ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 8, pp. 1347–1348. © Pleiades Publishing, Inc., 2006.
Original Russian Text © N. Merkhatuly, S.K. Zhokizhanova, L.T. Balmagambetova, S.M. Adekenov, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 8, pp. 1403–1404.

LETTERS TO THE EDITOR

Reaction of the Sesquiterpene γ-Lactone α-Santonin with Alcoholic Hydrogen Chloride

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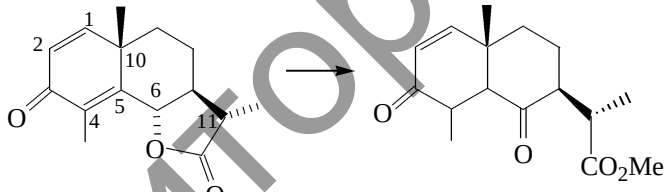
Received February 20, 2006

DOI: 10.1134/S107036320608038X

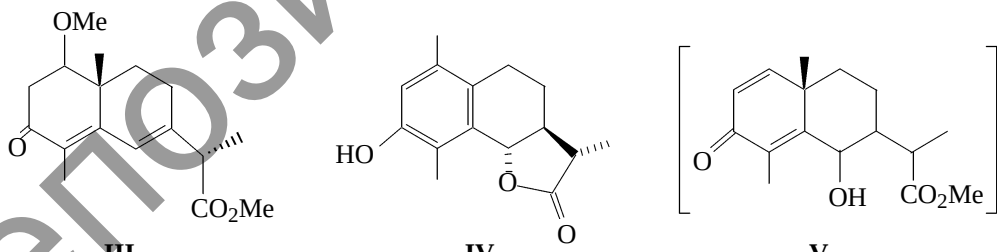
It is known that treatment of eudesmane sesquiterpene γ-lactone α-santonin (**I**) with acid gives ride to a dienone–phenol rearrangement to form desmatropesantonin **IV** [1–3].

In this study we showed that the reaction of α-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**.



I **II**



III **IV** **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 α-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 $NaHCO_3$ and dried with $MgSO_4$. 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, ν, cm^{-1}: 1730 (ester C=O), 1710 (ketone C=O), 1630 (C=C). ^1H NMR spectrum, δ, ppm:

6.23 d (1H, HC^1, J_{HH} 9.0 Hz), 6.45 d (1H, HC^2, J_{HH} 9.0 Hz), 1.15 d (3H, CH_3–C^4, J_{HH} 6.5 Hz), 1.01 s (3H, CH_3–C^{10}), 1.26 d (3H, CH_3–C^{11}, J_{HH} 6.0 Hz), 3.34 s (3H, CO_2–CH_3). Found, %: C 68.87; H 7.81. $C_{16}H_{22}O_4$. Calculated, %: C 69.06; H 7.91.

Compound III, yield 0.035 g (15%), colorless oil. IR spectrum, ν, cm^{-1}: 1740 (ester C=O), 1715 (ketone C=O), 1650, 1630 (C=C). ^{1}H NMR spectrum, δ, ppm: 3.18 q (1H, HC^1, J_{HH} 10.0, 6.0 Hz), 2.06 br.s (3H, CH_3–C^4), 6.34 br.s (1H, HC^6), 1.28 s (3H, CH_3–C^{10}), 1.99 d (3H, CH_3–C^{11}, J_{HH} 6.0 Hz), 3.53 s (3H, OCH_3), 3.62 s (3H, CO_2CH_3). Found, %: C 69.68; H 8.11. $C_{17}H_{24}O_4$. Calculated, %: C 69.86; H 8.21.

Compound IV, yield 0.009 g (5%), colorless crystals, mp 175–177°C. The physicochemical characteristics and ^{1}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-β instrument in ethanol. The ^{1}H NMR spectra were obtained on a Bruker WP-200SY instrument (200.13 MHz) in $CDCl_3$, internal reference TMS.

REFERENCES

1. Barton, D.H.R., *J. Org. Chem.*, 1950, vol. 15, p. 466.
2. Flohlich, A., Maura, P., Ishikowa, K., McMurry, T.B.H., and Ranc, D., *Proc. R. Ir. Acad.*, 1983, vol. 83, p. 65.
3. Kulyyasov, A.T., Seitembetov, T.S., and Adekenov, S.M., *Khim. Pripodn. Soedin.*, 1997, no. 2, p. 247.