SESQUITERPENE LACTONES OF Tanacetum vulgare

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The sesquiterpene lactones tanacetin, 1β-hydroxyarbusculin A, and reynosin have been isolated from Tanacetum vulgare L. (common tansy) previously [1, 2]. We have studied the lactones of the same plant collected during the period of flowering in the environs of the town of Lepsinsk (Kazakh SSR). The dried epigeal part (14 kg) was extracted with chloroform. The concentrated extracts were treated with 50% ethanol and the precipitate that formed was precipitated off. The lactones were extracted from the aqueous ethanolic solution with chloroform, the chloroform extracts were combined, and the solvent was distilled off in vacuum. The residue (94 g) was chromatographed on a column of type KSK silica gel and was eluted with hexane–ethyl acetate with a gradient increase in the concentration of the latter. The following lactones were isolated:

I. $C_{20}H_{26}O_5$, mp 209–211°, M^+ 346, R_f 0,82; yield 1.2 g.
II. $C_{15}H_{18}O_4$, mp 167–168°, M^+ 262, R_f 0,64, yield 6.7 g.
III. $C_{15}H_{20}O_4$, mp 160–161°, M^+ 264, R_f 0,60, yield 2.5 g.
IV. $C_{15}H_{20}O_4$, mp 158–159°, M^+ 264, R_f 0,57, yield 4.3 g.

The R_f values were determined on Silufol plates in ethyl acetate.

On the basis of mixed melting points with authentic samples and a comparison of their IR spectra, lactones (I), (II), and (IV) were identified as chrysanin [3], tamirin [4], and tanachin [5], respectively. A sample of tamirin was kindly provided by V. A. Mnatsakalyan and L. V. Revazova.

Lactone (III) [$C_{15}H_{20}O_4$, mp 160-161°C (from hexane–ethyl acetate), $[\alpha]_D^{25}$ −32°C 1.0; methanol)] proved to be new and we have called it tavulin. The IR spectrum of tavulin has absorption bands at 3370 cm^{-1} (OH group), 1760 cm^{-1} (carbonyl of a γ-lactone), and 1670 cm^{-1} (double bond); and the mass spectrum has peaks with the following m/e values: 264 (M^+), 246 ($M - H_2O$), 236 ($M - CO$), 231 ($M - H_2O - CH_3$), and 228 ($M - 2H_2O$). This nature of the fragmentation shows the presence of two hydroxy groups in the molecule of (III).

The PMR spectrum of tavulin (taken on a JNM-4H-100/100 instrument in C_5D_5N, δ scale, 0 – HMDS) has three-proton singlets at 1.56 and 1.80 ppm belonging to two methyl groups at double bonds. Two doublets in the regions of 5.1 ppm (1 H, J = 10 Hz) and 5.27 ppm (1 H, J = * Hz) correspond to olefinic protons, and a doublet at 6.72 ppm (1 H, J = 5 Hz) to the signal of the proton of a hydroxy group. In this part of the spectrum two more signals appear, at 6.4 ppm (2 H) and 6.24 ppm (1 H) (the protons of an exocyclic methylene group and of a secondary hydroxy group).

The signals of the hemihydroxylic protons and of the lactone proton are superposed and appear in the form of a multiplet at 4.45-4.85 ppm.

Both hydroxy groups are secondary, as was confirmed by the acetylation of tavulin with acetic anhydride in the presence of pyridine. This gave diacetyltavulin (V), $C_{19}H_{24}O_6$, mp 204°C (from ethanol), M^+ 348. The IR spectrum of (V) lacks the absorption bands of hydroxy groups. The PMR spectrum of (V) clearly shows the signal of a lactone proton in the form of a doublet at 4.76 ppm (J = 10 Hz). This shows the trans linkage of the lactone ring relative to the ten-membered ring.

The reduction of (V) with $NaBH_4$ in methanol gave dihydrodiacetyltavulin (VI), $C_{19}H_{26}O_6$, mp 184-185°C, M^+ 350. The PMR spectrum of (VI) lacked the signals of the protons of the exocyclic methylene group and contained a doublet at 1.28 ppm (J = 7 Hz) due to a secondary methyl group, and its IR spectrum (1780 cm^{-1}) showed that the γ-lactone ring was saturated.

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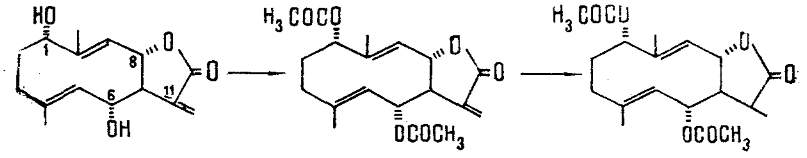
A comparative study of the PMR spectra of tavulin and its derivatives and of tanachin [5] showed that these lactones differ only by the substituent at C_{10}. Apparently, tavulin is isomeric with tatridin A [6-8] and is 1,6α-dihydroxy-1β,6β,7α,8β-H-germacra-4,9,11(13)-trien-8,12-olide:



III V VI

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STEROID GLYCOSIDES

XXII. ROCKOGENIN GLYCOSIDES

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The preparation from the leaves of Agava americana of glycosides of hecogenin – agavosides – has been reported previously. This plant is one of the sources of steroid glycoside. However, in view of the detection of ever new properties of representatives of this class [2] it is necessary to seek other methods for extending the variety of steroid glycosides.

In the present communication we describe new glycosides obtained by the chemical modification of agavosides A, B, and C[1]. These compounds were treated with $NaBH_4$ in methanolic solution at 50°C for three hours.

The reaction products were freed from inorganic impurities on Sephadex LH-20 (eluent CH_3OH) and from residues of the starting material on a column of silica gel in the $CHCl_3-CH_3OH-H_2O$ (13 : 5 : 1), system. In all cases the yield was not less than 90%.

The reduction of the keto group in the genin of the agavosides – hecogenin – that took place as the result of the reaction was shown by a study of the products of complete acid hydrolysis of the new compounds. In all cases, the aglycone isolated was identified as rockogenin from its melting point (217-220°C), $[\alpha]^{20}_D$ value (63°), and its R_f value in the presence of an authentic sample [3].

The study of the monosaccharide fraction of the hydrolyzate by paper chromatography and GLC of the aldononitrile acetates derived from the monosaccharides show that the carbohydrate moiety in each of the glycosides had remained unchanged.

Below we give the physicochemical characteristics of the rockosides (aglycone – rockogenin):

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