LACTONES OF Achillea micrantha AND A. vermicularis

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From the epigeal green part of Achillea micrantha Willd., collected in the Petrovskii region of Stavropol' territory, by aqueous extraction followed by chromatography we have isolated a new sesquiterpene lactone, micranthin, with the composition $C_{19}H_{26}O_7$, mp 284-286°C (from ethyl acetate) $[\alpha]_D^{20}$ +123.1° (c 1.4; chloroform).

IR spectrum: $\nu_{max}^{paraffin\ oil}$, cm^{-1}: 1770 (γ-lactone), 1730-1720 and 1260-1240 (2 $OCOCH_3$), and 1665 cm^{-1}. (C=C).

NMR spectrum (in $CDCl_3$), ppm: doublet at 1.12 – secondary methyl; singlet at 1.20 – methyl attached to an epoxide ring; feebly resolved double at 1.83 ppm – methyl on a double bond; 6H singlet at 2.05 ppm – protons of two acetyl groups; triplet at 4.78 ppm (J = 10 Hz) – lactone proton; quartet at 4.28 ppm – hemiacyl proton; 2H multiplet at 5.4 ppm – hemiacyl and vinyl protons; the signal of an epoxide proton is located in the 2.7-ppm region (superimposition of signals).

The hydrogenation of micranthin over Pt (from PtO_2) in acetic acid gave two substances. Substance A, mp 130-132°C (from a mixture of petroleum ether and diethyl ether), $C_{19}H_{28}O_6$. IR spectrum: $\nu_{max}^{par.\ oil}$, cm^{-1}: 1760 (γ-lactone), 1735-1720 and 1260-1240 (2 $OCOCH_3$), and 1665 (C=C).

The NMR spectrum of substance A, in contrast to that of the initial substance, has no signal of a methyl group attached to an epoxide ring, and in place of this the signal of a secondary methyl has appeared (doublet at 1.18 ppm); the structure of the lactone proton has also changed: in place of a triplet a multiplet has appeared; the chemical shifts and structures of the other signals have remained almost unchanged.

The composition of the substance and the characteristics of its IR and NMR spectra permit the conclusion that on hydrogenation only the epoxide ring was reduced.

Substance B has mp 174-176°C (from petroleum ether – ether) and the composition $C_{19}H_{28}O_7$. IR spectrum, $\nu_{max}^{par.oil}$, cm^{-1}: 1765 (γ-lactone), 1735 and 1235-1260 (2 $OCOCH_3$).

The NMR spectrum of substance B, in comparison with that of the initial substance, lacks the signals of a methyl group on a double bond and of a vinyl proton and has an additional doublet at 1.20 ppm; the signal of the methyl attached to an epoxide ring has been retained (singlet at 1.32 ppm), i.e., only the reduction of the double bond has taken place.

The composition of the substance and also the presence of only one double bond permits the assumption of a germacranolide structure for micranthin, and the change in the structure of the signal of the lactone proton indicates the immediate propinquity of the epoxy group to the lactone ring. The acetyl groups are located at C_3 and C_8, since no formation of a deacetyl derivative took place on hydrogenation, which excludes the α position of an acetoxy group with respect to the double bond. The structure of the signals of the geminal protons also agrees with the positions of the acetoxy group at C_3 and C_8. On the basis of the facts given above, we propose structure (I) as the most probable for micranthin.

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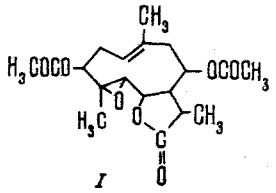

I

From the epigeal part of Achillea vermicularis Trin., collected in June in the Ordubarskii region of the Armenian SSR by aqueous extraction we have isolated a crystalline substance with the composition $C_{15}H_{18}O_4 \cdot H_2O$. The properties and spectral characteristics of this substance, and a comparison of them with those given in the literature [1, 2] have permitted the conclusion that the substance isolated is austricin (deacetylmatricarin), and this is the first time that it has been isolated from this species.

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THE LACTONES OF Achillea biebersteinii

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We have investigated the widely distributed plant Achillea biebersteinii Afan. for its lactone content [1]. The epigeal part of the plant collected in the flowering period in May in the environs of Tashkent was extracted with chloroform. The extract was treated with 50% alcohol and extracted with chloroform. The purified extract was deposited on a column of silica gel and eluted successively with benzene, chloroform, and chloroform–ethanol. The rechromatography of these eluates yielded five sesquiterpene lactones. Lactone (I) had the composition $C_{15}H_{18}O_4$, mp 164-165°C (benzene), M^+ 262, R_f 0.51 [TLC, fixed layer of silica gel, benzene–ether–methanol (5 : 1 : 1) system here and below]. According to its IR and NMR spectra, the substance has two OH groups, two methyl groups or double bonds, and an exomethylene group in a lactone ring.

Lactone (II), $C_{15}H_{18}O_4$, mp 142-143°C (benzene, M^+ 262, R_f 0.46. According to its IR and NMR spectra, the substance has two OH groups, one methyl group on a double bond, and two exomethylene groups.

Lactone (III), $C_{15}H_{20}O_4$, mp 220-221°C (benzene), M^+ 264, R_f 0.6. According to its IR spectrum, the lactone contains an OH group, a lactone C=O, a ketonic C=O, and double bonds. The NMR spectrum contains the signals of an angular methyl group, a secondary methyl group, a lactone proton, and one exomethylene group. On acetylation with acetic anhydride in pyridine, a monoacetyl derivative was obtained. Treatment of the lactone (III) with a mixture of acetic anhydride and acetic acid (2 : 1) gave an anhydro derivative. In their physicochemical properties, the lactone and its derivatives are similar to the lactone artecalin and its derivatives [2]. Mixed melting points showed no depression and their IR spectra were identical.

Lactone (IV), $C_{15}H_{20}O_4$, mp 197-199°C (ethanol), M^+ 264, R_f 0.37. According to its IR spectrum, it has an OH group, a lactone C=O, and double bonds. On acetylation with acetic anhydride in pyridine, a diacetyl derivative was obtained with mp 136-138°C. According to the NMR spectrum, (IV) has one methyl on a double bond, two hydroxyls, and two exomethylene groups.

Lactone (V), $C_{15}H_{18}O_6$, mp 312-314°C (ethanol), M^+ 294, R_f 0.4. In the IR spectrum there are absorption bands at 3455 and 3495 cm^{-1} (OH), 1745 cm^{-1} (lactone C=O), and 1645-1660 cm^{-1} (C=C bond). The NMR

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