FIELD-DESORPTION MASS SPECTRA OF FLAVONOID ACYLGLYCOSIDES.

II. NATURAL CINNAMOYL AND BENZOYL DERIVATIVES

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The field-desorption mass spectra of 14 flavonoid glycosides esterified with p-coumaric, ferulic, caffeic, p-hydroxybenzoic, and gallic acids have been studied. For all the compounds the molecular ions and the ions of the aglycone (A) were obtained as the main peaks. The spectra also contained a number of other fragmentary ions, including the ion of the acylated anhydrosugar. For flavonol glycosides in which the carbohydrate is esterified by cinnamic acids, the (A + Ac), and for the diacylglycosides the (A + 2 Ac), ions are diagnostic. The formation of these strong ions corresponding in mass to the molecules of the mono- and diacylated aglycone permits the assumption of the existence of acyl migration in the breakdown of the initial molecular ion.

Using a procedure described in the preceeding paper [1] we have measured and studied the field-desorption mass spectra (FD spectra) of a series of natural flavonoid glycosides esterified in the carbohydrate moiety with p-coumaric, caffeic, ferulic, gallic, and p-hydroxybenzoic acids.

Some conclusions from this work have been published previously in the form of theses [13] and have been used to some extent in the structural analysis (to confirm the composition) of a large group of flavonoid acylglycosides [14]. The literature contains details of the FD spectra of only three compounds of similar structure, of which one included a sinapic acid residue (kaempferol 3-(2"'-sinapoylsophoroside)-7-glycoside) [15], the second a gallic acid residue (quercetin 3-(2"-galloylglucoside)) [16], and the third a caffeic acid residue (quercetin 3-(6"-caffeoylgallactoside)) [17]. In the first two cases, the authors reported the presence of the molecular ions and the ions of the aglycone and of the acylated anhydrosugar in the spectra, and in the third FD-MS was used only to confirm the molecular formula.

Monohydroxycinnamoyl Derivatives of Monoglycosides of Flavonols and Flavones

In this group, we studied the FD spectra of six flavonol 3-glycosides acylated with p-coumaric or ferulic acids (1-6) and one flavone 7-glycoside acylated with caffeic acid (7); their structures are shown in Figs. 1 and 2:

Compound	Literature reference
1. Kaempferol 3-(2"-O-p-coumaroylarabinofuranoside) = 2"-coumaroyljuglanin	2
2. Kaempferol 3-(3"-O-p-coumaroylglucoside) = 3"-coumaroyl-astragalin	
3. Kaempferol 3-(6"-O-p-coumaroylglucoside) = 6"-coumaroyl-astragalin = tiliroside	3
4. Kaempferol 3-(6"-O-feruloylglucoside) = 6"-feruloylastragalin	
5. Kaempferol 3-(6"-O-p-coumaroylgalactoside) = 6"-coumaroyltrifolin	
6. Quercetin 3-(3"-O-p-coumaroylglucoside) = 3"-coumaroylisoquercitrin	6
7. 6-Methoxychrysoeriol 7-(6"-O-caffeoylglucoside)	
8. Kaempferol 3-(3",6"-di-O-p-coumaroylgalactoside) = 3",6"-dicoumaroyltrifolin	5

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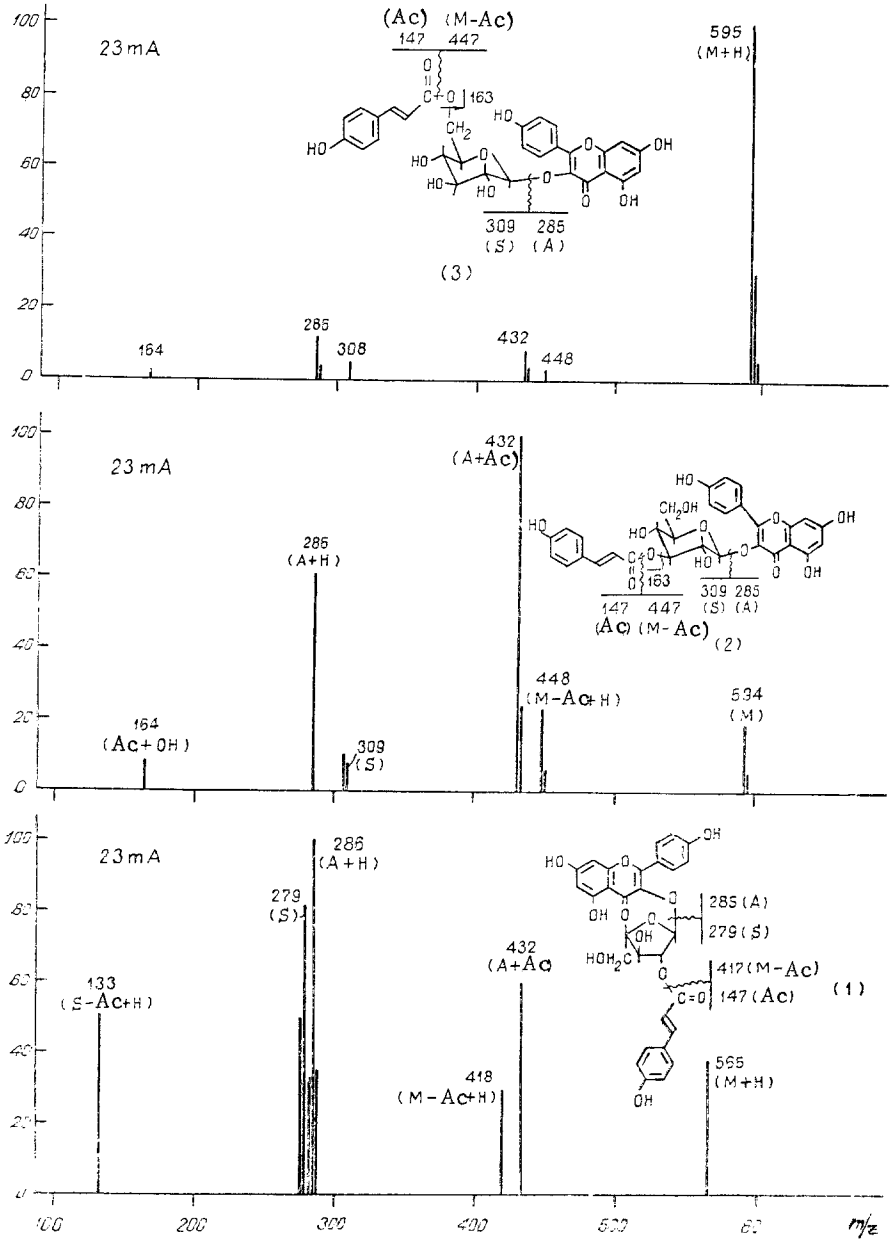

Fig. 1. FD spectra of compounds (1), (2), and (3).

	Compound	Literature reference
9.	Kaempferol 3-(3"-O-p-coumaroyl-6"-O-feruloylglucoside) = 3"-coumaroyl-6"-feruloylastragalin	4
10.	Quercetin 3-(3",6"-di-O-p-coumaroylglucoside) = 3",6"-di-coumaroylisoquercitrin	8, 9
11.	Quercetin 3-(6"-O-p-hydroxybenzoylgalactoside) = 6"-hydroxy-benzoylhyperin	10
12.	Myricetin 3-(2"-O-galloylrhamnoside) = 2"-gallomyricitrin	11
13.	Myricetin 3-(6"-O-galloylglucoside)	12
14.	Myricetin 3-(6"-O-galloylgalactoside)	12

For all the compounds (1-7) intense molecular (M) or (M + H) ions were obtained. In contrast to the acetylated flavonols [1], the FD spectrum of compounds (1-7) contained the peaks of the deacylated glycosides (the (M — Ac + H) ions). One of the main peaks in the

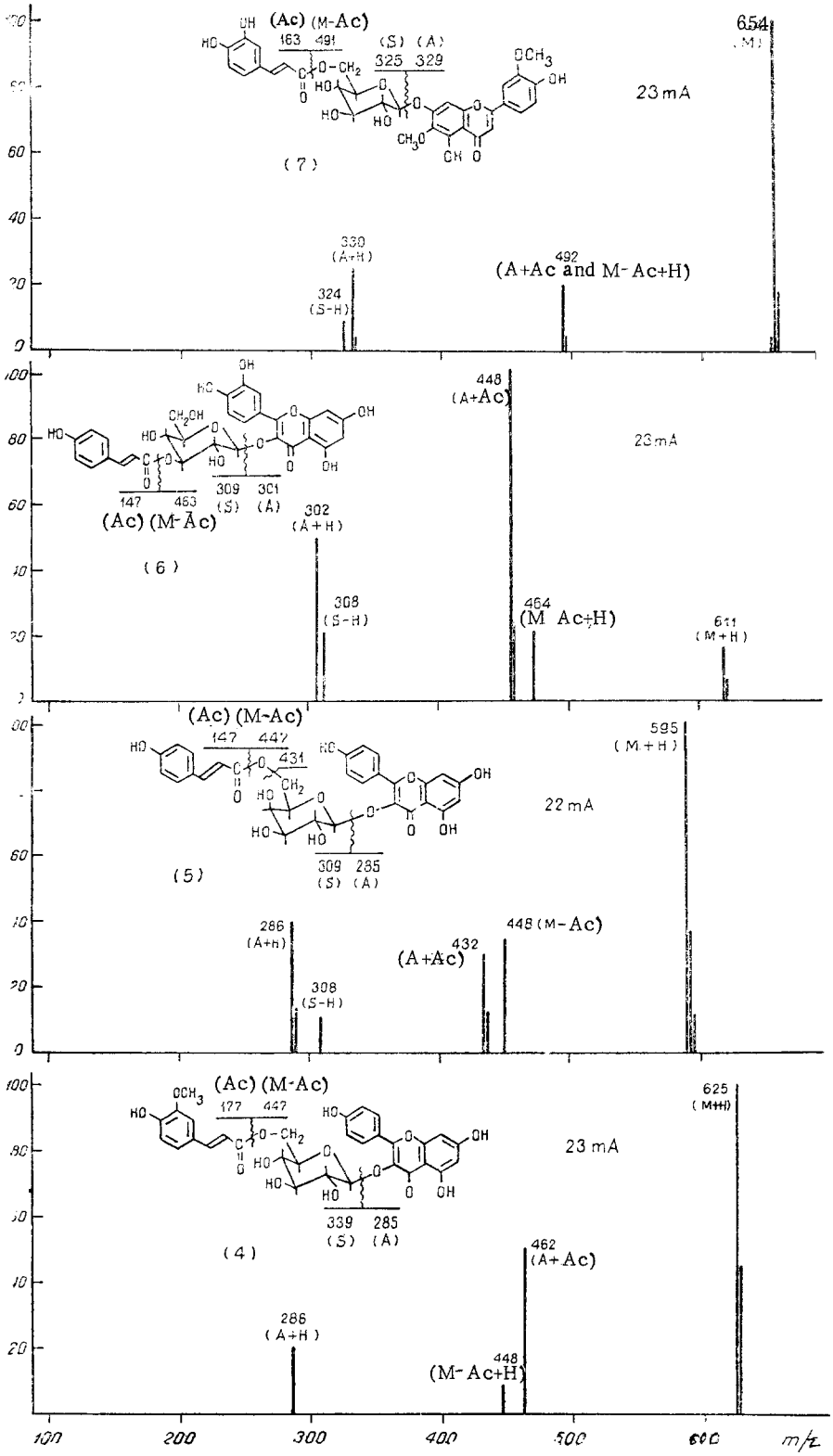

Fig. 2, FD spectra of compounds (4), (5), (6), and (7).

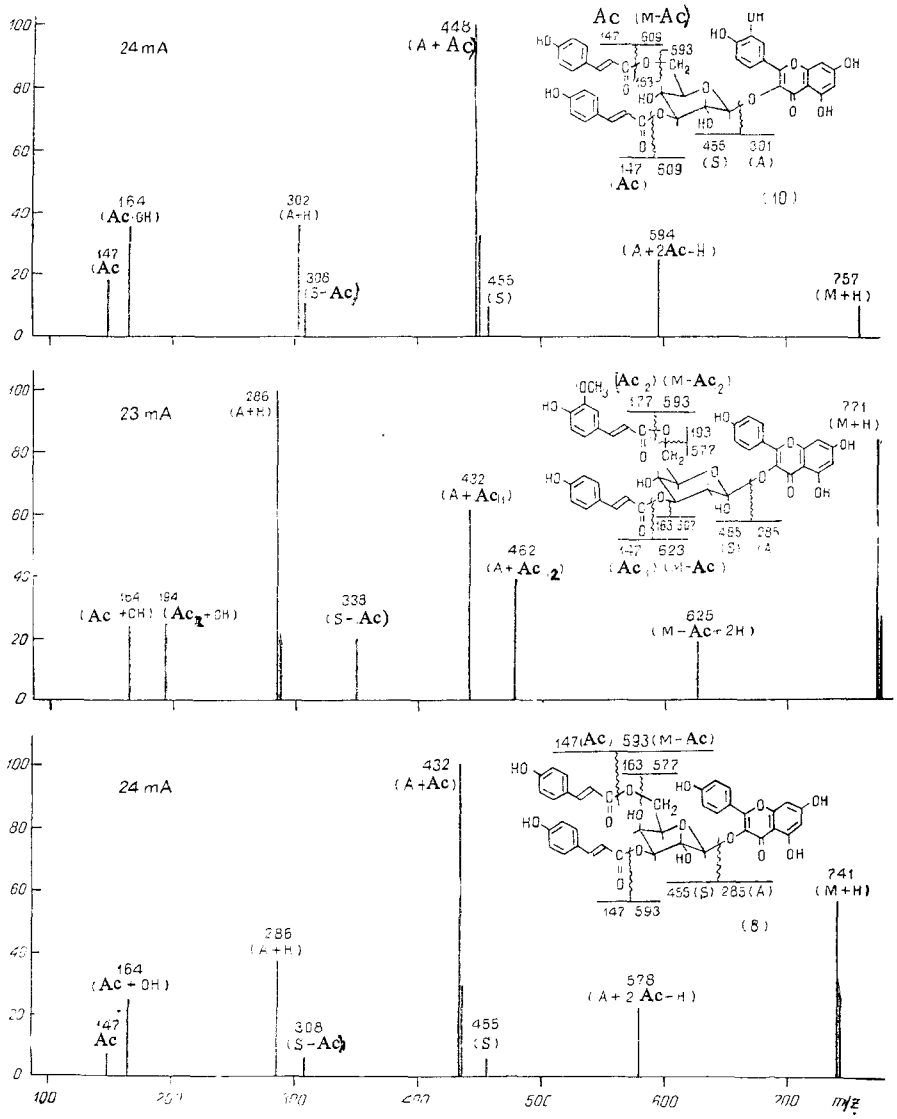

Fig. 3. FD spectra of compounds (8), (9), and (10).

spectra was that of the ion of the aglycone (A + H). Corresponding to its detachment from the molecule, the ion of the acylated anhydrosugar (S or (S − H)) was present in all the spectra but had a low intensity, with the exception of the fragmentation of the arabinofuranoside (1) where the intensity of the fragmentary peak S reached 80%. This spectrum also contained the ion of the deacylated anhydrosugar (S − Ac + H) (m/z 133, 51%). In individual cases, we observed the appearance of the ions of p-coumaric acid (m/z 164), which is the acylating agent.

But particularly interesting and unexpected was the fact which we discovered of the migration of an acyl residue from the carbohydrate moiety into the aglycone, leading to the appearance of ion with a mass corresponding to aglycone + acyl residue in the course of the ionization of the molecule. The corresponding rearrangement (A + Ac) peak is diagnostic for flavonoid glycosides acylated in the carbohydrate fragment by hydroxycinnamic acids.

In a number of substances the (A + Ac) and the (M − OAc + H) ions (compounds 2, 3, 5, and 6) or the (M − Ac + H) ions (compound 7) would have the same mass. However, in the case of compounds (1) and (4) these ions would have different masses, and only the ions with the (A + Ac) value of the mass were present in the spectra. Thus, it has been shown that in the process of field desorption acyl migration takes place, and this far more readily (the (A + Ac) ion has a greater intensity) in the case of the 2- and 3-O-acyl derivatives of the sugars than in the case of the 6- derivatives (for example, compare the 2- and 3- position isomers in Fig. 1).

With an increase in the anode heating current, the (A + Ac) ion became the main peak in the spectra, while in some compounds (4, 5) under these conditions the ion of the aglycone (A or (A + H)) was absent.

As was to be expected, in the case of a flavone 7-glycoside (7, Fig. 2), the molecular ion was very stable — its peak was the main one in the spectra over a wide range of variation of the current through the emitter (20, 23, 24, and 25 mA).

Dihydroxycinnamoyl Derivatives of Flavonol Monoglycosides

The dicinnamoyl monoglycosides (8-10; their structures are shown in Fig. 3) gave a complex fragmentation pattern. In these compounds the molecular ion is far less stable and its intensity considerably lower than for the monoglycosides esterified with one hydroxycinnamic acid residue (1-7). (It must be mentioned that in the monoglycosides with two and three acetic acid residues (diacetylrhodalin, triacetylrhodalin [1]) the peak of the molecular ion is the main one in the spectra in spite of the high intensities of the fragmentary ions).

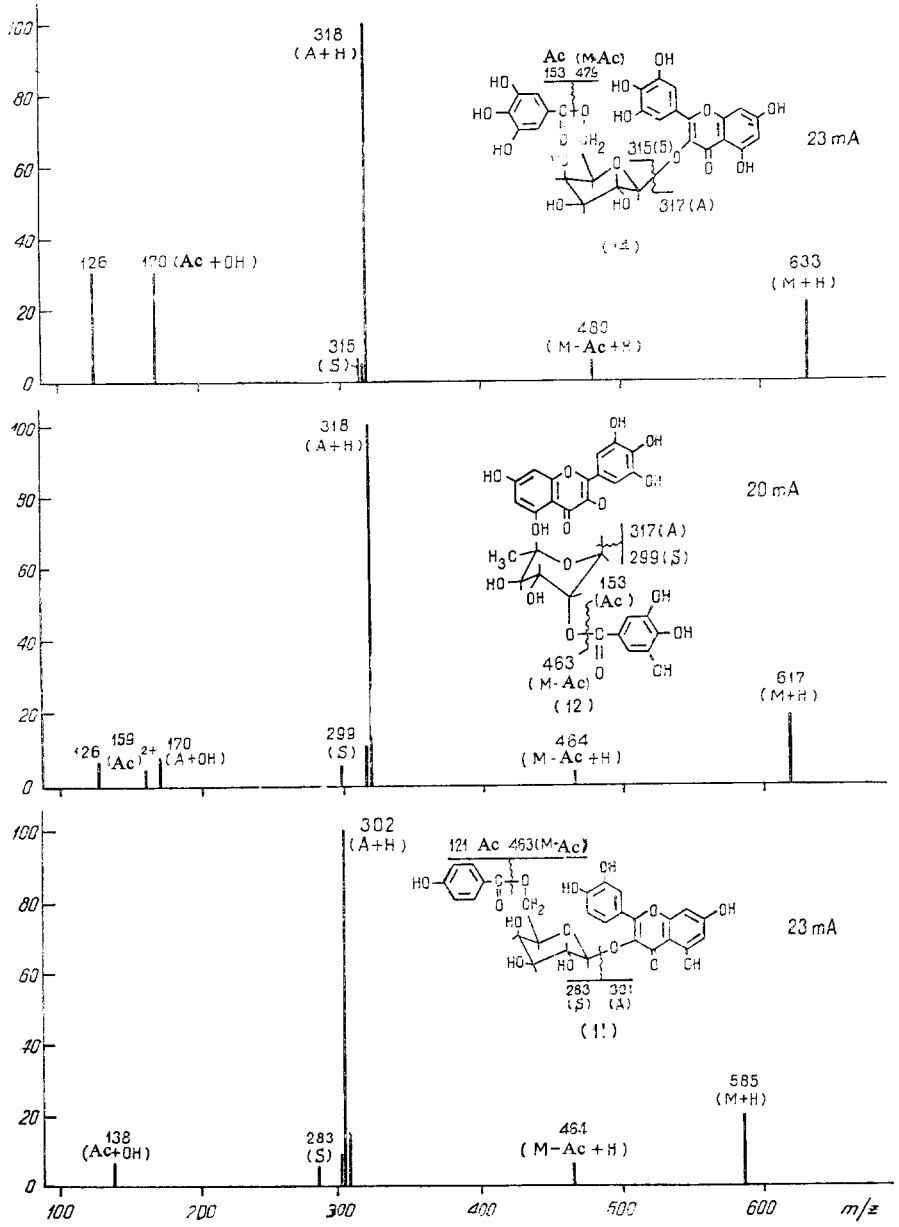

Fig. 4. FD spectra of compounds (11), (12), and (14).

In the 3,6-diacyl derivatives of the glycosides, the acyl residue present in position 6 of the sugar residue was retained more strongly, and therefore the spectra lacked the (M − 2 Ac) ions but the (M − 1 Ac) ions were formed − with the splitting out of the acyl group in position 3. This is particularly striking in compound (9) (Fig. 3), where the acyl residues had different masses: the ($M - Ac_1 = 2$ h) ion with m/z 625 was formed while the ($M - Ac_2 + 2H$) ion with m/z 595 was not; the feruloylanhydroglucose ($S - Ac_1$) ion with m/z 338 was present and the coumaroylanhydroglucose ($S - Ac_2$) ion with m/z 308 was absent.

The ion of the diacylated carbohydrate residue (S) had a low intensity in the spectra of compounds (8) and (10) (m/z 455) and was completely absent from the spectrum of compound (9).

In the spectra of Fig. 3 the molecular ions of p-coumaric acid (m/z 164) and ferulic acid (m/z 194) are fairly strong, although among the fragmentary ions there is also a coumaroyl residue (Ac) with m/z 147.

The highest intensities in the spectra are those of the peaks of the aglycone (A + H) and of the acylated aglycone (A + Ac) ions. In addition, the FD spectra of compounds (8-10) contain the peaks of the ions of the diacylated flavonol (A + 2 Ac − H), which were not formed in the spectra of the monoacylated compounds (1-7).

We must dwell particularly on the properties of compound (9). The migration of two acyl groups in it did not take place at 23 mA (Fig. 3) and was observed only at higher temperatures (I = 28 mA). Since the acyl residues in this substance had different masses, their migration could give rise to three ions of the diacylated aglycone, m/z 578 ($A + 2Ac_1 - H$), m/z 608 ($A + Ac_1 + Ac_2 - H$), and m/z 638 ($A + 2 Ac_2 - H$). All these ions were observed in the spectrum of compound (9) at 28 mA, but the intensity of the peak with m/z 608 was several times higher than those of the ions with identical acyl residues (m/z 578 and 638). These results may obviously indicate a preferred intramolecular mechanism of migration. And if it is assumed that the migration of an acyl group represents a rearrangement process of the molecular ion in the gas phase, double migration under these conditions appears unlikely and is far more likely to take place on the surface of the emitter.

Thus, for the flavonoid diacylglycosides esterified in the carbohydrate fragments with hydroxycinnamic acid, the rearranged peaks (A + Ac) and (A + 2 Ac) are diagnostic.

Flavonol Hydroxybenzoylglycosides

In this group we analyzed compounds (11-14). Some of the field desorption mass spectra of these substances that were measured are given in Fig. 4.

For the flavonol 3-glycosides acylated with p-hydroxybenzoic and gallic acids the following features are characteristic:

absence of the acyl migration observed for the cinnamoylglycosides;

splitting out and stabilization of the p-hydroxybenzoic and gallic acid residues in the form of the molecular ions (m/z 138 and 170, respectively) and the subsequent carboxylation of the gallic acid (ion with m/z 126);

The presence of a fragment of the acylated anhydrosugar S, the mass of which corresponds to hydroxybenzoylanhydrogalactose (m/z 283), galloylanhydrorhamnose (m/z 299), or a galloylanhydrohexose (m/z 315);

ions of the aglycone (A + H) and, in some cases, its doubly charged ion $(A + H)^{2+}$;

low-intensity ions of the acylglycosides (M − Ac + H); and

with an increase in the emitter heating current, the protonated molecular ion (M + H) becomes the main and only peak of each spectrum.

CONCLUSIONS

The field desorption mass spectra of 14 flavonoid glycosides esterified with p-coumaric, ferulic, caffeic, p-hydroxybenzoic, and gallic acid residues have been studied. In all the compounds the molecular ions and the ions of the aglycone (A) and of the acylated anhydrosugar (S) were obtained as the main peaks.

For flavonol monoglycosides in which the carbohydrate is acylated by hydroxycinnamic acids, migration of the acyl residue (Ac) to the aglycone, leading to the appearance of

strong (A + Ac) ions in the course of the ionization of the monoacylglycosides, and, additionally, the (A + 2 Ac) ions in the case of the diacylglycosides, was observed.

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