

SHORT
COMMUNICATIONSStereoselective Transformations of (–)- α -Santonin
in the Course of Alkaline Transesterification

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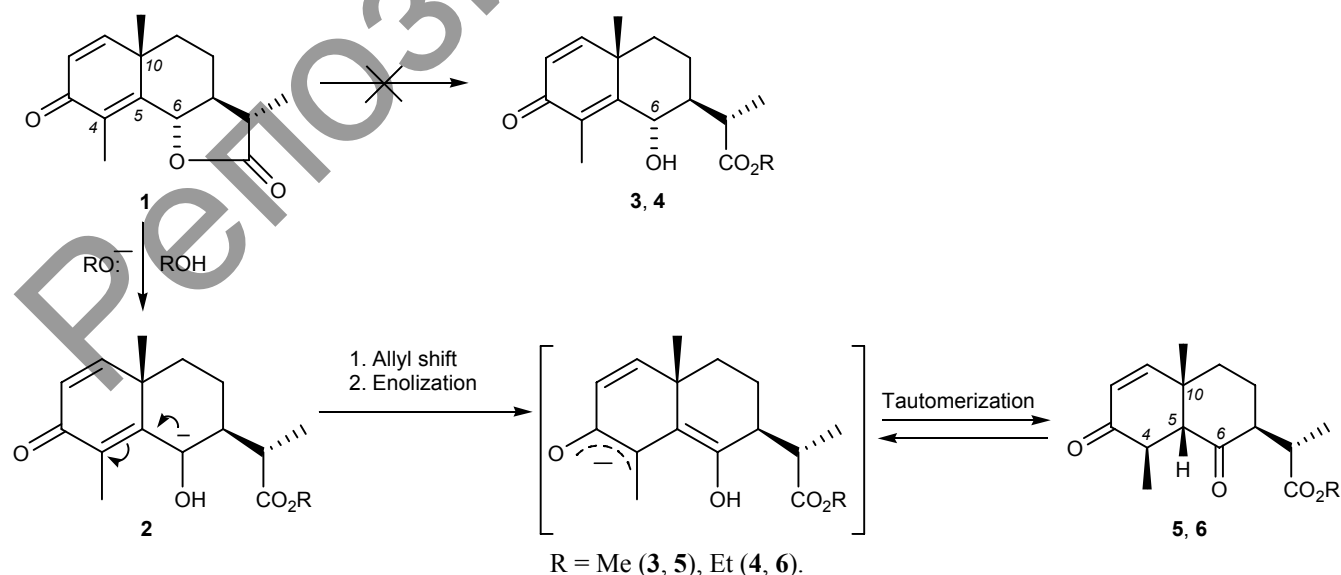
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In extension of research on the chemistry of diene eudesmanolides [1–4] we explored the reaction of alkaline transesterification of a natural eudesmanolide, (–)- α -santonin **1**. Reactions of eudesmanolide **1** with MeOH and EtOH in the presence of sodium alcoholates stereoselectively led to the formation instead of expected 6-hydroxyesters **3** and **4** of new practically important *cis*-fused 10 β (CH₃), 5 β (H), 4 β (CH₃)-6-oxoeudesmane esters **5** and **6** in 96 and 94% yields respectively.

Under the conditions of alkaline transesterification of compound **1** γ -lactone ring the primary stage of the formation of eudesmane anion **2** initiates the subsequent stages of intramolecular electrophilic rearrangements that proceed strictly stereoselectively leading

finally to *cis*-fused ketoeudesmane esters **5** and **6** in nearly quantitative yields.

Transesterification of α -santonin (1). To a solution of sodium methylate in MeOH or sodium ethylate in EtOH (prepared from 0.046 g of sodium metal and 1 mL of alcohol) under an argon atmosphere at room temperature was added a solution of 0.5 g (2 mmol) of compound **1** in 5 mL of MeOH or EtOH. The reaction mixture was stirred at room temperature for 1 h. Then alcohol was distilled off in a vacuum, the residue was dissolved in ethyl acetate, the solution was washed with water (3 \times 10 mL) and dried with MgSO₄. The solvent was evaporated in a vacuum, the residue (0.55 g) was chromatographed on a column packed with silica gel (eluent hexane–ethyl acetate, 4 : 1).



Eudesmane methyl ester (5). Yield 0.534 g (96%). R_f 0.67 (hexane–ethyl acetate, 3 : 2). Colorless oil, $[\alpha]_D^{20} -106^\circ$ (c 0.05, CHCl_3). IR spectrum, ν , cm^{-1} : 1730 (C=O), 1710 (C=O), 1630 (C=C). ^1H NMR spectrum, δ , ppm: 5.94 d (1H, H^1 , J 10.0 Hz), 6.58 d (1H, H^2 , J 10.0 Hz), 1.05 d (3H, CH_3C^4 , J 6.6 Hz), 1.06 s (3H, CH_3C^{10}), 1.26 d (3H, CH_3C^{11} , J 6.0 Hz), 4.10 s (3H, H^{16}). Mass spectrum, m/z (I_{rel} , %): 278 (40.4) $[\text{M}]^+$. Found, %: C 68.87; H 7.81. $\text{C}_{16}\text{H}_{22}\text{O}_4$. Calculated, %: C 69.06; H 7.91. M 277.98.

Eudesmane ethyl ester (6). Yield 0.550 g (94%). R_f 0.65 (hexane–ethyl acetate, 3 : 2). Colorless crystals, mp 94–96°C. $[\alpha]_D^{18} -90^\circ$ (c 0.05, CHCl_3). IR spectrum, ν , cm^{-1} : 1732 (C=O), 1710 (C=O), 1630 (C=C). ^1H NMR spectrum, δ , ppm: 5.94 d (1H, H^1 , J 10.0 Hz), 6.58 d (1H, H^2 , J 10.0 Hz), 1.05 d (3H, CH_3C^4 , J 6.6 Hz), 1.06 s (3H, CH_3C^{10}), 1.18 d (3H, CH_3C^{11} , J 7.1 Hz), 4.20 m (2H, H^{16}), 1.27 t (3H, H^{17} , J 7.2 Hz). Mass spectrum, m/z (I_{rel} , %): 292 (41) $[\text{M}]^+$. Found, %: C 69.57; H 8.10. $\text{C}_{17}\text{H}_{24}\text{O}_4$. Calculated, %: C 69.86; H 8.22. M 291.99.

IR spectra were recorded on a spectrophotometer Avatar-360 from pellets with KBr. ^1H NMR spectra were registered on a spectrometer Jeol ECA-500 (operating frequency 500.15 MHz), solvent CDCl_3 . Mass spectra were measured on an instrument Agilent 7890A. The specific rotation was determined on a polarimeter Perkin Elmer 141. Melting points were obtained on a small Boëtius heating block. TLC was performed on Sorbfil PTSKh-AF-UF.

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