NEGATIVE- AND POSITIVE-ION MASS SPECTRA OF ARYL GLYCOSIDE ACETATES

Yu. N. El'kin, V. G. Voinov, and Ya. V. Voznyi

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The low specificity of the electron-impact positive-ion mass spectrum in relation to the structure of an aromatic aglycone has been shown. The glycosidic moiety is determined unambiguously from the pattern of the mass spectrum. The dissociative electron-capture mass spectra are sensitive to the nature of the substituents of the aromatic nucleus of the aglycone. The influence of the aglycone is most pronounced in cases with substituents having high electron affinities.

Early results from the study of the laws of the breakdown under electron impact of aryl glycoside acetates amount to the following. Regardless of the nature of the aglycone, acylated aryl glycosides give very complex mass spectra. An aroxyl radical is readily split off from the molecular ion (M^+), and M^+ itself is not recorded [1]. The ion current is due to glycosyl-cationic products or, more accurately, their proportion in the total ion current is not less than 60% [2]. It has been noted that in the case of Me and Ac glycosides the yields of these ions are substantially smaller than those of the products of the splitting out of the the monosaccharide ring. The explanation of this phenomenon was based on the greater stability of an aroxyl radical as compared with the OMe and OAc radicals [3]. The peak of the ion characterizing the aglycone (Agl + OH) was determined by an accurate mass measurement. This was the only indication of the aglycone in the mass spectrum. The information given was obtained for the case of phenyl β-glucoside tetraacetate [2]. On the other hand, the mass spectra of derivatives of aryl glycosides with aglycones having complex structures contain both the M^+ peaks and also the peaks of Agl + OH ion. The existence of an ester bond in benzyloxycarbonylmethylphenyl aglycones is responsible for appreciable peaks of the M — OBzl ion [4]. It can be seen from the information given above that the products of the decomposition of glycosides under electron impact contain practically no ions determining the structure of the aglycone. This observation forced us to some extent, in later period, to use other methods for ionizing glycosides. The biological importance of glucuronides has stimulated the development of their analysis and control by the methods of mass spectrometry with chemical ionization [5] and with bombardment by fast atoms [6]. In the last-mentioned paper, in addition to cationic products, the anionic products were also studied. The negative-ion mass spectra from the bombardment of aryl glycosides with fast atoms include the peaks of the ions $[M - H]^-$ and $[Agl + O]^-$. The same ions unambiguously characterizing the size of the aglycone have also been detected in the dissociative electron-capture (DEC) mass spectrum of phenyl glucoside tetraacetate [7]. As a study of the capture of thermal electrons by esters of glucose tetraacetate have shown, the yields of negative ions from the aglycone moiety predominate [8]. However, no results showing the structure of the aglycone were found. The question of whether it is possible to establish the position and nature of a substituent in the aromatic aglycone of an aryl glucoside from mass-spectrometric characteristics therefore remains open.

The positive-ion mass spectra of the aryl glycosides were practically insensitive to the aglycone, as already mentioned, since the proportion of the $[Agl + OH]^+$ ion was insignificant in the total ion current. If the internal energy of M^+ decreased, the positive ions produced by its breakdown contained not only the glycosyl moiety but also, to a considerable extent, the aglycone moiety. Further, the yields of ions from the aglycone moiety were correlated with Hammett constants for the substituents of the aromatic aglycone. These results were obtained from the field-ionization mass spectra of unmodified aryl glycosides with substituents of different types in the aromatic nucleus of the aglycone [9]. The differences in the yields

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TABLE 1. Electron-Impact Mass Spectra (partial) of Per-O-Ac Aryl Aldopyranosides 1-12, %

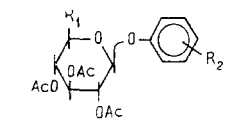
Ion	1	2	3	4	5	6	7	8	9	10	11	12
A_1	22	43	10	24	12	35	30	33	74	47	11	0,5
A_2^1	0,4	0,6	0,2	0,3	0,3	—	0,4	—	1,6	—	0,1	0,7
A_2	6	0,9	3,1	3,6	3	11	6	6	25	7	2,6	—
A_3^1	3,3	4,6	2,2	3,3	2,6	36	19	19	27	19	2,5	1,4
A_3	5	4,3	3,1	2,6	3,2	78	66	70	100	74	3,4	0,4
A_4^1	100	100	100	100	100	100	100	100	91	100	100	—
A_4^2	2,6	3,2	3,1	3,0	2,8	10	12	12	6	12	2,8	c
A_4	—	—	—	—	—	16	41	44	20	47	—	—
A_5^1	60	68	86	70	87	—	—	—	—	—	88	c
A_5^2	25	38	30	26	-	—	—	—	—	—	34	—
E_3	7	5	7	7[a]	8	—	—	—	—	—	7	8
C_1	2	1,5	0,9	1,2	0,8	2[b]	1,3	1,3	2,7	1,9	0,8	42
C_2^1	4	7	5	9	5	3,2[b]	3,2	3,6	2,2	3,9	6	84
Agl +OH	40	25	2,7	3	3,6	3,8	44	58	3,4	35	13[d]	—
Agl +OAc	1,3	1,8	—	—	0,4	—	11	4,9	—	7	—	—

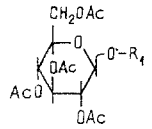
a) Agl + OH and E_3 have the same m/z value, and their yield was estimated for E_3 as an average for hexosides 2, 3, 5, and 11; b) C_1 and C_2^1, and A_3^1 and A_4^2, have the same m/z values, respectively, and the yields of C_1 and C_2^1 were estimated as the means for the 6-deoxyhexosides 8, 9, and 10; c) the yield was not estimated because of overlapping with other types of ions; d) for the chlorine-35 isotope.

of the negative ions $(Agl + O)^-$ in Table 2 [8] show that M^- is sensitive to the nature of the aglycone. On the basis of this information, we have suggested that it is possible from the DEC mass spectra to obtain information on the nature of a substituent in an aromatic aglycone, since the negative ions formed have no appreciable excess of internal energy.

Two groups of aryl glycosides were taken as model compounds. One group having substituents in the aromatic nucleus with nominally low electron affinities — H, CH_3, OCH_3 — and the other with high electron affinities — OAc, NO_2, Cl. The compounds studied had as the glycosyl moieties completely acetylated D-glucose, L-rhamnose, and D-arabinose residues (scheme). The electron-impact mass spectra in fact show that, regardless of the nature of the substituent in the aglycone and the type of glycosyl residue, the main proportion of the ion current was due to glycosyl cations of series A (Table 1). The M^+ peak was absent and, with the exception of compounds with a nitrophenyl aglycone, no fragments heavier than the A_1 ion were detected. Why is this? The reference made above to the stability of the aroxyl radical does not fully explain what takes place. In the spectrum of an analogue having no aglycone whatever, (12), the proportion of ions of series A amounted to only one percent of the total ion current and its main part was due to fragments of the monosaccharide ring. (See scheme on next plate.)

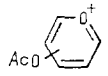
This contrast is due to the low-energy state of M^+ formed by the loss of π-electrons of the aromatic nucleus. This state is below the ionization energy of the oxygen atoms of the glycosyl residue. Consequently, the maximum of the distribution of molecular ions with respect to their internal energies is due to the energy of the state of the ionized aromatic nucleus. In these ions, the rapid cleavage of the glycosidic bond with the transfer of an electron to the aryl cation leads to the glycosyl cations of series A. The excess energy of the glycosyl residue of M^+ is sufficient only for low-energy rearrangements with the loss of ketene or acetic acid molecules, but not for the breakdown of the carbohydrate skeleton of



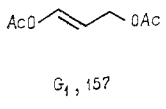


2. $R_1 = CH_2OAc$ $R_2 = H$
3. $R_1 = CH_2OAc$ $R_2 = o\text{-}OAc$
4. $R_1 = CH_2OAc$ $R_2 = p\text{-}NO_2$
5. $R_1 = CH_2OAc$ $R_2 = m\text{-}OAc$
6. $R_1 = H$ $R_2 = p\text{-}OAc$
7. $R_1 = CH_3$ $R_2 = p\text{-}Me$
8. $R_1 = CH_3$ $R_2 = o\text{-}OMe$
9. $R_1 = CH_3$ $R_2 = o\text{-}NO_2$
10. $R_1 = CH_3$ $R_2 = H$
11. $R_1 = CH_2OAc$ $R_2 = Cl$

1. $R_1 = 2\text{-Nph}$
12. $R_1 = H$



E_3, 139



A_1, 331

G_1, 157

the monosaccharide ring. Consequently, the mass spectrum of an aryl glycoside acetate consists of several peaks of A ions and of not one peak of an A_1 ion. In this connection one more fact must be mentioned. The mass spectra of the acetylated sugars are characterized by the peak of the acetoxonium ion with m/z 43, the intensity of which is an order of magnitude higher than the intensity of the fragmentary ions of the monosaccharide ring and is less than that of the strong peaks of rearranged acetoxonium ions with m/z 103 and 145. In the spectra of the acetylated aryl glycosides (1-11) their proportion is small in comparison with that which is observed in the mass spectrum of glucose tetraacetate (12), and also in the spectra of methyl and acetyl glycosides. The high yield of acetoxonium ions in the last three compounds is due to the predominant formation of molecular ions with localization of the charge on the oxygen atoms of the acetoxy groups. Thus, the mass spectrum of an aryl glycoside shows an aglycone with a low ionization energy but says nothing about the structure of the aglycone.

The DEC spectra of the compounds studied are given in Table 2. A consideration of this Table shows that the dissociation affects the ester and ether bonds in the substituents of the pyranose ring (OAc and OAgl). The most important results of our study of the DEC spectra of compounds (1-12) are given below.

1. The peaks of the negative ions $[M - H]^-$ are recorded. An exception is 2-naphthyl glycoside (1). The yield of $[M - H]^-$ ions depends strongly on the nature of the substituent in the aromatic nucleus of the aglycone. The presence of an ester bond in the aglycone — a OAc substituent — leads to the situation that in the case of compounds (5) and (6) only the $[M - H]^-$ ion is recorded. At the same time, the loss of Ac from the aglycone leads to the strongest peaks in the DEC spectra of these compounds. The negative ions $[M - Ac]^-$ are also formed at the expense of the acetoxy groups of the glycosyl residue. In this case, their yield is smaller and depends on the nature of the aglycones. In the spectra of the glycosides with a nitrophenyl aglycone (4, 9) the $[M - Ac]^-$ ion is not detected at all, just like the anion from the subsequent ejection of a ketene molecule. This reaction is completed by the degradation of the glycosyl residue of the aryl glycoside molecule. However, the dissociation of the molecules of Me and Ac glycosides [10] or of compounds (12) affects all four acetoxy groups. The product of the most far-reaching degradation is the $[M - Ac - CH_2CO - AcOH - AcOH]^-$ ion.

2. The yield of negative ions that are formed from the acetoxy group themselves $[H(OAc)_2]^-$ and $[OAc]^-$ does not depend appreciably on the nature of the aglycone, and the peaks due to them are the strongest for the aryl glycosides and also for the three glycosides mentioned

TABLE 2. Dissociative Electron-Capture Mass Spectra of Aryl Per-O-Ac-aldonopyranosides 1-12 with the Values of the Yields of the Anions at the Resonance Energy of Capture with the Maximum Cross-Section, %

Ion	1	2	3	4	5	6	7	8	9	10	11	12
M—H	—	10	P*	100	P*	P*	10	10	100	15	5	5
M—Ac	60	10	100	P*	100	100	70	45	P*	30	35	10
M—Ac—CH_2CO	30	10	70	—	70	20	30	25	—	15	25	P*
AcOHOAc	25	5	5	—	30	—	—	40	—	—	10	25
OAc	100	100	70	60	70	40	100	100	50	100	80	100
AgI+O	60	15	30	90	30	50	50	60	80	50	40	—
O_2	—	—	—	10	—	—	—	—	70	—	—	—
	—	—	—	40	—	—	—	—	20	—	—	—
	—	—	—	—	—	—	—	—	—	—	100	—

*The yields of negative ions are low, but they are recorded.

above. Consequently, the peak of the $[OAc]^-$ ion is taken as the main one for estimating intensities.

3. In the DEC products of the compounds studied the $[AgI + O]^-$ ion has an appreciable proportion and the peaks due to it possess an intensity of not less 30%. In the spectra of the nitrophenyl glycosides the intensity of the $[AgI + O]^-$ ion is even higher than that of the $[OAc]^-$ ion. The nature of substituents with high electron affinities — OAc, NO_2, Cl — is shown in a whole series of fragmentary negative ions, the product of the splitting out of these substituents or of atoms present in them. Some of them — $[M - Ac]^-$, NO_2^-, and Cl^- — are responsible for the strongest peaks in the DEC spectra.

4. The dissociation of M^- for sugar derivatives is more sensitive to stereochemical factors than the decomposition of M^+ under electron impact [10]. In actual fact, the spectra of both types of ions from o- and m-OAc-phenyl glycosides (3) and (5) are identical, but in the DEC spectrum of the ortho isomer there is a pronounced metastable peak corresponding to the transition

$$[M-43]^{-\cdot}\rightarrow[M-85]^- + CH_2CO,$$

i.e., the rate constant of the rearrangement reaction of the loss of a ketene molecule has a considerable component controlled by the geometry of the fragmenting $[M - OAc]^-$ ion. This observation confirms the sensitivity of rearrangement reactions to the geometry of feebly excited decomposing ions [11] and it is just the products of field, chemical, and electron-capture ionizations that have an insignificant excess internal energy.

EXPERIMENTAL

The preparation of compounds (1-10) has been described previously [2]. Compounds (11) and (12) were kindly provided by E. R. Novik (KhTI [Institute of Chemical Technology], Leningrad) and by N. I. Belogortseva (TIBOKh [Pacific Ocean Institute of Bioorganic Chemistry], Vladivostok), respectively. The mass spectra of the positive ions were recorded on a LKB-9000 chromato-mass spectrometer with introduction through a SE-30 column having a temperature over its whole length of 250°C (2, 3, 5-8, 10-12)) and by direct introduction into the ion source (compounds (1, 4, 9)). The dissociative electron-capture spectra were recorded on a RMU-6D mass spectrometer adapted for this purpose, also with the direct introduction of the substances into the ion source.

CONCLUSIONS

1. The study of dissociative electron-capture mass spectra has shown the possibility of establishing on their basis the nature and positions of substituents in the aromatic aglycones of aryl per-OAc-glycosides.

2. The nature of the glycosidic residue is clearly shown in the electron impact mass spectra.

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ALKALOIDS OF *Hypecoum erectum*. THE STRUCTURE OF HYPERECTINE

M. E. Perel'son, G. G. Aleksandrov,
L. D. Yakhontova, O. N. Tolkachev,
D. A. Fesenko, M. N. Komarova,
and S. E. Esipov

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The structure of a new spirobenzylisoquinoline alkaloid from *Hypecoum erectum* L. has been established by spectral methods and also by the x-ray structural analysis of its methiodide. It has been shown that the alkaloid, which has been called hyperectine, has a pentacyclic structure in which the tetrahydroisoquinoline fragment has the sofa conformation and the indan fragment the envelope conformation. The natural alkaloid is a mixture of the enantiomeric C-8(S), C-16(R), and C-8(R), C-16(S) forms.

In preceeding communications [1, 2] we have described the isolation from the herb *Hypecoum erectum* L. of two new alkaloids hypecorine and hypecorinine, the determination of their structure, and some of their transformations. In a further study of the alkaloid composition of this plant by fractional separation according to basicities we have isolated another new compound which has been called hyperectine. Hyperectine (I) is a yellow base with the composition $C_{24}H_{21}N_3O_6$, mp 237-238°C (decomp., from a mixture of methanol and chloroform), optically inactive. The alkaloid undergoes hydrolysis in an alkaline medium but is stable to acid hydrolysis and to acetylation with acetic anhydride. Its reaction with diazomethane formed a N-methyl derivative, $C_{25}H_{23}N_3O_6$, mp 258-259°C (decomp.).

The PMR spectra of hyperectine (Fig. 1 and Table 1) contained the signals of four aromatic protons located in pairs in the ortho and para positions with respect to one another, of two aromatic methylenedioxy groups, of a N-methyl group, of a methylene group located between an aromatic nucleus and a saturated quaternary carbon atom, and of three mobile hydrogen atoms.

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