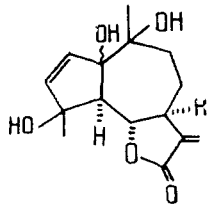
H-3 and H-6 signals was due to homoallyl spin—spin coupling between them (J ~ 1 Hz) and to allyl coupling with the protons of a methyl group at a double bond (J ~ 1 Hz), as has been observed in the case of cyclopumilin —10β-hydroxyguaia-4,13-dien-6,12-olide [4]. The structure of the splitting of the signal at 4.80 ppm mentioned above indicates a vicinal coupling of a proton geminal to a secondary OH group with not more than two protons. From this it followed that the secondary hydroxy group was located at C-3.

The facts given above taken all together permit the structure of pyrethroidinin to be established as 3,10-(di)hydroxy-6β(H)m7α(H)-guaia-4,11(13)-dien-6,12-olide.



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STRUCTURE OF SANCHILLIN

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UDC 547.314

We have previously [1] reported the isolation from the epigeal part of *Achillea santolina* L., together with leucomisin, austricin, chrysartemin B, and santachin, of a lactone (V) with the composition $C_{15}H_{10}O_5$, mp 233°C (acetone), M^+ 280, R_f 0.5 silica gel; benzene—ethanol (9:1). This lactone is new and we have called it sanchillin.

Sanchillin is readily soluble in chloroform and pyridine and sparingly soluble in benzene, acetone, and ether, and it readily polymerizes in ethanol and on boiling in benzene. When the lactone was treated with selenium, the reaction mixture acquired a blue color, which is characteristic for compounds of the guaiane series. This was confirmed by the composition and by the presence of a peak with m/z 111 in the mass spectrum [2].

The IR spectrum of the compound (KBr tablets) showed absorption bands at (cm^{-1}) 3325-3480 (hydroxy groups), 1750 and 1660 (C=O and C=C in a conjugated γ-lactone system), and 1630 (isolated C=C bond).

In the PMR spectrum of sanchillin (C_5D_5N, 0 — HMDS, H_o = 100 MHz, doublets with an intensity of 1 H each at 5.98 and 6.23 ppm corresponded to two olefinic protons interacting vicinally in the manner of a AB system with ^3J = 5.9 Hz. The value of the spin—spin coupling constant showed that the isolated double bond was present in a five-membered ring [3-5], which unambiguously indicated that sanchillin belonged to the guanolide group. In such a skeleton, the double bond can be formed only at C-2 and C-3.

There were broad singlets of 1 H each at 5.50, 6.38, and 6.57 ppm which broadened even more and shifted upfield with a rise in the temperature of the solution under investigation,

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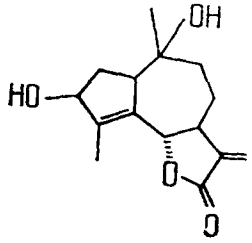
this showing that they belonged to the protons of three OH groups. They were tertiary, since there were no signals in the spectrum characteristic for protons located geminally with respect to hydroxy groups.

Singlets with an intensity of 3 H at 1.54 and 1.23 ppm were characteristic for the protons of methyl groups and two CH_3—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 ($^3J \simeq 10.9$ 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 ($^3J \simeq 10.8$ and 9.6 Hz). The second value, $^3J \simeq 9.6$ 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-5α,7α(H),6β(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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