H-12) as a broad singlet; the olefinic proton at  $\delta$  5.27 (br d,  $J=11$  Hz, H-3) and another one proton doublet of doublets at  $\delta$  4.92 ( $J=4$  Hz and 11 Hz, H-1 $\alpha$ ) indicated the proton next to the acetyl group. The iso-

lated methylene at C-9 ( $\delta$  2.27, d,  $J=12$  Hz, H-9 and  $\delta$  2.08, d,  $J=12$  Hz, H-9') clearly indicated the suggested structure. The stereochemistry at C-1 was determined by measuring the  $J$  values of H-1 ( $J_{1a,2a}=11$  Hz and  $J_{1a,2e}=4$  Hz) and by studying a Dreiding model.

The mass spectrum of 1 $\beta$ -acetoxy-8-hydroxyeudesma-3,7-dien-8,12-olide (7) indicated a molecular formula C<sub>17</sub>H<sub>22</sub>O<sub>5</sub> (M<sup>+</sup>, m/z 306). The ir spectrum showed hydroxyl at 3450 cm<sup>-1</sup>, lactone carbonyl at 1755 cm<sup>-1</sup>, acetyl carbonyl at 1725 cm<sup>-1</sup>, and unsaturation at 1640 cm<sup>-1</sup>. The structure of 7 was established by the <sup>1</sup>H-nmr spectrum. Two methyl singlets were observed at  $\delta$  1.29 (H-14) and 1.60 (H-15), a methyl doublet at  $\delta$  1.96 ( $J=1$  Hz) (H-13), and a one proton doublet of doublets at  $\delta$  4.97 ( $J=4$  Hz and 11 Hz, H-1 $\alpha$ ) was assigned to the proton geminal to the acetyl group at C-1. Another one proton doublet of doublets at  $\delta$  5.08 ( $J=4$  Hz and 11.5 Hz, H-3) indicated the presence of an olefinic proton at C-3. The lack of a lactone proton and the presence of an isolated methylene group at C-9 ( $\delta$  2.42, d,  $J=12$  Hz, H-9 and 2.08, d,  $J=12$  Hz, H-9') suggested that the hydroxyl group should be at C-8. The stereochemistry at C-1 was decided by measuring the  $J$  values of H-1 ( $J_{1a,2a}=11$  Hz and  $J_{1a,2e}=4$  Hz) and by studying a Dreiding model.

The molecular ion peak at m/z 248 suggested a molecular formula C<sub>15</sub>H<sub>20</sub>O<sub>3</sub> for 1-oxo-eudesm-7(11)-en-8,12-olide (8). The ir spectrum showed a lactone carbonyl at 1750 cm<sup>-1</sup>, a ketone carbonyl group at 1715 cm<sup>-1</sup>, and no hydroxyl peak. The <sup>1</sup>H-nmr spectrum showed two methyl doublets at  $\delta$  1.95 ( $J=1$  Hz) (H-13) and at  $\delta$  0.8



( $J=7$  Hz) (H-15) and a methyl singlet at  $\delta$  0.97 (H-14). The lactone proton was at  $\delta$  4.96 (dd,  $J=5$  Hz and 10 Hz, H-8 $\beta$ ) and the other peaks were between 1.1 and 2.5 ppm. The stereochemistry at C-8 was decided by measuring the  $J$  values for H-8 ( $J_{8a,9a}=10$  Hz and  $J_{8a,9e}=5$  Hz) and by studying a Dreiding model.

## EXPERIMENTAL

**PLANT MATERIAL.**—The same plant material that was used in the previous study (1) was also used here.

**EXTRACTION AND ISOLATION OF THE COMPOUNDS.**—The compounds were extracted by Et<sub>2</sub>O-petrol (1:2) and fractioned from a Si gel column using petrol and a gradient of Et<sub>2</sub>O as elution solvents. The compounds obtained from the column were further purified on preparative tlc plates using petrol for **5** and Et<sub>2</sub>O-petrol (1:1 and 2:1) for **7** and **8**; all reported compounds were homogeneous by tlc in three different solvent systems [C<sub>6</sub>H<sub>6</sub>-Et<sub>2</sub>O (1:1), petrol-Et<sub>2</sub>O (8:2), and petrol]. The spectra were recorded as follows: uv, Varian Techtron model 635; ir, Perkin-Elmer 577; <sup>1</sup>H nmr WM 400 MHz; ms, Varian MAT 711.

**1 $\beta$ -Acetoxyeudesma-3,7,11-trien (5).**—Amorphous, yield 5 mg, Rf (petrol-Et<sub>2</sub>O, 8:2) 0.80; uv  $\lambda$  max (EtOH) 218 nm; ir  $\nu$  max (KBr) 2940, 2860, 1725, 1650, 1460, 1385, 1250, 1120, 1075, 960, 880 cm<sup>-1</sup>; <sup>1</sup>H nmr given in the text; ms  $m/z$  (rel. int.) (M)<sup>+</sup> 274 (C<sub>17</sub>H<sub>22</sub>O<sub>3</sub>) (8), 259

(M-Me)<sup>+</sup> (20), 214 (M-AcOH)<sup>+</sup> (5), 151 (60), 109 (C<sub>7</sub>H<sub>9</sub>O)<sup>+</sup> (48).

**1 $\beta$ -Acetoxy-8-hydroxyeudesma-3,7(11)-dien-8,12-olide (7).**—Amorphous, yield 8 mg, Rf (petrol-Et<sub>2</sub>O, 8:2) 0.25; uv  $\lambda$  max (EtOH) 220 nm; ir  $\nu$  max (KBr) 3450, 2950, 2840, 1755, 1725, 1640, 1450, 1380, 1245, 1100, 1080, 980 cm<sup>-1</sup>; <sup>1</sup>H nmr given in the text; ms  $m/z$  (rel. int.) (M)<sup>+</sup> 306 (C<sub>17</sub>H<sub>22</sub>O<sub>5</sub>) (5), 263 (M-COMe)<sup>+</sup> (5), 246 (M-AcOH)<sup>+</sup> (8), 236 (80), 220 (30), 205 (100), 151 (60), 107 (C<sub>7</sub>H<sub>7</sub>O)<sup>+</sup> (40).

**1-Oxoeadesm-7(11)-en-8,12-olide (8).**—Amorphous, yield 10 mg, Rf (petrol-Et<sub>2</sub>O, 8:2) 0.16; uv  $\lambda$  max (EtOH) 220 nm; ir  $\nu$  max (KBr) 2950, 2860, 1750, 1715, 1640, 1480, 1365, 1100, 1080, 960 cm<sup>-1</sup>; <sup>1</sup>H nmr given in the text; ms  $m/z$  (rel. int.) (M)<sup>+</sup> 248 (C<sub>15</sub>H<sub>20</sub>O<sub>3</sub>) (8), 220 (M-CO)<sup>+</sup> (20), 205 (M-CO-Me)<sup>+</sup> (20), 159 (20), 109 (C<sub>7</sub>H<sub>9</sub>O)<sup>+</sup> (30), 108 (C<sub>7</sub>H<sub>8</sub>O)<sup>+</sup> (70).

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