

LETTERS  
TO THE EDITOR

Reaction of the Sesquiterpene  $\gamma$ -Lactone  $\alpha$ -Santonin  
with Alcoholic Hydrogen Chloride

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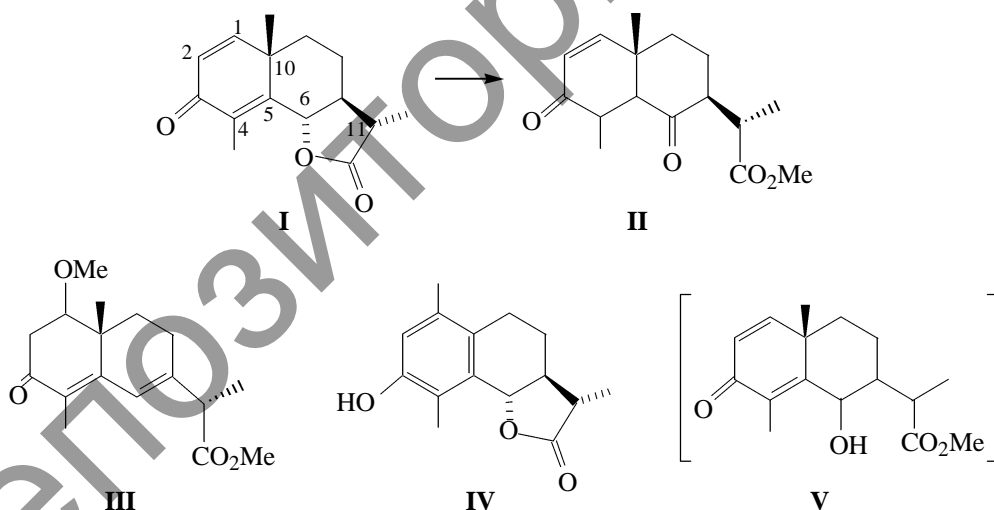
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It is known that treatment of eudesmane sesquiterpene  $\gamma$ -lactone  $\alpha$ -santonin (I) with acid gives rise to a dienone–phenol rearrangement to form desmatropesantonin IV [1–3].

In this study we showed that the reaction of  $\alpha$ -santonin (I) with methanolic HCl under reflux results in preferential formation of a transesterification

product, oxo ester II, in 60% yield. The minor reaction products are derivative III and desmatropesantonin IV (yields 15 and 5%, respectively).

The 6-C=O group in compound II is probably formed by the prototropic allyl rearrangement of intermediate hydroxy ester V.



Methyl-3,6-dioxoeudesm-1(2)-en-11-oate (II), methyl-1-methoxy-3-oxoeudesma-4(5),6(7)-dien-11-oate (III), and desmatropesantonin IV. To a solution of 0.2 g of  $\alpha$ -santonin in 1 ml of methanol, we added 4 ml of 0.1 N methanolic HCl. The mixture was refluxed for 1 h, the solvent was then removed in a vacuum, and the residue was dissolved in ethyl acetate. The solution was treated with a solution of

NaHCO<sub>3</sub> and dried with MgSO<sub>4</sub>. The solvent was removed in a vacuum, and the residue was subjected to column chromatography on silica gel, eluent hexane–ethyl acetate.

Compound II, yield 0.133 g (60%), colorless oil. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1730 (ester C=O), 1710 (ketone C=O), 1630 (C=C). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm:

6.23 d (1H, HC<sup>1</sup>,  $J_{\text{HH}}$  9.0 Hz), 6.45 d (1H, HC<sup>2</sup>,  $J_{\text{HH}}$  9.0 Hz), 1.15 d (3H, CH<sub>3</sub>-C<sup>4</sup>,  $J_{\text{HH}}$  6.5 Hz), 1.01 s (3H, CH<sub>3</sub>-C<sup>10</sup>), 1.26 d (3H, CH<sub>3</sub>-C<sup>11</sup>,  $J_{\text{HH}}$  6.0 Hz), 3.34 s (3H, CO<sub>2</sub>-CH<sub>3</sub>). Found, %: C 68.87; H 7.81. C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>. Calculated, %: C 69.06; H 7.91.

**Compound III**, yield 0.035 g (15%), colorless oil. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1740 (ester C=O), 1715 (ketone C=O), 1650, 1630 (C=C). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 3.18 q (1H, HC<sup>1</sup>,  $J_{\text{HH}}$  10.0, 6.0 Hz), 2.06 br.s (3H, CH<sub>3</sub>-C<sup>4</sup>), 6.34 br.s (1H, HC<sup>6</sup>), 1.28 s (3H, CH<sub>3</sub>-C<sup>10</sup>), 1.99 d (3H, CH<sub>3</sub>-C<sup>11</sup>,  $J_{\text{HH}}$  6.0 Hz), 3.53 s (3H, OCH<sub>3</sub>), 3.62 s (3H, CO<sub>2</sub>CH<sub>3</sub>). Found, %: C 69.68; H 8.11. C<sub>17</sub>H<sub>24</sub>O<sub>4</sub>. Calculated, %: C 69.86; H 8.21.

**Compound IV**, yield 0.009 g (5%), colorless crystals, mp 175–177°C. The physicochemical character-

istics and <sup>1</sup>H NMR, IR, and UV spectra of compound **IV** are consistent with those reported in [1–3].

The IR spectra were measured on an Avatar-360 instrument in thin films or KBr pellets. The UV spectrum was taken on a Helios- $\beta$  instrument in ethanol. The <sup>1</sup>H NMR spectra were obtained on a Bruker WP-200SY instrument (200.13 MHz) in CDCl<sub>3</sub>, internal reference TMS.

## REFERENCES

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