SECONDARY-ION MASS SPECTRA OF PENNOGENIN GLYCOSIDES

Yu. M. Mil'grom, Ya. V. Rashkes, L. I. Strugina, and V. L. Sadovskaya

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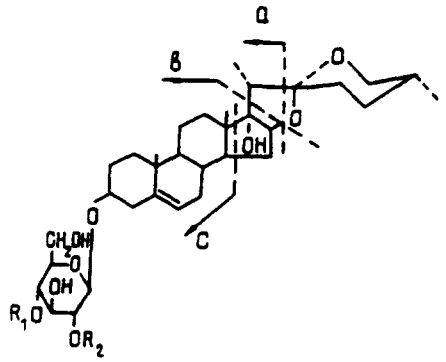
LSIMS mass spectra of pennogenin glycosides have been studied; the most characteristic ions are $(M + H - H_2O)^+$ (with glycerol as the liquid matrix) and $(M + Na)^+$ (with glycerol + NaCl as matrix). In both cases the peaks of ions formed as the result of the successive elimination of the carbohydrate units, the breakdown of the bonds of the terminal pyranoses, the cleavage of the bonds of the rings D and E, and the peaks of the ions Agl^+ and $(Agl - H_2O)^+$ were observed.

By studying the mass spectra of pennogenin glycosides we have established that the stability of these compounds under electron impact is determined not only by the number of carbohydrate units but also by their nature [1]. In the search for a more reliable method of determining molecular masses, we have dwelt upon secondary-ion mass spectrometry (LSIMS) [2] which has been used successfully for the analysis of spirostanol tetra- and pentaosides [3].

The LSIMS mass spectra of five pennogin glycosides – the 3-O-β-D-glucopyranoside (I), the progenin (II), and polygonatosides B^3 (III), C^2 (IV), and C^1 (V) – were obtained with the use as liquid matrices of pure glycerol and glycerol with the addition of NaCl. The main characteristic ions of these spectra are given in Table 1.



I. $R_1 = R_2 = H$
II. $R_1 = \alpha$-L-Rha$_p$; $R_2 = H$
III. $R_1 = H$; $R_2 = \alpha$-L-Rha$_p$
IV. $R_1 = R_2 = \alpha$-L-Rha$_p$
V. $R_1 = \alpha$-L-Ara$_f$; $R_2 = \alpha$-L-Rha$_p$

The spectra of glycosides (II), (IV), and (V) obtained using the glycerol matrix did not show the peaks of the $(M + H)^+$ ions, while in the spectra of compounds (I) and (III) these peaks were greatly inferior in intensity to the peaks of the $(M + H - H_2O)^+$ ions. This feature of the spectra was apparently due to the presence of an OH group at C-17 in each of the molecules of compounds (I-V). The molecular region of the spectra obtained by the use of the "glycerol + NaCl" matrix contained the peaks of the $(M + Na)^+$ and $(M + H - H_2O)^+$ ions.

The Agl^+ and $(Agl - H_2O)^+$ ions with m/z 413 and 395 were identically characteristic for the spectra recorded with the use of both matrices, but in the case of the employment of the glycerol matrix they were relatively more intense. In the same spectra, the peaks of ions in the protonated aglycon with m/z 413 had a low intensity, in contrast to the lycotetraosides of the spirostan series [3]. In some of the spectra (with glycerol + NaCl as matrix),

Institute of Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. All-Union Scientific-Research Institute for Agricultural Biotechnology, All-Union Academy of Agricultural Sciences, Moscow. Pacific Institute of Bioorganic Chemistry, Far Eastern Branch, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 523-525, July-August, 1991. Original article submitted September 3, 1990; revision submitted February 7, 1991.

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TABLE 1. Characteristic Ions Observed in the LSIMS Spectra of Compounds (I)-(V) when using a Glycerol Matrix and a Glycerol + NaCl Matrix

Compound	Glycerol			Glycerol + NaCl				Other ions
	$(M+H)^+$	$(M+H-H_2O)^+$	A	$(M+Na)^+$	$(AglOH+Na)^+$	$(Agl-H+Na)^+$	A	
I	593	575	441	615	453	435	481	575,413(Agl)$^+$, 395(Agl$-H_2O)^+$ 281 269,251,213
II	—	721	603	761	—	—	643	721,615(761$-Rha_p$ $+H)^+$, 575(721 $-Rha_p+H)^+$, 413,395,281,269, 251,213
III	739	721	603	761	453	435	643	615,575,413,395, 281,269, 251,213
IV	—	867	749	907	453	435	789	761(907$-Rha_p+$ $H)^+$, 743(761$-$ $H_2O)^+$, 721(867$-$ $Rha_p+H)^+$,703(721 $-H_2O)^+$,575,413 395,281,269,251, 213
V	—	853	749 735	893	—	—	789 775	761(893$-Ara_f$ $-H)^+$, 747(893$-$ $Rha_p+H)^+$, 743, 721(853$-Ara_f+$ $H)^+$,707(853$-$ $Rha_p+H)^+$, 703, 689,575,413,395, 281,269,251,239, 213

the peaks of the ions $(AglOH + Na)^+$ with m/z 453 and of the products of their dehydration with m/z 435 appeared (Table 1).

In all the spectra, without exception, the peaks of ions characterizing processes of the successive elimination of the carbohydrate units were observed, but when a glycerol matrix was present the peaks of the corresponding ions (m/z 575, 707, 721) were more intense than the peaks of analogous origin in the spectra obtained with the use of the glycerol + NaCl matrix (m/z 615, 747, 761).

An unusual property of the spectra under consideration is the cleavage at the C_5–O and C_1–C_2 of the terminal pyranose units [in compound (V) the terminal furanose undergoes cleavage at the C_4–O and C_1–C_2 bonds] (ions A), which is characteristic for the electron-impact spectra of these compounds [1]. It leads to the splitting out from the $(M + H - H_2O)^+$ or the $(M + Na)^+$ ions of fragments with 134, 118, and 104 m.u. when glucose, rhamnose, and arabinose, respectively appear as the terminal units.

All the spectra contained the peaks of ions characterizing the breakdown of the aglycon moiety of the molecule at bonds of rings D and E after the loss of the carbohydrate units. An ion with m/z 281 may be considered a consequence of breakdown of type a in the $(Agl - H_2O)^+$ ion with m/z 395. Ions with m/z 269 and 251 arise on fragmentation of type b, and an ion with m/z 213 by that of type c. Ions with the given mass numbers are characteristic in the EI spectra of compounds (I)-(V) [1].

At the same time, in the secondary-ion spectra of compounds (I)-(V) there were no peaks of ions characterizing the carbohydrate moiety of the molecules (in contrast to the spectra of the lycotetraosides of the spirostan series [3] in which they were of considerable intensity).

Thus, in the case of the LSIMS spectra of pennogenin glycosides it can be seen that mass spectra of this type give substantial information of the molecular masses and structures of the carbohydrate and aglycon moieties of the molecules. One more characteristic feature of the LSIMS spectra must be mentioned – the possibility of clearly fixing the presence of impurities of the same nature as the known compound. Thus, in the spectra of

progenin (II), in addition to the peak of an ion with m/z 721 $(M + H - H_2O)^+$ of the main component there were the peaks of ions with m/z 735, 737, 753 (with glycerol as the matrix), and, together with the peak of the $(M + Na)^+$ ion with m/z 761 there were the peaks of ions with m/z 775, 777, and 793 (with glycerol + NaCl as the matrix). Their intensities amounted to 40-70% of the intensity of the peak of the ion with m/z 761. This fact showed the presence of impurities with molecular masses of 752, 754, and 770.

The auxiliary compounds are products of the oxidation of aglycon moiety of progenin (II), since in the central part of the spectrum of this compound there are the peaks of the corresponding ions with m/z 427, 429, and 445, the first of which is the strongest. This agrees with the presence in the EI spectrum of progenin (II) of the peak of an ion with m/z 426 in the composition of which there are four hydrogen atoms fewer than in the M^+ ion of pennogenin. Consequently, this ion may be the product of the dehydration of the aglycon part of a molecule containing a larger number of OH groups than pennogenin.

EXPERIMENTAL

The LSIMS mass spectra were obtained on a Hitachi M-80A mass spectrometer (Japan) at a resolving power of the instrument of 1000, with an accelerating voltage of 3 kV. The collection of the results and their processing were performed with the aid of a M-003 computer system. Glycerol and glycerol with the addition of trace amounts of an aqueous solution of NaCl were used as the matrices. The target was bombarded with a beam of Xe^+ ions having an energy of 8 keV.

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TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS

XXXIX. CYCLOARALOSIDE D FROM Astragalus amarus

M. I. Isaev

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The structure of a triterpene glycoside of the cycloartane series – cycloaraloside D, isolated from the roots of Astragalus amarus Pall. (Leguminosae) – has been established on the basis of chemical transformations and spectral characteristics. Cycloaraloside D is 20R,24S-epoxycycloartane-3β,6α,16β,25-tetraol 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranoside].

Continuing a study of glycosides of Astragalus amarus Pall. (Leguminosae), we have established the structure of substance 7 [1], which we have called cycloaraloside D (I).

The presence in the PMR spectra of glycoside (I) of two one-proton doublets interconnected in the manner of an AB system, at 0.19 and 0.55 ppm, permitted the glycoside under consideration to be assigned to the triterpenoids of the cycloartane series [2, 3]. This conclusion was confirmed by the formation of cyclosieversigenin (II) on the acid hydrolysis of glycoside (I).

In the carbohydrate fraction of a hydrolysate, D-glucose and L-rhamnose were detected by PC and GLC [4]. GLC showed the glycoside (I) contained one residue each of these monosaccharides.

Institute of Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent.

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