MASS SPECTRA OF ACETYLATED PENNOGENIN GLYCOSIDES

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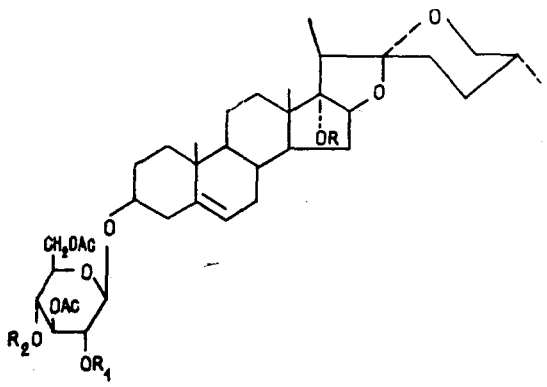
Continuing investigations of the mass spectra of glycosides of the spirostanol pennogenin [1], we have obtained the spectra of the acetylated derivatives (I-VII).



I. R=H; R_1=$(OAc)_3Rha_p$; R_2=$(OAc)_3Ara_f$

II. R=H; R_1=R_2 =$(OAc)_3Rha_p$

III. R=H; R_1=$(OAc)_3Rha_p$; R_2=Ac

IV. R=H; R_1=Ac; R_2=$(OAc)_3Rha_p$

V. R=H; R_1=R_2=Ac

VI. R=Ac; R_1=$(OAc)_3Rha_p$; R_2=$(OAc)_3Ara_f$

VII. R=Ac; R_1=R_2 =$(OAc)_3Rha_p$

The informativeness of these spectra is higher, since unlike those of the native glycosides, all the spectra contain the M^+ peaks. In addition to these, the products of the successive splitting out of carbohydrate units are clearly isolated in the spectra, which creates the prerequisites for deducing the structure of unknown compounds.

The fragmentation of the acetylated carbohydrate units proceeds in two alternative directions [2], which have been shown by the method of metastable defocussing. In one case, $(OAc)_3 \cdot Rha_p$ is split out with the loss by the molecular ion of 273 amu (in compounds (I) and (VI) the splitting out of $(OAc)_3Ara_f$ with the loss by M^+ of 259 amu also takes place); in the other case, $(OAc)_3Rha_pO$ is split out with the loss of 289 amu (in compounds (I) and (VI) of $(OAc)_3Ar_fO$ with the loss of 275 amu).

The splitting out of $(OAc)_3Rha_pO$ from M^+ in the case of compound (III) takes place with the migration of hydrogen to the ejected fragment with the formation of an ion having m/z 700, in contrast to the similar process in compound (IV), in which an ion with m/z 701 is formed.

In the acetates of trisaccharides, the splitting out of the second pyranose ring takes place less intensively than of the first and leads to the formation of ions with m/z 658 (I and II).

All the spectra contained the peaks of the ions of the carbohydrate units [2] and also those of the products of their fragmentation.

In the literature [1, 3], reference is made to the presence in the spectra of unesterified glycosides of ions formed by the breakdown of the terminal pyranose rings at C–C and C–O bonds. We detected similar decompositions in the spectra of compounds (I-VII).

The spectra of compound (I): 1206 (M^+; 0.01); 1188 (M − H_2O; 0.08); 1173 (1188 − CH_3 0.02); 1146 (M − AcOH; 0.02); 1116 (M − b − H_2O; 0.02); 1072 (C − H_2O; 0.01); 1000 (B − H_2O 0.01); 944 (A − H_2O; 0.02); 931 (M − $(OAc)_3Ara_fO$; 0.11); 777 (M − AglO; 0.04); 743 (P; 0.02); 687 (A; 0.04); 685 (M − $(OAc)_3Ara_fO$ − $(OAc)_3Rha_p$; 0.03); 561 (0.25); 547 (0.7); 426 (AglOH − 4H; 10.4); 412 (10.4); 395 (11.3); 379 (0.44); 377 (0.61); 340 (0.88); 298 (2.80); 287

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(1.31); 273 (31.1); 269 (2.06); 259 (20.7); 257 (1.84); 241 (1.31); 239 (1.75); 214 (3.85); 213 (7.00); 199 (3.15); 197 (3.5); 171 (9.1); 153 (100.0); 126 (93.2).

Experimental Procedure. MKh 1310 mass spectrometer; SVP-5 system for direct introduction of the sample; temperature of the heater bulb and ionization chamber 150-200°C; collector current 40 μA; ionizing voltage 50 V. The masses of the ions were determined with an accuracy of $5 \cdot 10^{-6}$, the reference substance being perfluorokerosine.

LITERATURE CITED

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HEDERAGONIC ACID FROM *Dipsacus azureus*

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Triterpene glycosides — dipsacosides A and B — have been isolated previously from the roots of *Dipsacus azureus* Schrenk [1, 2].

We have studied the roots of *D. azureus* collected in the Chimgan mountains, Tashkent province. The ground raw material (5 kg) was extracted with chloroform at room temperature. After the chloroform had been evaporated off, a resinous mass (225 g) was obtained in which by TLC in the ethyl acetate—ethanol—water (100:17:13) system the spots of four substances were detected, with R_f 0.65, 0.70, 0.75, and 0.9.

Part of the chloroform extract (50 g) was chromatographed on a column of cellulose powder with elution by petroleum ether. The fractions containing triterpenoids were rechromatographed on a column of type KSK silica gel with chloroform as eluent. This gave a compound (R_f 0.70) with mp 214-216°C (from methanol) and $[\alpha]_D^{24}$ +60.4 ± 2° (s 1.01; chloroform). Its molecular weight (M^+ 470, corresponded to the composition $C_{30}H_{46}O_4$.

The presence in its PMR spectrum (100 MHz, C_5D_5N, δ, ppm, 0 — HMDS) of the signals of the protons of six methyl groups (0.81-1.07 ppm), of an olefinic proton at a trisubstituted double bond (5.39 ppm), and also the fragments formed in mass-spectrometric decomposition (peaks with m/z 248, 222, and 203) indicated that the substance which we had isolated was a triterpenoid of the olean-12-ene series.

The triterpenoid contained a primary hydroxy group, as was shown by two one-proton doublets in the PMR spectrum at 3.51 and 3.88 ppm with a spin-spin coupling constant of ^2J = 10 Hz.

In the spectrum of the acetyl derivative, which was obtained in amorphous form, these protons appeared in the shape of a singlet in the 4.17 ppm region.

On the IR spectrum of the substance, in addition to absorption bands in the 3380-3450 cm^{-1} region, bands were observed of a six-membered cycic ketone (1715 cm^{-1}) and of the carbonyl of a carboxy group (1695 cm^{-1}).

A peak in the mass spectrum with m/z 222 clearly showed that the hydroxy and keto groups were localized in rings A and B.

From its spectral characteristics, the substance that we have isolated corresponded to hederagonic, or 23-hydroxy-3-oxolean-12-en-28-oic, acid. This triterpenoid has been detected previously by Rastogi et al. in *Viburnum erubescens* (family *Caprifoliaceae*) and *Caltha polustrus* (family *Ranunculaceae*) [3, 4].

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