SESQUITERPENE LACTONES OF *Ajania fastigiata*

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We have studied the lactones of the plant *Ajania fastigiata* (C. Winkl.) Poljak., family Compositae [1], collected in the flowering phase in August, 1978, in the Chon-Kemin region, Kirghiz SSR. The epigeal part of the plant was extracted with chloroform. The resin so obtained was treated with 50% ethanol, the soluble fraction was taken off, and extraction was performed with petroleum ether, benzene, and chloroform, successively. The chloroform extract was chromatographed on a column of type KSK silica gel. Elution with benzene—acetone (30:1) yielded a lactone (I). On elution with chloroform—acetone (20:1), eluates 7-9 yielded a lactone (II), 26-30 a lactone (III), and 32-40 a lactone (IV). Rechromatography on silica gel in diethyl ether—petroleum ether (4:6) of the fraction obtained by elution with benzene—acetone (30:1) yielded the lactone (V).

Lactone (I), composition $C_{15}H_{18}O_5$, mp 242-243°C (benzene—ethyl acetate), M^+ 278. The IR spectrum contained the absorption bands of a hydroxy group (3440 cm^{-1}), of a lactone carbonyl conjugated with an exomethylene group (1745 cm^{-1}), and a double bond (1665 cm^{-1}). The physicochemical properties of this lactone corresponded to those of chrysartemin B [2]. Identification was checked with an authentic sample and a comparison of IR spectra.

Lactone (II), composition $C_{15}H_{18}O_6$, mp 312°C (benzene—ethanol). The given melting point was determined in a previously heated metal block. M^+ 294. The IR spectrum showed absorption bands of hydroxy groups (3495-3455 cm^{-1}), of a γ-lactone ring conjugated with an exomethylene group (1745 cm^{-1}), and of a double bond (1660-1645 cm^{-1}).

Acetic anhydride in pyridine formed a monoacetyl derivative with mp 216-219°C. This lactone was identified by direct comparison with an authentic sample as rupin A [3]. Their IR spectra were identical.

Lactone (III), composition $C_{15}H_{20}O_5$, mp 186-188°C (benzene—ethyl acetate), M^+ 280. The IR spectrum contained the absorption bands of hydroxy groups (3440-3410 cm^{-1}), of an α-methylene-γ-lactone ring (1750 cm^{-1}), and of double bonds (1670-1640 cm^{-1}). With acetic anhydride in pyridine it formed a diacetyl derivative with mp 127-129°C. Its IR spectrum showed the absorption bands of a hydroxy group (3480 cm^{-1}), of a lactone carbonyl (1778 cm^{-1}), of an ester group (1742 and 1245 cm^{-1}), and of double bonds (1665 and 1640 cm^{-1}). This means that there are three hydroxy groups in the molecule. The lactone proved to be new, and we have called it ajanin.

Lactone (IV), composition $C_{15}H_{20}O_6$, mp 162-164°C (benzene—ethyl acetate), M^+ 296 (mass spectrometry). The IR spectra contained the absorption bands of hydroxy groups (3300-3560 cm^{-1}), of a lactone carbonyl conjugated with an exomethylene group (1760 cm^{-1}), and of double bonds (1670 and 1632 cm^{-1}). The physicochemical constants of this lactone differed from those described in the literature and therefore it was called ajafinin.

Lactone (V), composition $C_{15}H_{18}O_4$, mp 104-105°C (diethyl ether—hexane), M^+ 26, $[\alpha]_D^{20}$ +111.1° (c 0.9; chloroform). The IR spectrum showed absorption bands of hydroxy groups (3440, 3540 cm^{-1}), of a lactone carbonyl (1756 cm^{-1}), and of double bonds (1660, 1640 cm^{-1}). The lactone has proved to be new and has been called ajadin.

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

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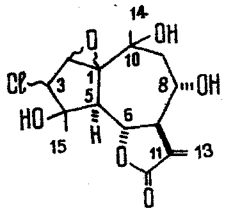
Continuing a study of the lactones of *Achillea biebersteinii* [1] and *A. santolina*, from the mother liquors [2, 3] by means of the systems chloroform–ethanol (30:1) and benzene–ethyl acetate (1:1) we have isolated a new chlorine-containing sesquiterpene lactone with the composition $C_{15}H_{19}O_6Cl$ (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, 0 — 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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