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Cumambrins A and B, artecalin, rupicolins A and B, and the new sesquiterpene lactone tansanin have been isolated from the epigeal part of *Tanacetum santolina* C. Winkl. For tansanin the structure and configuration of 3-keto-4 $\beta$ ,6 $\beta$ (H)-germacra-1(10),11-(13)-dien-6,12-olide has been established.

From the epigeal part of *Tanacetum santolina* C. Winkl. [1] collected in the period of incipient flowering (June 5, 1979, environs of Kababdai, KKASSR Karachai-Cherkess Autonomous SSR), by the chromatography of a benzene extract on a column of alumina we have isolated six sesquiterpene lactones.

Sesquiterpene lactone (I),  $C_{15}H_{20}O_3$ , mp 131-132°C (from a mixture of hexane and ethyl acetate),  $R_f$  0.61,  $[d]_D^{22} + 161.8^\circ$  (c 0.67; methanol), proved not to have been described in the literature, and we have called it tansanin.

The IR spectrum of (I) (Fig. 1) contains absorption bands at ( $cm^{-1}$ ) 1765 (C=O of a  $\gamma$ -lactone), 1710 (ketone carbonyl), and 1670 (C=C). Its UV spectrum (taken in ethanolic solution) exhibits maxima at  $\lambda_{max}$  210 and 295 nm ( $\log \epsilon$  4.11 and 2.39, respectively) showing the presence of conjugation of the lactone ring and of an isolated carbonyl group.

The PMR spectrum of (I) (Fig. 2, taken in deuteropyridine) showed the signals of the protons of a secondary methyl group (doublet, 0.85 pp,  $J = 7$  Hz) and of a methyl group on a double bond (singlet, 1.40 ppm). The signal of the lactone proton appeared in the form of a multiplet at 3.64 ppm. In the 5.52 and 6.27 ppm regions there were two one-proton singlets assigned to an exocyclic methylene group. In addition, this region of the spectrum contained the signal of an olefinic proton (triplet, 5.29 ppm,  $J = 9$  Hz).

By comparing the UV, IR, and PMR spectra of tansanin with the spectra of the ketopelenolides [2, 3], we came to the conclusion that tansanin also has germacrane carbon skeleton and differs only by the constituent at  $C_{11}$ . To confirm this, we performed catalytic hydrogenation in the presence of platinum oxide. Two substances were formed:  $C_{15}H_{24}O_3$ , mp 92-93°C,

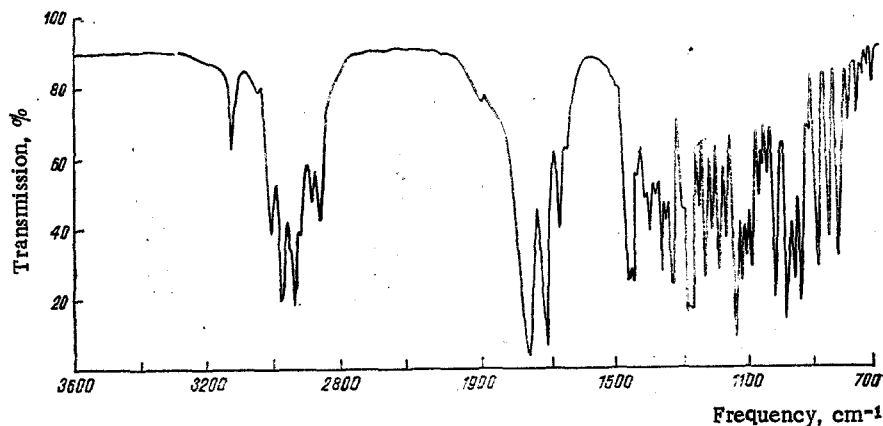


Fig. 1. IR Spectrum of tansanin.

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$M^+$  252, and  $C_{15}H_{22}O_3$ , mp 113–114°C,  $M^+$  250, and by their physicochemical constants these were identical with dihydroketopelenolide A and with ketopelenolide A, respectively.

Consequently, tansanin has the structure and configuration of 3-keto-4 $\beta$ ,6 $\beta$ (H)-germacra-1(10),11(13)-dien-6,12-olide.

Compounds (II),  $C_{17}H_{22}O_5$ , mp 186–187°C,  $R_f$  0.38, and (III),  $C_{15}H_{20}O_4$ , mp 178–179°C,  $R_f$  0.24 corresponded to the known lactone cumambrin A and cumambrin B.

Substance (IV),  $C_{15}H_{20}O_4$ , mp 232°C (preheated metal block), with  $R_f$  0.15, formed a monoacetate with the composition  $C_{17}H_{22}O_5$ , mp 215°C,  $M^+$  306. From its IR and PMR spectra, (IV) was identical with artecalin [4–6].

Substances (V),  $C_{15}H_{18}O_4$ , mp 164–165°C,  $R_f$  0.12, and (VI),  $C_{15}H_{18}O_4$ , mp 143–144°C,  $R_f$  0.10, were identified by direct comparison with authentic samples of rupicolin A and rupicolin B, respectively [7–8].

This is the first time that any of the known lactones have been isolated from this plant.

#### EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer (KBr), UV spectra on a Hitachi spectrometer, mass spectra on a MKh-1303, and PMR spectra on a JNM-4H-100 MHz instrument the chemical shifts being given on the  $\delta$  scale from the signal of HMDS taken as 0. Thin-layer chromatography (TLC) was performed on Silufol-UV-254 plates, and the spots were revealed with sulfuric acid containing 1% of vanillin. The eluent used was benzene-methanol (9:1). The results of elementary analyses corresponded to the calculated figures.

**Isolation of the Lactones.** The epigeal part of *Tanacetum santolina* (16 kg) was extracted with chloroform (1:5) five times for 24 h each, and the solvent was distilled off in vacuum. The yield of chloroform resin on the air-dry weight of the plant was 3.5%. The resin was treated with 40%, and then with 70%, ethanol. The lactones were extracted from the 40% ethanolic solution with benzene and chloroform. The benzene-extracted resin (78.9 g) was chromatographed on neutral alumina (activity grade IV) at a ratio 1:30. It was eluted with hexane and hexane-benzene (9:1) with a gradual increase in the concentration of the benzene.

Fractions with a volume of 700 ml each were collected. Tansanin was isolated from fractions 6–8 and cumambrin A and cumambrin B, respectively, from fractions 16–24 and 30–43. The benzene eluates yielded artecalin (fractions 60–65), rupicolin A (fractions 72–80), and rupicolin B (fractions 92–104).

**Hydrogenation of Tansanin.** A mixture of 70 mg of tansanin in 5 ml of ethanol and 10 mg of  $PtO_2$  was hydrogenated for 30 min. After the catalyst and ethanol had been eliminated, a noncrystallizing product was obtained which, on TLC, gave two spots with  $R_f$  0.63 and 0.65. By chromatography on a column (45 cm  $\times$  1 cm) containing KSK silica gel with hexane-ethyl acetate (9:1), 18 mg of tetrahydrotansanin with mp 92–93°C and 10 mg of dihydrotansanin with mp 113–114°C were isolated.

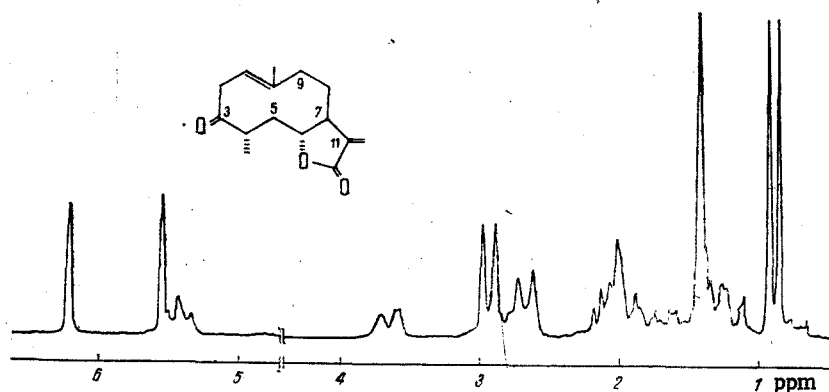


Fig. 2. PMR spectrum of tansanin.

## SUMMARY

A new sesquiterpene lactone  $C_{15}H_{20}O_3$  with mp 131-132°C, which has been called tansanin, and the known sesquiterpene lactones cumambrin A, cumambrin B, artecadin, rupicolin A, and rupicolin B have been isolated from the epigeal part of *Tanacetum sanitolina* C. Winkl.

On the basis of spectral characteristics and conversion into the known ketopelenolide A, the structure and configuration of 3-keto-4 $\beta$ ,6 $\beta$ (H)-germacra-1(10),11(13)-dien-6,12-olide have been established for tansanin.

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## MASS SPECTRA OF ARTABIN, HANPHYLLIN, AND SOLONITOLIDE

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The processes of fragmentation of the germacranolides artabin, hanphyllin, and solonitolide have been considered from the points of view of various methods of migration of the  $\pi$ -bonds of the ten-membered macrocycle, such as the retrodiene reaction, and the MacLafferty and Cope rearrangements. The occurrence of a thermal rearrangement has been detected for artabin. The influence of the additional OH group in the solonitolide molecule on the nature of its fragmentation is discussed.

The absence of a preferred direction of fragmentation under electron impact for the majority of sesquiterpene lactones creates certain difficulties both in establishing their structures and in elucidating the laws of fragmentation of these compounds. Even the germacranolides do not form an exception in this sense. The presence of two  $\pi$ -bonds in a ten-membered ring, on the one hand, ensures the stability of the molecular ions. The possibility of double-bond migration in them is one of the reasons for the multiline nature of their spectra. In addition to the probable formation of fragments with identical composition from different sections of the germacrane skeleton, an additional complication is introduced by the multiplet nature of practically each one of the main peaks of the spectrum under high-resolution conditions. Of course, measurements of the fine masses of the ions and the introduction of chemical and isotopic labels will lead to the elucidation of the origin of almost all the component multiplets. However, in essence, the most characteristic directions of fragmentation cannot be isolated, and this all the more because of the introduction of substituents into different positions of a skeleton considerably changes the overall pattern of the spectrum.

All of the above-mentioned features of the spectra of the germacranolides appeared in an investigation of costunolide (I) and its derivatives [1, 2]. The authors concerned analyzed the elementary compositions and relative intensities of the components of the multiplets corresponding to the elimination of chains of 1-6 carbon atoms from the  $M^+$  ions. Other authors

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