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BIEBSANIN — A NEW SUSQUITERPENE LACTONE FROM *Achillea biebersteinii* AND *A. santolina*

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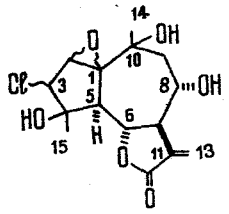
Continuing a study of the lactones of *Achillea biebersteinii* [1] and *A. santolina*, from the mother liquors [2, 3] by means of the systems chloroform–ethanol (30:1) and benzene–ethyl acetate (1:1) we have isolated a new chlorine-containing sesquiterpene lactone with the composition $C_{15}H_{19}O_6Cl$ (ethyl acetate), mp 258-259°C (in a preheated metal block), $[\alpha]_D^{20}$ −34° (c 1.0; pyridine), M^+ 330, which we have called biebsanin (I).

The IR spectrum of (I) has the following absorption bands: ν_{max}^{KBr} 3500 and 3440 cm^{-1} (OH group), 1755 cm^{-1} (lactone C=O conjugated with an exocyclic double bond), and 1662 and 1633 cm^{-1} (C=C). The PMR spectrum of (I) (deuteropyridine, O—HMDS, JNM-14H-100) included singlets at 1.22 and 1.64 ppm corresponding to tertiary methyl groups — 2 (HO—C—CH_3). A doublet at 3.12 ppm with J = 10 Hz was assigned to a proton at C_5. Signlets at 3.97 and 4.62 ppm were due to protons at C_2 and C_3. The signal of the lactone proton was present in the form of a triplet at 4.55 ppm with ^3J 10 Hz. The nature of the splitting of the signal and the magnitude of the spin–spin interaction show that the lactone ring is attached to C_6-C_7 and has the trans linkage. The protons of the exomethylene group appeared in the form of a broadened singlet at 6.02 ppm.

The acetylation of biebsanin with acetic anhydride in pyridine yielded a monoacetyl derivative (II) with the composition $C_{17}H_{21}O_7Cl$, mp 223-224°C (benzene–ethyl acetate), M^+ 372 (mass spectrometry). The IR spectrum of (II) contained absorption bands at (cm^{-1}) 3500 (OH), 1755 (C=O of a γ-lactone), 1662 and 1630 (C=C), and 1740 and 1255 ($OCOCH_3$). Thus, the presence of one secondary and two tertiary hydroxy groups has been shown.

The PMR spectrum of (II) showed the signal of the protons of the methyl part of an acetyl group at 1.86 ppm, and the signal of a hemiacyl proton at 5.40 ppm. The signals of the protons of the exomethylene group appeared in the form of doublets at 5.52 and 6.12 ppm with J = 3 Hz. This fact shows that the secondary hydroxy group is located in the β position relative to the exomethylene group, i.e., at C_8, and it has an α orientation [4]. The facts obtained and a comparative study of the spectra of our lactone and of rupin A enables us to put forward the following structure for biebsanin:



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