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SHORT COMMUNICATIONS

Stereocontrolled Acid Cyclization of (+)-Hanphillin

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In extension of our research in the field of biomimetic transformations of germacranic sesquiterpene γ-lactones [1, 2] we performed by the action of formic acid a stereocontrolled transannular carbocyclization of *E,E*-germanocranolide hanphillin (**I**) isolated from Noble Yarrow (*Achillea nobilis L.*), and obtained new *trans*-fused 5α(H),10β(CH_3)-eudesmanolides **II** and **III** in the yields of 65 and 30% respectively.

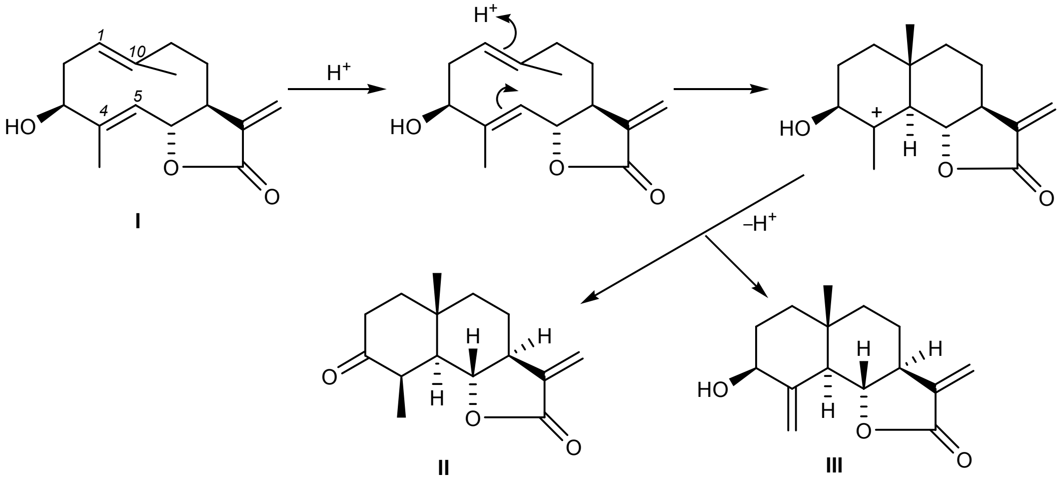
As shown in the scheme the acid-catalyzed 5,10-carbocyclization of compound **I** proceeds evidently through a regioselective protonation of the most electron-donor and spatially available $\Delta^{1,10}$-double bond of compound **I** followed by a stereospecific nucleophilic attack by the $\Delta^{4,5}$-double bond leading via a tertiary carbocation to the *trans*-fused eudesmanolides **II** and **III** (Scheme 1).

The stereocontrolled 5,10-carbocyclization of compound **I** occurs also in the presence of CH_3CO_3H and $C_6H_5CO_3H$ in CH_2Cl_2 at room temperature giving *trans*-eudesmanolides formerly isolated from plant sources [3, 4] epiartekalin (**IV**) and ridentin-B (**V**) in 45 and 53% yields (Scheme 2).

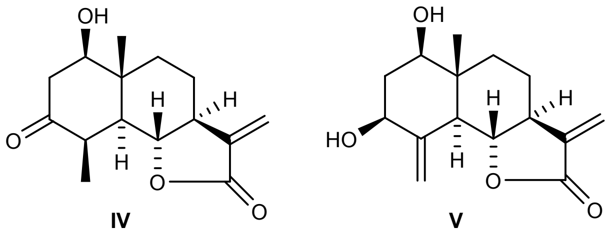
Compounds II and **III**. To a solution of 0.3 g (1.2 mmol) of compound **I** in 15 mL of $CHCl_3$ was added dropwise at room temperature 4.6 mL of 99% HCO_2H. The reaction mixture was stirred at room temperature, then washed with 10% solution of $NaHCO_3$ (2 × 10 mL), with water (3 × 10 mL), dried with $MgSO_4$, the solvent was distilled off in a vacuum. The residue (0.33 g) was chromatographed on a column packed with silica gel (eluent hexane–ethyl acetate, 2 : 3 and 1 : 4).

3-Oxoeudesm-11(13)-en-6,12-olide, or (3a*S*,5a*S*,9*R*,9a*S*,9b*S*)-5a,9-dimethyl-3-methylidene-octahydronaphtho[1,2-*b*]furan-2,8(3*H*,4*H*)-dione (II). Yield 0.193 g (65%). R_f 0.54 (hexane–ethyl acetate, 2 : 3). Colorless crystals, mp 136–138°C.

Scheme 1.



Scheme 2.



IV V

$[\alpha]_D^{18}$ +96° (*c* 0.02, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1760 (C=O), 1700 (C=O), 1640 (C=C). ^1H NMR spectrum, δ, ppm: 1.43 s (3H, CH_3-C^{10}), 1.68 br.s (3H, CH_3-C^4), 4.12 q (1H, H^6, *J* 10, 8.5 Hz), 5.52 d (1H, H^{13}, *J* 3.5 Hz), 6.26 d (1H, H^{13}, *J* 3.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 248 (32.4) $[M]^+$. Found, %: C 72.38; H 7.87. $C_{15}H_{20}O_3$. Calculated, %: C 72.58; H 8.06.

3-Hydroxyeudesma-4(15),11(13)-dien-6,12-olide, or (3a*S*,5a*S*,9a*R*,9b*S*)-8-hydroxy-5a-methyl-3,9-dimethylidenedecahydronaphtho[1,2-*b*]furan-2(3*H*)-one (III). Yield 0. 074 g (30%). R_f 0.37 (hexane–ethyl acetate, 1 : 4). Colorless crystals, mp 175–177°C. $[\alpha]_D^{18}$ +106° (*c* 0.02, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1760 (C=O), 1650, 1640 (C=C). ^1H NMR spectrum, δ, ppm: 1.43 s (3H, CH_3C^{10}), 4.12 q (1H, H^6, *J* 10, 8.5 Hz), 5,26 d (1H, H^{15}, *J* 1 Hz), 5.52 d (1H, H^{13}, *J* 3.5 Hz), 5,92 d (1H, H^{15}, *J* 1 Hz), 6.26 d (1H, H^{13}, *J* 3.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 248 (44.7) $[M]^+$. Found, %: C 72.33; H 7.81. $C_{15}H_{20}O_3$. Calculated, %: C 72.58; H 8.06.

IR spectra were recorded on a spectrophotometer Avatar-360 from pellets with KBr. ^1H NMR spectra were registered on a spectrometer Bruker Avance-400 (operating frequency 400.13 MHz), solvent $CDCl_3$, internal reference TMS. Mass spectra were obtained on an instrument Agilent 7890A. Specific rotation was measured on a polarimeter Perkin-Elmer 141. Melting points were determined on a small heating block Boëtius. TLC was carried out on Silufol UV-254 plates.

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