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LETTERS TO THE EDITOR

OXIDATION OF BRITANIN

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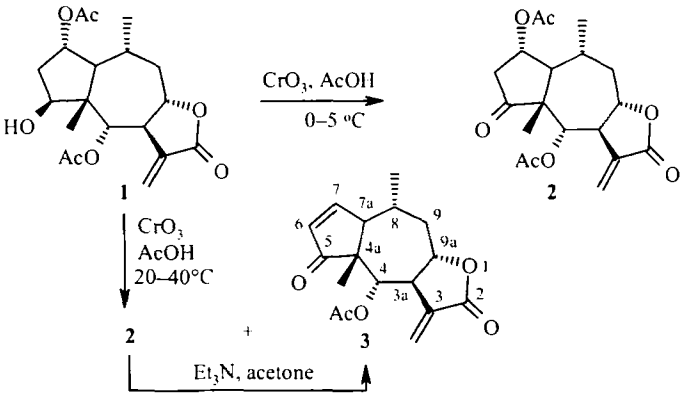
The oxidation products of the sesquiterpene lactone britanin (**1**) from *Inula britannica* L. are of considerable interest as starting compounds for obtaining a whole range of physiologically active substances [1]. Also literature data on its oxidation are ambiguous. Under identical conditions, dehydrobritanin (**2**) [2] or bigelovin (**3**) [3] have been obtained by treating lactone **1** with chromium oxides. We have investigated this reaction and established that formation of compounds **2** and **3** is controlled by the reaction temperature. Oxidation of lactone **1** by CrO_3 in acetic acid at a reaction temperature of 0-5°C quantitatively leads to the dehydro derivative **2**; if the temperature is raised to 20-40°C, mixtures of compounds **2** and **3** are always formed. The data obtained were confirmed by HPLC analysis (column 4 × 250 mm, packed with 5 μm Diasorb 130 C16/T, the eluent was an acetonitrile gradient in water; detection by UV at 254 nm) and ^1H NMR spectra of the isolated compounds and reaction mixtures. Vigorous stirring of equimolar amounts of britanin and CrO_3 in AcOH at 20°C for 3 h leads to a 1:1 mixture of compounds **2** and **3**, and the content of the latter increases slightly when the reaction time is increased. Lactone **3** is formed quantitatively only in dehydroacetylation of compound **2** by treatment with bases.



4-Acetoxy-3,3a,4,4a,7a,8,9,9a-octahydro-4a,8-dimethyl-3-methyleneazuleno[6,5-*b*]furan-2,5-dione (Bigelovin, 3). CrO_3 (54.6 mg, 0.55 mmol) was added in small portions to a solution of lactone **1** (200 mg, 0.55 mmol) in acetic acid (3 ml). The mixture was vigorously stirred at 20°C for 3 h, diluted with water (15 ml), and extracted with chloroform (5 × 10 ml). The extract was dried over Na_2SO_4 and evaporated under vacuum. The residue was boiled for 2 h in acetone (10 ml) containing triethylamine (0.42 g, 4.1 mmol). The oxidation product was purified on silica gel; eluent hexane–acetone, 2:1. Obtained 157 mg (94%) of bigelovin; mp 191-192°C;

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according to data in [4], mp 190-191°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.2 (3H, s, 4a-CH_3); 1.3 (3H, d, J = 7.2 Hz, 8-CH_3); 1.54 (1H, q, J = 11.8 Hz, 9-H); 1.95 (3H, s, CH_3CO); 2.03 (1H, m, 9-H); 2.58 (1H, m, 8-H); 3.05 (2H, m, 3a-H and 7a-H); 4.6 (1H, ddd, J_1 = 11.6, J_2 = 10.5, J_3 = 3.0 Hz, 9a-H); 5.58 (1H, d, J = 7.5 Hz, 4-H); 5.9 (1H, d, J = 3.1 Hz, CH_2=); 6.1 (1H, dd, J_1 = 6.0, J_2 = 2.9 Hz, 6-H); 6.2 (1H, d, J = 3.5 Hz, CH_2=); 7.7 (1H, dd, J_1 = 6.0, J_2 = 1.8 Hz, 7-H). Found, %: C 66.64; H 6.22. $C_{17}H_{20}O_5$. Calculated, %: C 67.11; H 6.58.

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