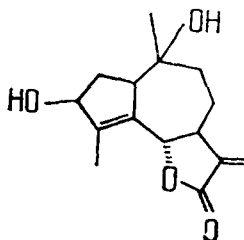


this showing that they belonged to the protons of three OH groups. They were tertiary, since there were no signals in the spectrum characteristic for protons located geminally with respect to hydroxy groups.

Singlets with an intensity of 3 H at 1.54 and 1.23 ppm were characteristic for the protons of methyl groups and two $\text{CH}_3\text{-C-OH}$ groupings. They were formed with the participation of two OH groups at C-4 and C-10, since the signal of the exocyclic methylene function appeared in the form of two doublets at 5.35 and 6.16 ppm ($^4J = 2.5$ and 3.4 Hz, respectively, with the H-7 signal at 3.3 ppm), and, consequently, were located in the lactone ring.

The doublet splitting of the signal at 3.20 ($^3J \approx 10.9$ Hz) belonging to H-5 was due to its interaction with the H-6 lactone proton which gave a signal in form of a quartet at 4.45 ppm ($^3J \approx 10.8$ and 9.6 Hz). The second value, $^3J \approx 9.6$ Hz, corresponds to the spin-spin coupling of H-6 with H-7. On the basis of these facts, we found that the lactone ring was located at C-6 and C-7 and was trans-linked to the main guaiane skeleton where the H-5 and H-7 protons had the relative α orientation. The doublet nature of the splitting of the signals of H-5 and of the H-2 and H-3 olefinic signals unambiguously showed the position of the tertiary hydroxy group at C-1 in the molecules of the lactone under investigation.

The facts given above permit us to propose for sanchillin the structure of 1,4,10-trihydroxy-5 α ,7 α (H),6 β (H)-guai-2-en-6,12-olide.



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SESQUITERPENE LACTONES OF *Polychrysum tadshicorum*

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We have studied the terpenoids of *Polychrysum tadshicorum* (S. Kudr.), S. Kovalevsk., family Asteraceae, collected in July, 1982, in the environs of Komsomolabad, TadzhSSR. The lactones were extracted from the epigeal part with chloroform by steeping for 24 h five times. The combined extract was evaporated to dryness and the residue was treated with 60% ethanol. The precipitate that deposited was separated off, and the compounds to be investigated were extracted from the filtrate with chloroform.

By column chromatography from silica gel in hexane-ethyl acetate with increasing concentrations of the latter, four compounds of terpenoid nature were isolated, including cumambrin A [1], cumambrin B [2], and handelin [3]. For the identification of the substances of the substances we used IR and PMR spectroscopy and also direct comparison with authentic samples.

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The fourth substance had the composition $C_{17}H_{24}O_5$, mp $179^\circ C$, $[\alpha]_D^{20} +45.3^\circ$ (c 1.0; CH_3OH), M^+ 308. The spectral characteristics were close to those of the sesquiterpene lactone cumambrin A. IR spectrum, ν_{max}^{KBr} , cm^{-1} : 3490, 1780, 1740, 1260. PMR spectrum (δ scale, C_5D_5N , ppm): 1.17 (s, CH_3-C_{10}); 1.21 (d, $J = 7$ Hz, CH_3-C_{11}); 1.86 (s, CH_3-C_4); 4.06 (t, 3J 10 Hz each, H-6); 5.12-5.30 (m, H-3, H-8); 5.80 (br.s, $OH-C_{10}$). The PMR spectrum differed from that of cumambrin A only by the absence of the signals of an oxycyclic methylene group. By reducing cumambrin A with sodium tetrahydroborate we obtained dihydrocumambrin A [4], which proved to be identical with our substance. This is the first time that dihydrocumambrin A has been isolated from a plant.

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NEW GUAIANOLIDES FROM *Artemisia absinthium*

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From the epigeal part of *Artemisia absinthium* L. collected in the Tashkent province, by extraction with chloroform and separation of the purified extract on silica gel, we have isolated two new guaianolides: (I) - $C_{15}H_{22}O_4$, M^+ 266, mp $203-205^\circ$, λ_{max}^{KBr} , cm^{-1} : 3400-3470 (OH), 1750 (C=O of a γ -lactone); and (II) - $C_{15}H_{20}O_4$, M^+ 264, mp $205-207^\circ$, λ_{max}^{KBr} , cm^{-1} : 3420 (OH), 1780 (C=O of a γ -lactone).

In the PMR spectrum of (I) ($CDCl_3$, 0 - HMDS), the resonance signals were characterized by the following CS values (δ , ppm): 1.21 (3 H, d, $^3J = 6.8$ Hz, CH_3-C-OH); 1.31 (3 H, c, CH_3-C-OH); 1.89 (3 H, br.s, $CH_3-C=C$); 2.68 (1 H, br.s, $^2J = 14.5$ Hz, H-2); 3.23 (1 H, br.s, $^3J = 11.1$ Hz, H-5); 4.18 (1 H, q, $^3J = 11.1$ and 9.7 Hz, H-6); 5.43 (1 H, br.s, $H-C=CH_3$).

Using the double proton-proton resonance procedure, we found that the broadened doublet at 2.68 ppm belonged to the proton of a methylene group which experienced spin-spin coupling (SSC) with the proton geminal to it having $^2J = 14.5$ Hz and interacted similarly only with an olefinic proton (5.43 ppm) having $^3J = 2$ Hz, which is characteristic for a guaianolide with a double bond in the cyclopentane ring [1-3].

We also made an assignment of the broadened doublet at 3.23 ppm to H-5 and of the multiplet at 2.27 ppm to H-7, which interacted trans-diaxially with the lactone proton with $^3J = 11.1$ and 9.7 Hz, respectively. Consequently, H-5 interacted vicinally only with H-6. Furthermore, we detected the existence of a long-range SSC between the protons of a methyl group at a double bond and H-2, H-3, and H-5, which explained the broadened signals at 2.68, 5.43, 3.23, and 1.89 ppm. The magnitude of the SSCC between H-7 and H-11 measured with suppression of the SSCC of the $CH(11)-CH_3$ protons was 11 Hz.

It followed from all that had been said that compound (I) had a guaiane structure with a double bond at C-3-C-4, a tertiary group at C-1 with the formation of a CH_3-OH group at C-10 and the trans-linkage of the lactone ring at C-6 and C-7. The value of $^3J = 11$ Hz between C-7 and C-11 showed the α -orientation of the second methyl group at C-11.

Thus, (I) has the structure of 1,10-dihydroxy-5,7 α (H)-6,11 β (H)-guai-3-em-6,12-olide and was identical with arlatin [4].

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