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ELECTRON-IMPACT MASS SPECTRA OF NATURAL PHENYLETHANOIDS

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The electron-impact mass spectra of a number of phenylpropanoids and iridoid glycosides containing a phenylethanoid fragment in their structure have been studied. This has revealed features of the formation of fragments of 4-hydroxyphenylethyl and 3,4-dihydroxyphenylethyl alcohols and also of fragments of phenylethylamine and indolylethylamine derivatives present in the structures of the compounds investigated.

In the course of a study of the chemical composition of the bark of comon lilac, the herbage of *Aerva lanata*, the rhizomes of rose-root stonecrop [1-4], and safflower fruit, a number of substances have been isolated that contain phenylethanoid fragments in their structures: phenylethanol derivatives (1-4), phenylpropanoids (5, 6), iridoid glycosides (7-10), and feruloyl- and coumaroylamides (11-13).

In a study of the electron-impact mass spectra of compounds (1-13) a number of features of the formation of fragments of 4-hydroxyphenyethyl alcohol (tyrosol) (1) and 3,4-dihydroxyphenylethyl alcohol (hydroxytyrosol) (2), and also of fragments of phenylethylamine and indolylethylamine derivatives present in the structures of the above-mentioned compounds have been observed.

The fragmentation of compounds (1) and (2) takes place with the formation of 100% (base) ions with $(M - 31)^+$ through the cleavage of the C—C bond of the side-chain (Table 1). Here the molecular ions have a low intensity and no peaks of the **b** and (**b** − H) ions are observed, although in all the glucosides (3-10) they are fairly intense, and in compounds (3) and (4) breakdown at the C—O bond (ion **b**) predominates (see Table 1).

TABLE 1. Intensities of Fragments of Phenylethyl Alcohol, Phenylethylamine, and Indolylethylamine in the Mass Spectra of Various Derivatives of Them (3-13)

Compound	Recording temperature, °C	Fragments in the mass spectra (%)			
		c + H	b	b—H	a
Tyrosol (1)	70	138 (M^+) (24)	—	—	107(100)
Hydroxytyrosol (2)	60	154 (M^+) (39)	—	—	123(100)
Salidroside (3)	160	138(12)	121(100)	120(89)	107(26)
Hydroxysalidroside (4)	140	154(7)	137(100)	136(91)	123(17)
Acteoside (5)	260	154(53)	137(46)	136(39)	123(100)
Forsythiaside (6)	270	154(52)	137(49)	136(35)	123(100)
Oleuropein (7)	200	—	137(84)	136(100)	123(25)
Dimethyloleuropin (7a)	180	182(23)	165(13)	164(100)	151(30)
Demethyloleuropein (8)	210	—	137(77)	135(100)	123(33)
Ligustroside (9)	210	—	121(92)	120(100)	107(14)
Nüzhenide (10)	180	138(4)	121(47)	120(38)	107(35)
Feruloyltyramine (11)	160	—	121(14)	120(100)	107(56)
Feruloylhomovanillylamine (12)	100	—	151(41)	150(100)	137(38)
Coumaroylserotonin glucoside (13)	250	176(16)	160(6)	159(40)	146(100)

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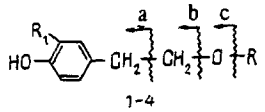

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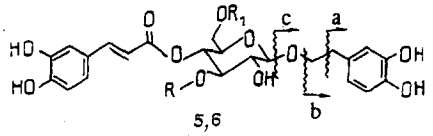

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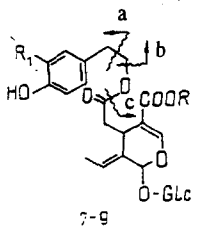

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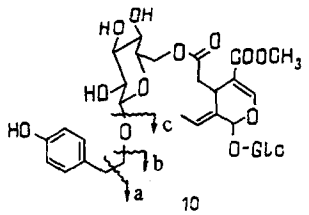

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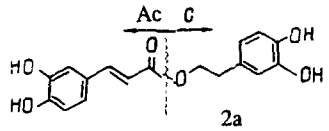
1. Tyrosol: R = R_1 = H
2. Hydroxytyrosol: R = H; R_1 = OH
3. Salidroside: R_1 = H; R = β-*D*-glucopyranoside
4. Hydroxysalidroside: R_1 = OH; R = β-*D*-glucopyranoside
5. Acteoside: R = Rha; R_1 = H
6. Forsythiaside: R = H; R_1 = Rha
7. Oleuropein: R = CH_3; R_1 = OH
8. Demethyloleuropein: R = H; R_1 = OH
9. Ligustroside: R = CH_3; R_1 = H
10. Nüzhenide

In the more complex glycosides – acteoside (5) and forsythiaside (6), the recording of the mass spectra of which requires higher temperatures, these processes become equivalent and the peaks of both ions (**b** with *m/z* 137 and **a** with *m/z* 123) have higher intensities (see Table 1).

We must mention the formation in the mass spectra of the phenylpropanoid glycosides (5, 6) of a fragment with *m/z* 316 (13%), which corresponds in mass (Ac + **c**) to caffeoylhydroxytyrosol (2a)



2a

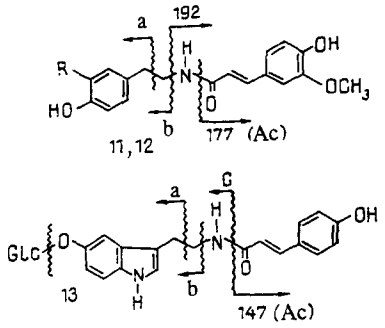
This process can be explained by acyl migration from carbohydrate to aglycone. An analogous phenomenon has been reported previously for cinnamoylglycosides of flavonoids [5], in which acyl migration was one of the dominating processes on ionization by a strong electric field, although in a number of cases ions with the mass of (aglycon + acyl) were also obtained in the electron-impact mass spectra. Moreover, in the thermolysis of compounds (5) and (6) the molecular ion of caffeic acid (M^+ 180) and its characteristic fragments (*m/z* 163 and 136) are formed.

In the iridoid compounds (7-9), where tyrosol (1) and hydroxytyrosol (2) are bound with the carboxy group of a secoiridoid (oleoside), the molecular ions of these alcohols (**c** + H) have not been detected and the ions **b** and (**b** – H) are formed predominantly, together with low-intensity ions **a** (see Table 1).

In the iridoid nüzhenide (10), where a carbohydrate hydroxyl is bound with the carboxyl of oleoside, a tyrosol fragment is formed by the same scheme as in the fragmentation of salidroside (3).

So far as concerns the fragmentation of the iridoid moiety, it must be mentioned that in all the secoiridoids (5-10) insignificant peaks of the ions of the aglycon (A) are formed. Their further breakdown takes place in accordance with known schemes of the fragmentation of iridoids [6-8]. Thus, in the case of compounds (7-9) ions are formed both with the splitting out of water (A – 18) and with the splitting out of hydroxyl (A – 17). In the case of compound (10) only the (A – 18) ion is formed, and this then loses a CO group and gives an (A – 46) fragment – the most intense peak in the mass spectrum.

In the case of the cinnamoylamides (11) and (12), the phenylethyl fragment is split out mainly in the form of the (**b** – H) ion (100%). At the same time, the mass spectrum also contains fairly intensive peaks of the ions **b** and **a**, but no peak of a (**c** + H) ion has been detected (see Table 1).



11. Feruloyltyramine; R = H
12. Feruloylhomovanillylamine; R = OCH_3
13. *p*-Coumaroylserotonin glucoside.

As already mentioned, in compounds (11) and (12) breakdwon at the CH—NH bond predominates, with the formation of intense peaks of (M − **b**) ions with *m/z* 192 and of an acyl residue (Ac) with *m/z* 177, which agrees with the scheme of fragmentation described in [9]. In contrast to this scheme, in the related compound (13) breakdown at the NH—CH bond predominates, and the mass spectrum contains intense peaks of the (**c** + H) ions with *m/z* 146 (100%) and **a** with *m/z* 146 (100%) and also of the Ac fragment with *m/z* 147 (42%). The (M − **b**) ion that is characteristic for compounds (11) and (12) is not observed for substance (13), and the **b** ion has a low intensity (Table 1).

Thus, the electron-impact mass spectra have revealed some laws of the fragmentation of the phenylethanoids that can be used in structural investigations of compounds of this series.

EXPERIMENTAL

We isolated compounds (1-10) from the roots of common lilac [1, 2]. Compound (7a) was obtained by methylating oleuropein with diazomethane. Compounds (11) and (12) were isolated in a study of the chemical composition of the herbage of *Aerva lanata* [3]. The idenitification of compounds (1-12) is described in the literature [1-4]. Compound (13) was isolated from the fruit of safflower *Carthamus tinctorius* L. and consisted of white crystals with the composition $C_{25}H_{23}N_2O_8$, mp 227-230°C, ν_{max} 1660 cm^{-1} (amide C=O). Under the conditions of enzymatic hydrolysis by β-glucosidase, compound (13) split to form glucose (PC) and coumaroylserotonin (M^+ 322). The characteristics given, and also the ^1H NMR spectrum of the substance, permitted compound (13) to be identified as *p*-coumaroylserotonin glucoside [10].

Electron-impact mass spectra were taken on a CH-8 mass spectrometer (Varian) at energies of the ionizing electrons of 30 eV (compound (10)) and 70 eV (compounds (1-9, 7a, 11-13)). The temperature of the ion source ranged from 30 to 300°C; the temperatures at which the specimens were recorded are given in Table 1.

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