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LETTERS TO THE EDITOR

Stereoselective Carbocyclization of Hanphyllin with *N*-Bromosuccinimide

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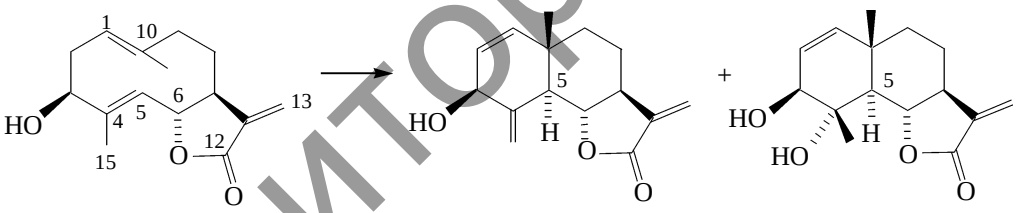
It is known that sesquiterpene γ-lactones of the germacrane structure (germacranolides) in acid media undergo facile intramolecular cyclization to form bicyclic (eudesmane, guaiane, etc.) sesquiterpenoids [1–3].

We performed a stereoselective transannular carbocyclization of 1(10)*E*,4*E*-germacranolide hanphyllin (**I**) with *N*-bromosuccinimide to obtain novel *trans*-fused (5α-*H*) eudesmane sesquiterpene γ-lactones **II** and **III** in 30 and 40% yields, respectively.

The stereoselectivity of the reaction is probably explained by the *chair–chair* conformation of hanphyllin (**I**) [4].



I **II** **III**

3β-Hydroxy-5,7α-*H*-eudesma-1(2),4(15),11(13)-trien-6,12-olide (II) and 3β,4α-dihydroxy-5,7α-*H*-eudesma-1(2),11(13)-dien-6,12-olide (III). To a solution of 2.2 g of hanphyllin in 5 ml of 5% aqueous acetone, 0.142 g of finely ground *N*-bromosuccinimide was added with stirring. The mixture was stirred for 1.5 h and then, at 25–30°C, poured into 3% HCl. The reaction products were extracted with ethyl acetate, the extract was dried with $MgSO_4$, the solvent was removed by vacuum distillation, and the residue was subjected to column chromatography on silica gel, eluent hexane–ethyl acetate.

Compound **II**, yield 0.059 g (30%), colorless crystals, mp 142–144°C. IR spectrum, ν, cm^{-1}: 3450 (HO), 1750 (C=O), 1650, 1640 (C=C). ^1H NMR spectrum, δ, ppm: 0.90 s (3H, CH_3–C^{10}), 5.28 d (1H, HC^1, J_{HH} 11.0 Hz), 5.40 q (1H, HC^2, J_{HH} 11.0, 9.0 Hz), 4.40 br.d (1H, HC^3, J_{HH} 9.0 Hz), 2.24 br.d (1H, HC^5, J_{HH} 11.0 Hz), 3.98 t (1H, HC^6, J_{HH} 11.0 Hz), 5.40 d (1H, HC^{13}, J_{HH} 3.0 Hz), 6.06 d (1H, HC^{13}, J_{HH} 3.0 Hz), 5.25 d (1H, HC^{15}, J_{HH} 1.0 Hz), 5.90 d (1H, HC^{15}, J_{HH} 1.0 Hz). Found, %: C 72.97; H 7.21. $C_{15}H_{18}O_3$. Calculated, %: C 73.17; H 7.31.

Compound **III**, yield 0.084 g (40%), colorless crystals, mp 161–163°C. IR spectrum, ν, cm^{-1}: 3450 (OH), 1750 (C=O), 1650 (C=C). ^1H NMR spectrum, δ, ppm: 1.26 s (3H, CH_3–C^4), 0.94 s (3H, CH_3–C^{10}), 5.29 d (1H, HC^1, J_{HH} 11.0 Hz), 5.41 q (1H, HC^2, J_{HH}

11.0, 9.0 Hz), 4.45 d (1H, HC^3, J_{HH} 9.0 Hz), 2.18 d (1H, HC^5, J_{HH} 11.0 Hz), 6.14 d (1H, HC^{13}, J_{HH} 3.0 Hz). Mass spectrum, *m/z* (I_{rel}, %): 265 (44.7) [*M* + H], 247 (61.8), 207 (100), 147 (28.9), 119 (19.7), 81 (25.0), 55 (25.0), 43 (69.7). Found, %: C 72.99; H 7.38. $C_{15}H_{20}O_4$. Calculated, %: C 73.17; H 7.57.

The IR spectra were measured on an Avatar-360 instrument in KBr. The ^1H NMR spectra were taken on a Bruker WP-200SY instrument (200.13 MHz) in $CDCl_3$, internal reference TMS. The mass spectrum was taken on a Finnigan MAT-8200 instrument, ionizing energy 70 eV.

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