Reviews

Mass spectrometry in structural studies of diterpene alkaloids

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Data on the use of electron impact mass spectrometry for the determination of the structures of diterpene alkaloids are surveyed and described systematically.

Key words: diterpene alkaloids, mass spectrometry.

Mass spectrometry plays an important role in establishing the structures of diterpene alkaloids. However, no reviews on this topic have yet been published.

In terms of their structures, the compounds under consideration can be divided into two large groups: C_{19}-diterpene or norditerpene alkaloids and C_{20}-diterpene alkaloids. The compounds of the former group are based on the aconane skeleton **1**, while the latter group is based on the perhydrophenanthrene skeleton **2**. The so-called C_{18}-diterpene alkaloids have the skeleton of norditerpene alkaloids in which the C(18) atom is absent. Alkaloids of the heteratisine type, whose skeleton **3** also consists of 19 carbon atoms, contain a lactone ring instead of five-membered ring *C*; C_{20}-diterpene alkaloids are more diverse. In the present study, we consider mass spectra of alkaloids of the songorine and denudatine type, whose structures resemble somewhat those of norditerpene alkaloids (there is a bond between the C(7) and C(20) atoms).

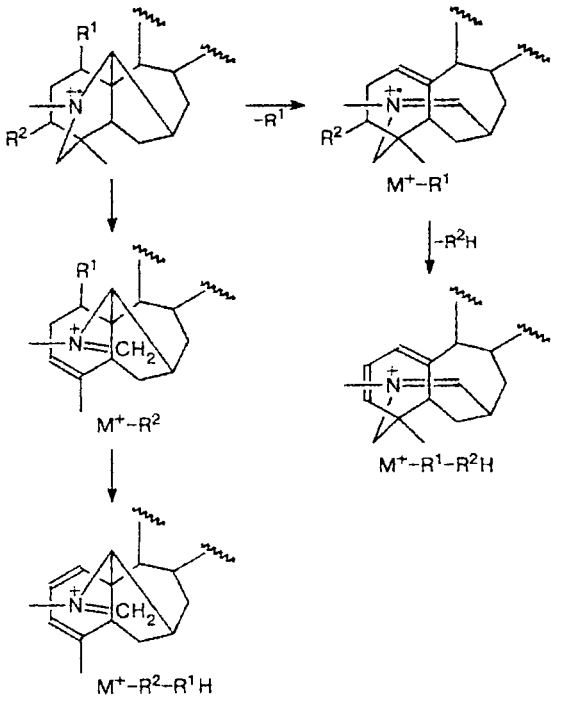
Mass spectra of norditerpene alkaloids contain several intense peaks in the region of large mass numbers and almost no peaks in other regions, except for some special cases. Fragmentation of compounds of this group mostly occurs as one-step abstraction of substituents in the form of free radicals. The major pathway of fragmentation involves, as a rule, cleavage of the C(11)—C(17) bond and the removal of the substituent from position 1 of the molecular ion; this results in the appearance of the most intense or one of the most intense peaks in the mass spectrum. If there is a substituent at C(3), the process mentioned above is followed by elimination of a molecule of water (R^2 = OH) or acetic acid (R^2 = OAc). If the C(3) atom carries an acetoxy group, the main process involving the abstraction of R^1 (Scheme 1) competes with the elimination of the substituent from the C(3) atom after cleavage of the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1096—1104, June, 1997.

1066-5285/97/4606-1047 $18.00

C(4)—C(19) bond; this is followed by the removal of a neutral molecule at the cost of the substituent at the C(1) atom.[1,2]

Scheme 1



The probability of the occurrence of one or another process is determined by the weight of the removed fragment (OH < OMe < OAc); this is demonstrated below.

The general route of destruction of norditerpene alkaloids to give the most intense peak of the M^+-R^1 ion is violated in the case of so-called pyro derivatives incorporating a C(8)=C(15) double bond (Scheme 2). In fact, the maximum peak in the spectra of pyrocaracolidine **4**, pyrocaracoline **5**, and monoacetylpyrocaracoline **6** corresponds to the M^+-31 ion resulting from the removal of the methoxy group from position 16.[3]

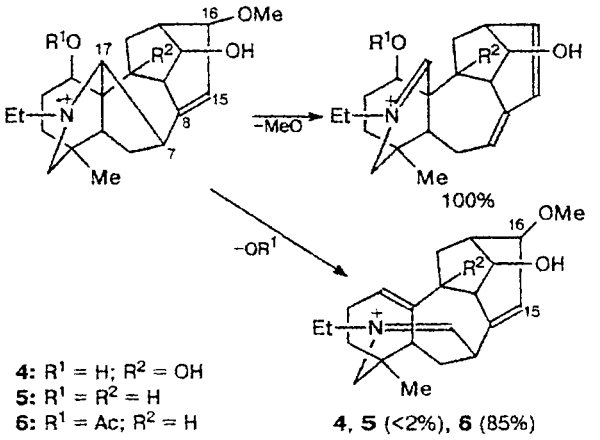
Thus, the main fragmentation pathway in the pyro derivatives involves cleavage of the C(7)—C(17) bond, apparently due to the strong strain in these molecules caused by the double bond.

It should be noted that the intensities of the M^+-OR^1 ion peaks in the mass spectra of compounds **4** and **5** do not exceed 2%, whereas in the case of monoacetylpyrocaracoline **6**, it amounts to 85%.*

The fragmentation of pyro derivatives described above can also be observed during mass spectrometry of

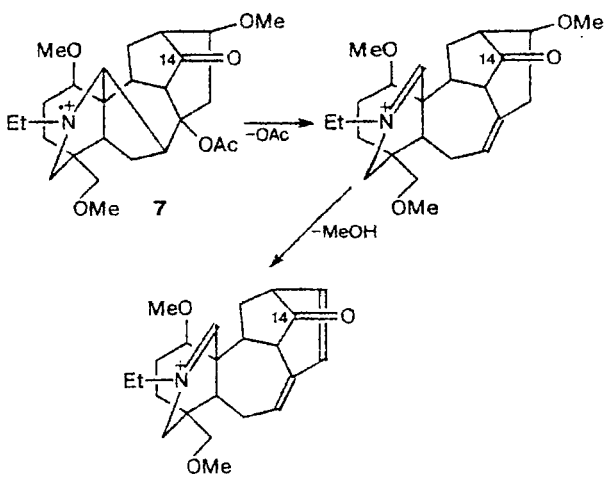
* From here on, the intensities of peaks are expressed in percent of the intensity of the maximum peak.

Scheme 2

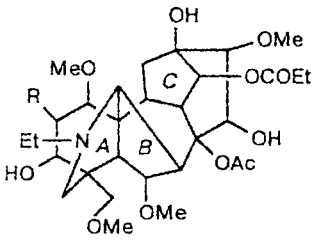


C(8)-acetoxy derivatives of norditerpene alkaloids, especially, at elevated temperatures or when the sample is kept in the injection unit for a long period.[3] This is due to the fact that these compounds readily eliminate an acetic acid molecule under pyrolytic conditions and are thus converted into pyro derivatives.[4—6] Notice also that mass spectra of the C(8)-acetoxy derivatives of norditerpene alkaloids can contain peaks of ions resulting from the abstraction of the acetoxy group. The height of the peak increases at low temperatures and when there is no bulky substituent at the C(14) atom. Thus the intensity of the peak of the M^+-OAc ion in the spectrum of dehydroacetyltalatisamine **7** at 75 °C amounts to 16% of the maximum intensity. The resulting ion eliminates an MeOH molecule due to the abstraction of the methoxy group from the C(16) atom (Scheme 3).[4]

Scheme 3



The alkaloid altaconitine **7a**, which differs from aconitine **7b** by an additional hydroxyl group at the C(2) atom, exhibits an unusual mass spectrum.[7]



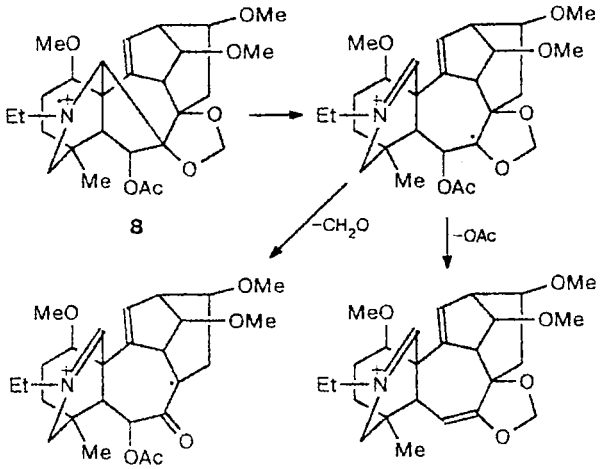
7a,b

R = OH (**a**), H (**b**)

The mass spectrum of compound **7a** differs sharply from those of aconitine **7b** and other norditerpene alkaloids containing an acetoxy group at the C(8) atom, a methoxy group at the C(1) atom, and a hydroxyl at C(3).[2] In the case of altaconitine **7a**, the peak of the M^+-OAc ion is the most intense, that of the M^+-OMe ion is of medium intensity (55%), and the peaks of the M^+-AcOH and $M^+-OMe-H_2O$ ions are not recorded. It is noteworthy that the molecular ion of **7a** (33%) is fairly stable, whereas that of aconitine **7b** is hardly manifested.[2,3] This route of fragmentation with preferred cleavage of the C(7)—C(17) bond is apparently caused by the specific conformation of the heterocycle and ring *A*, which is due to the presence of the hydroxyl group at the C(2) atom.

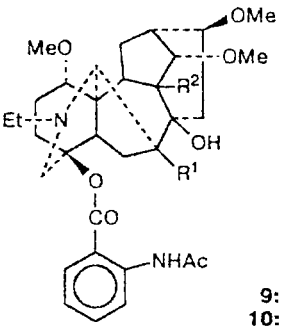
The presence of an acetoxy group at the C(6) atom normally results in the appearance of a medium-intensity (~20%) peak of the M^+-OAc ion in the mass spectrum.[8] However, for compounds with the C(10)=C(12) double bond, the peak due to this ion is the most intense. In this case, fragmentation starts with the cleavage of the C(7)—C(17) bond as shown in Scheme 4 for 10,12-anhydroeldeline **8**.[9]

Scheme 4



The presence of the C(7)—C(8) methylenedioxy group accounts for the competing process that involves elimination of a formaldehyde molecule. When the C(6) acetoxy group is replaced by a hydroxyl or a carbonyl group, abstraction of formaldehyde becomes the prevailing process, whereas its replacement by a methoxy group results in the predominant abstraction of OMe.[9]

The mass spectra of C_{18}-diterpene alkaloids with an acyloxy group at the C(4) atom are characteristic. In these cases, the most intense peak is due to the abstraction of a molecule of the ester-forming acid from the molecular ion.[10,11] For example, in the spectra of lappaconitine **9**, isolappaconitine **10**, and 9-desoxylappaconitine **11**, the peaks of the ions resulting from the elimination of a molecule of acetylanthranilic acid[12] are the most intense.



9—11

9: R^1 = H, R^2 = OH
10: R^1 = OH, R^2 = H
11: $R^1 = R^2$ = H

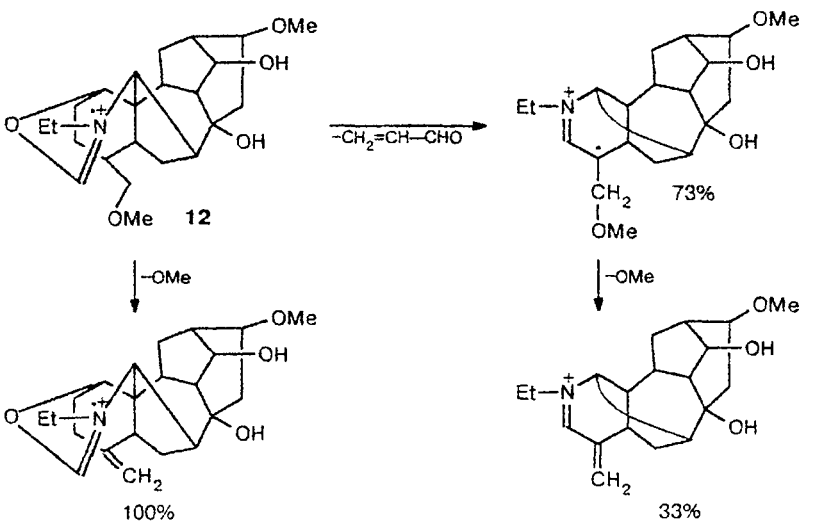
It should be noted that the process under consideration is induced only by electron impact, whereas in the case of C(8)-acyloxy derivatives, a molecule of the acid is eliminated by thermal treatment.

In elucidating the structures of diterpene alkaloids, quite a lot of information can be gained from the spectra of C(1),C(19)-epoxy compounds, which are readily obtained by oxidation of compounds having a C(1)—α-OH fragment by potassium permanganate.[13] The mass spectrum of isotalatisidine **12** can be considered as an example.[14] A significant characteristic feature of these compounds is elimination of an acrolein molecule from the molecular ion followed by the abstraction of the methoxyl radical from the C(18) atom (Scheme 5). Another pathway of the fragmentation of carbinolamine ethers is the removal of the methoxyl radical from the C(18) atom in the molecular ion. This virtually ends decomposition of this molecule.

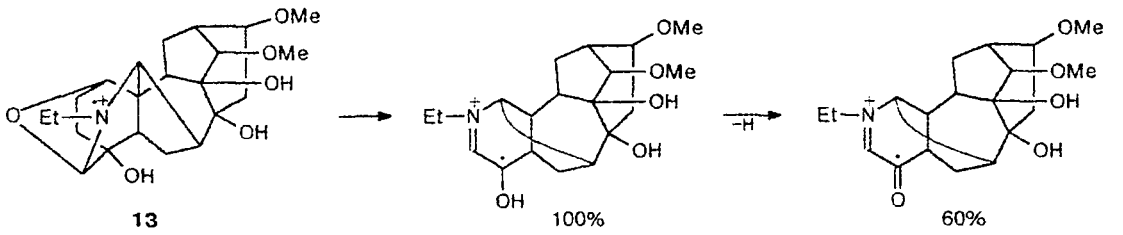
In the case of the epoxy derivative of lappaconitine **13**, the most intense peak corresponds to the M^+-56 ion, which subsequently eliminates an H atom (Scheme 6).

The elimination of an acrolein molecule starts with cleavage of the O—C(19) bond; then the C(1)—C(11) bond is cleaved. This is followed by migration of an H atom from C(2) to C(11) and rupture of the C(3)—C(4) bond.

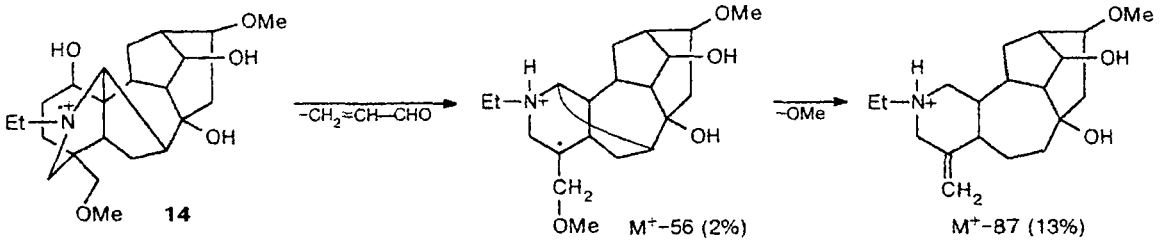
Scheme 5



Scheme 6



Scheme 7



A process involving liberation of an acrolein molecule occurs also in the case of alkaloids containing a 1-α-OH group, for example, isotalatisidine **14**. The formation of the corresponding ions involves the initial migration of the H atom of the α-OH group attached to C(1) to the N atom (Scheme 7); the subsequent destruction is similar to that described for C(1),C(19)-epoxides.

In the spectrum of the 1-β-OH isomer, this process is not observed.

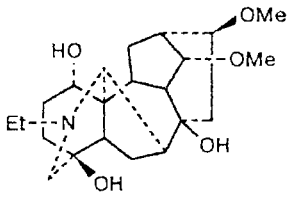
When a methoxymethyl residue is attached to the C(4) atom, the intensity of the peak of the M^+-56 ion decreases, because, in this case, it decomposes further to give a methoxyl radical and an M^+-87 ion.[15—19]

A substantial effect on the pathway of fragmentation of norditerpene alkaloids is exerted by the C(6)(OMe)—C(7)(OH)—C(8)(OH) fragment. Its presence largely suppresses all the main fragmentation stages and leads to a dramatic increase in the intensity of the M^+-Me ion peak resulting from the removal of the methoxy group from the C(6) atom, which has been confirmed in experiments with deuterated analogs.[15,20] This fragment has an effect on the fragmentation of the epoxy derivatives under consideration. The intensity of the peaks of ions resulting from the abstraction of an acrolein molecule and/or a methoxyl radical in the spectra of compounds containing this fragment is 39%. A similar tendency can be found in the case of C(1)—α-OH-norditerpene alkaloids.[15,21]

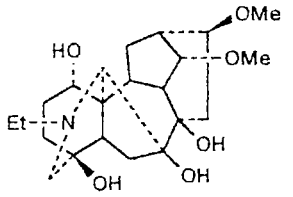
The dependence of the fragmentation on the presence or absence of the above-mentioned fragment at the C(6)—C(8) atoms is also markedly affected by the char-

acter of the substituent at C(1).[15] For example, for C(1)—OMe derivatives, the intensity ratio of the peaks of the $[M^+-Me]$ and $[M^+-C(1)OR]$ ions is (23 to 49) : 100 when the fragment in question is present in the molecule, while when the molecule contains no C(6)—OMe group, this ratio is 2 to 6 : 100. The same situation is observed for C(1)—OAc derivatives.[21] For C(1)—OH compounds, this ratio amounts to 100 : (28 to 52) and (54 to 74) : 100, respectively. Waller and coworkers, who studied the mass spectra of delcosine and its derivatives, also suggested that the methyl group eliminated from the molecular ion is removed from the methoxy group at the C(6) atom; however, they did not mention the role of the C(7)—C(8)-diol system.[22]

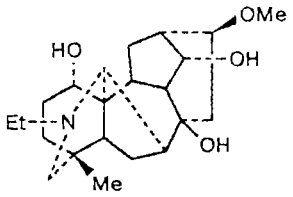
The presence of the C(7)—C(8)-diol system markedly increases the intensities of the peaks of M^+-Me ions, even in the absence of C(6)—OMe; this effect is especially pronounced in the mass spectra of compounds of the C(1)—α-OH series, in which the intensity of this peak amounts to 54—74%, whereas in the presence of only C(8)—OH, this intensity is as low as 22—36%.[15] This dependence is especially clearly manifested in the consideration of the following pairs of alkaloids: dihydromonticamine **15** and dihydromonticoline **16** (see Refs. 15 and 23) and cardiopetaline **17** and cardioletalidine **18** (see Refs. 15 and 24).



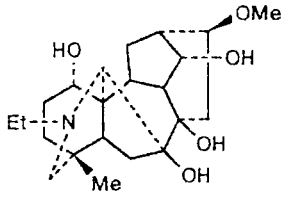
15 M^+-Me (28%)
M^+-OH (100%)



16 M^+-Me (70%)
M^+-OH (100%)



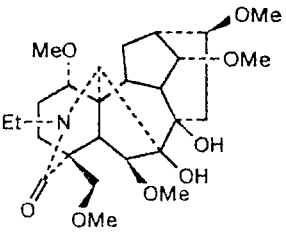
17 M^+-Me (27%)
M^+-OH (100%)



18 M^+-Me (74%)
M^+-OH (100%)

It is necessary to emphasize that when there is no oxygen function at the C(7) atom, the methoxy group at C(6) has no effect on the contribution of M^+-Me ions to the overall ionic current.[15] Analysis of the spectra taking into account the structures of the alkaloids makes it possible to believe that in these cases, the M^+-Me ions are mostly formed due to destruction of the N—Et group.

The intensity of the M^+-Me ion peak in the spectra of 19-oxo derivatives is markedly higher than those in the spectra of the initial bases; in the presence of a methoxy groups at the C(6) or C(18) atom, this peak becomes the most intense.[2,25,26] Experiments with the C(6)—OCD_3 and C(18)—OCD_3 deuterated analogs of the 19-oxo derivative of alkaloid delphatine **19** show that these groups are the main sources of the M^+-Me ions. In the case of oxolappaconine **20** [27] and oxoaconosine **21**, [15] which contain no methoxy groups at either the C(6) or C(18) atoms, the intensities of the peaks of the M^+-Me ions dramatically decrease.



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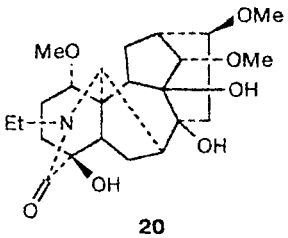

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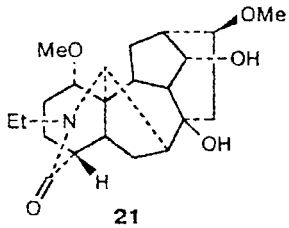
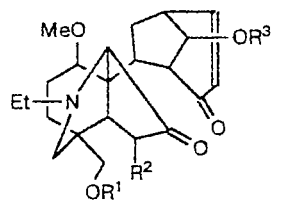


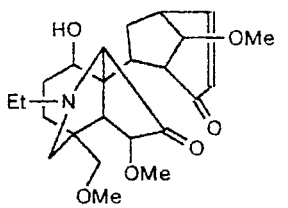
21

The mass spectra of seco-products of lycoctonine alkaloids are significant for elucidating the presence of a methoxy group at the C(6) atom; these spectra exhibit intense peaks in the region of low mass numbers. For example, the spectrum of demethylenesecodesmethanoldelcorine **22** contains a peak of the ion with m/z 100, and the spectrum of acetate **23** contains a peak with m/z 142. The mass spectra of the corresponding seco-products obtained from lycoctonine, brownine, and delsoline, *viz.*, **24**, **25**, and **26**, respectively, containing methoxy groups at the C(6) atom exhibit peaks of ions with m/z 114. Although the structures of these fragments were not identified, it is obvious that their formation involves the substituent at the C(6) atom.[25]



22—25

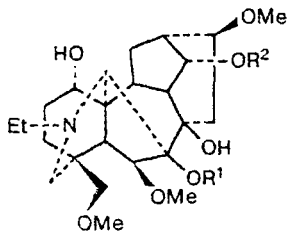
22: $R^1 = R^3 = Me$; $R^2 = OH$
23: $R^1 = R^3 = Me$; $R^2 = OAc$
24: $R^1 = H$; $R^2 = OMe$; $R^3 = Me$
25: $R^1 = Me$; $R^2 = OMe$; $R^3 = H$



26

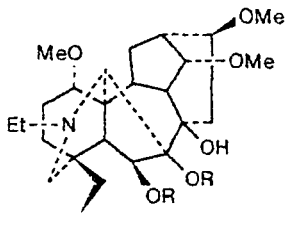
The intensity of the M^+-Me peak markedly increases on going from a C(7)—OH bond to a C(7)—OMe bond.

Thus methylation of delcosine **27** to give dimethyldelcosine **28** results in an increase in the intensity of this peak from 29.8 to 49.8% with respect to the overall ionic current, whereas the transformation of demethylenedelcorine **29** into its dimethyl derivative **30** increases the intensity of this peak from 2.9 to 26.1%.



27, 28

27: $R^1 = R^2 = H$
28: $R^1 = R^2 = Me$

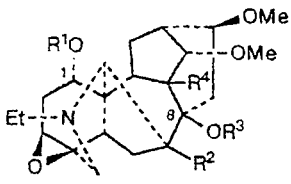


29, 30

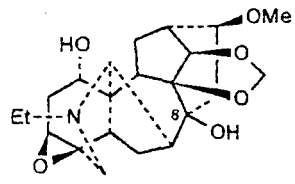
29: R = H
30: R = Me

The introduction of the C(3)—C(4)-epoxy group into molecules of C_{18}-diterpene alkaloids stabilizes their molecular ions; the main pathway of fragmentation of these ions involves elimination of a methyl radical mostly from the *N*-ethyl group and, to a lesser extent, from the OMe groups at the C(14) and C(16) atoms. Elimination of the substituent at the C(1) atom is less significant. Nevertheless, the main fragmentation pathway in the mass spectrum of 1-*O*-acetylexcelsin **31**, as in the spectra of most other 1-acetoxy derivatives of norditerpene alkaloids, is associated with the abstraction of an acetoxyl radical.

The spectrum of 8-*O*-acetylexcelsin **32** is characterized by a number of processes involving elimination of an acetoxy group (100%) or an acetic acid molecule (29%) from the molecular ion (83%); previously, this route of fragmentation has been observed for C(8)-acetylnorditerpene alkaloids. However, the presence of an epoxy group intensifies this process.[12]



31—35



36

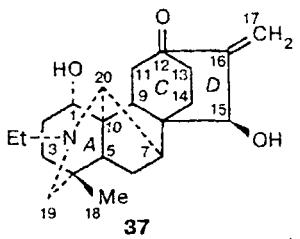
31: R^1 = Ac, $R^2 = R^3$ = H; R^4 = OH
32: $R^1 = R^2$ = H; R^3 = Ac; R^4 = OH
33: $R^1 = R^2 = R^3 = R^4$ = H
34: $R^1 = R^3 = R^4$ = H; R^2 = OH
35: $R^1 = R^2 = R^3$ = H; R^4 = OH

The spectra of compounds of this type containing no acetoxy group at the C(1) or C(8) atom (**33—36**) are characterized by increased intensities of the M^+-31 ion peaks, formed apparently *via* the removal of the OMe group from the C(16) atom. This process is hampered when an OH group is present at the C(7) atom and is facilitated when the same group is attached to C(9)[19,28] (Table 1).

Table 1. Intensities of the main fragment ions in the mass spectra of derivatives of norditerpene alkaloids

Alkaloid	I_{rel} (%)			
	M^+	M^+-15	M^+-17	M^+-31
Monticamine	41	100	17	70
N-Normonticamine	100	40	16	49
Monticoline	35	100	6	11
Excelsin	58	100	18	96
Acirine	100	60	43	60

To determine the contributions of various processes to the formation of a particular ion, the forms and intensities of metastable peaks have been studied by the method of ion beam defocusing in the first field-free space of a mass spectrometer.[19,29,30] It was found that the metastable peaks corresponding to the loss of identical species from the same positions are characterized by similar parameters, despite the different *m/z* values of the parent ions.[29,30]



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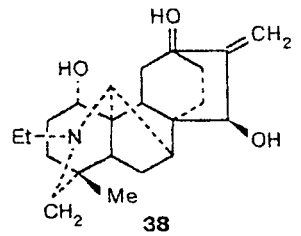

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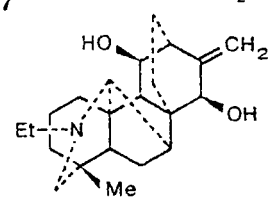
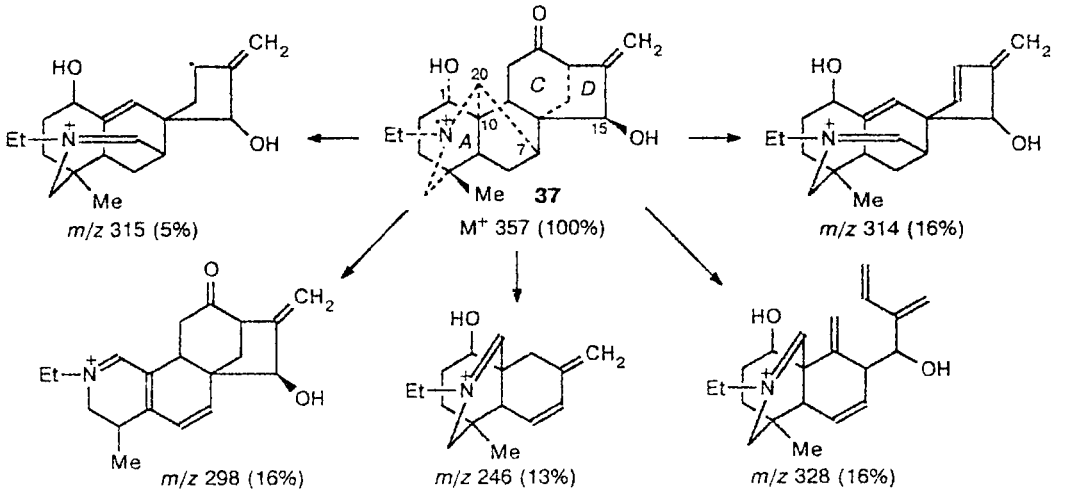


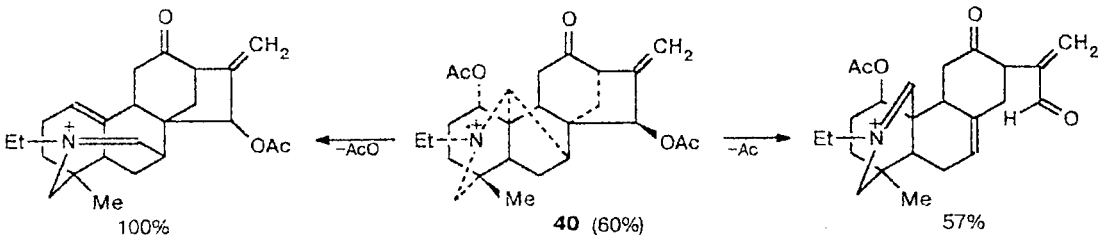
39

The mass spectra of C_{20}-diterpene alkaloids (songorine **37**, napelline **38**, denudatine **39**, and their derivatives) have some common features and differ appreciably from the spectra of C_{19}-diterpene alkaloids. In fact, compounds like songorine are highly resistant to electron impact, and their molecular ions decompose by several pathways[31,32] rather than by a single pathway as in the case of C_{19}-diterpene alkaloids. Along with the elimination of the substituent from the C(1) atom, cleavage of the C(10)—C(20) bond occurs accompanied by liberation of ketene or an acetyl radical and yields ions with *m/z* 315 and 314 (Scheme 8). Simultaneously with this processes, cleavage of the C(7)—C(20) bond occurs, which results, for example, in the loss of fragments of ring *A* (*m/z* 298) or the partial or complete loss of rings *C* and *D* (*m/z* 246, 328).

Scheme 8



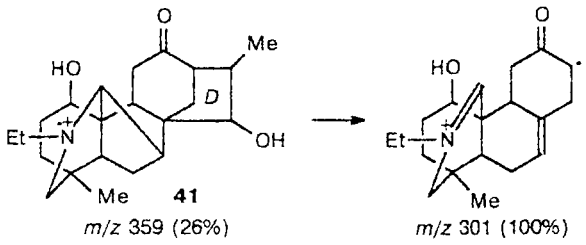
Scheme 9



The mass spectrum of songorine diacetate **40** is simpler than that of songorine **37**. The main routes of its fragmentation are due to cleavage of the C(10)—C(20), C(7)—C(20), and C(8)—C(15) bonds followed by abstraction of the acetoxyl radical from the C(1) atom and the acetyl radical from the C(15) atom (Scheme 9).

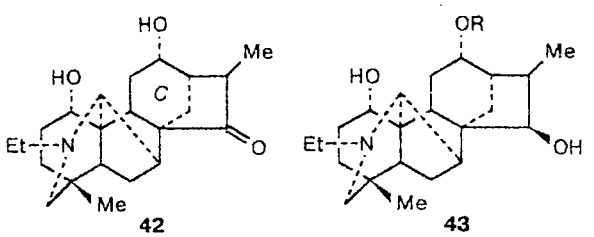
The most intense peak in the mass spectrum of dihydrosongorine **41** results from elimination of fragments of ring *D* (Scheme 10).

Scheme 10



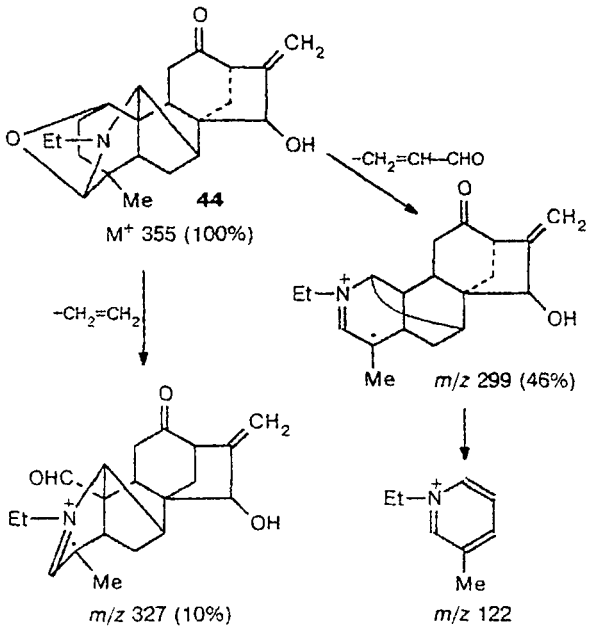
However, in the spectrum of diacetyldihydrosongorine, the peak of the M^+-59 ion resulting from the removal of the acetoxy group from the C(1) atom remains the most intense, while elimination of ring *D* fragments is less significant (28%). The maximum peak corresponding to the M^+-OAc ion is also observed in the spectra of all derivatives of napelline **38** that contain an acetoxy group at the C(1) atom.[33]

Elimination of ring *C* fragments accounts for a fairly intense peak of the M^+-56 ion (50%) in the spectrum of isonapelline **42**. The introduction of an acetoxy group to the C(12) atom hampers this process (23%), while the main fragmentation becomes associated with the loss of an acetoxyl radical. In the spectrum of the C(12)-acetyl derivative of napelline, the molecular ion peak has the maximum intensity, while the intensity of the peak corresponding to the M^+-OAc ion is only 41%. A similar mass spectral pattern is observed in the case of dihydroacetylnapelline **43** (R = Ac).[33]



The M^+-59 peak corresponding to fragmentation of ring *D* in the mass spectrum of dihydronapelline **43** (R = H), unlike that in the spectrum of dihydrosongorine

Scheme 11



41, has a medium intensity (51%), while the most intense peak is due to the molecular ion.

The molecular ions of the carbinolamine ethers derived from C_{20}-diterpene alkaloids, similarly to those of the ethers of norditerpene alkaloids, lose an acrolein molecule upon electron impact.[31] Simultaneously, an ethylene molecule is eliminated, and in the case of songoramine **44**, the pyridinium ion with *m/z* 122 is formed as the final product (Scheme 11). A similar ion is also formed upon decomposition of the corresponding ethers of norditerpene alkaloids.[20]

Mass spectra of diterpene alkaloids of the denudatine type have been studied in relation to the products of transformations of the alkaloids lappaconine and lappaconidine **45—50** (see Refs. 27, 34, and 35) and derivatives of the alkaloid dictisine **51** (see Ref. 36). The main pathways of their destruction, as in the case of alkaloids of the songorine type, involve cleavage of the C(7)—C(20) bond and elimination of fragments of ring *D*. For example, cleavage of the C(7)—C(20) bond in compounds **45** and **46** is accompanied by successive elimination of CO and Me (Scheme 12).[34]

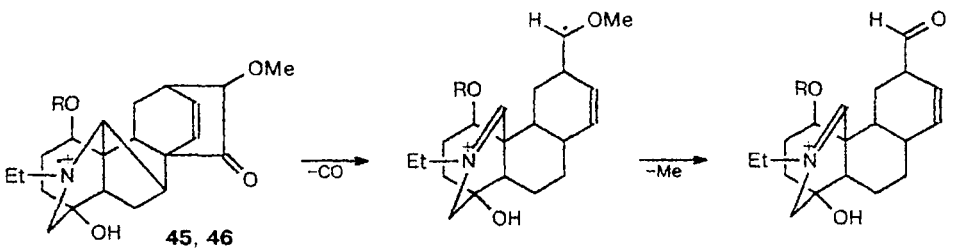
Reduction of the carbonyl group to a hydroxyl group (compounds **47** and **48**) results in the elimination of the functionalized ethylene bridge[34] or in the removal of a methoxyl radical[35] (Scheme 13).

The most intense peaks in the mass spectra of tetrahydro-derivatives **49** and **50** are due to the M^+—OMe ions (Scheme 14).[35]

Unlike the situation with the corresponding songorine derivatives considered above, in the case of compounds **45—50**, the substituent at the C(1) atom barely participates in fragmentation.[35]

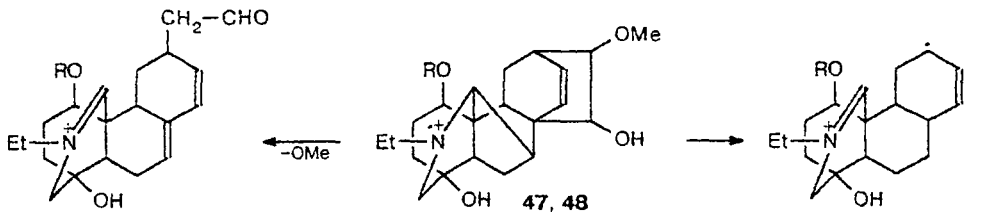
Study of the spectra of the alkaloid dictysine **51** and its derivatives **52—56** confirms the fact that the crucial role in the fragmentation of these compounds is played by the cleavage of the C(7)—C(20) bond, which leads

Scheme 12



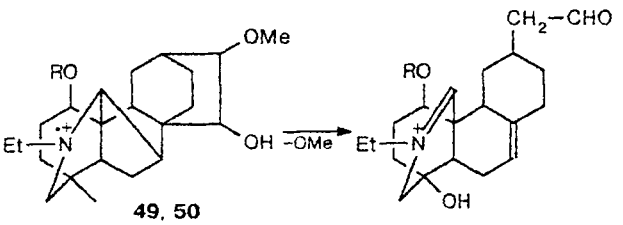
45: R = Me, M^+ 373 (4%)
46: R = H, M^+ 359 (7%)

Scheme 13



47: R = Me, M^+ 375 (34%)
48: R = H, M^+ 361 (33%)

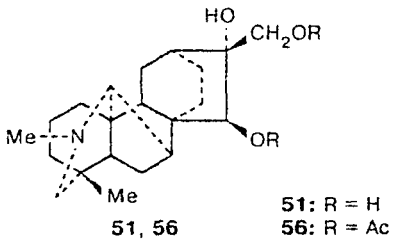
Scheme 14



49, 50

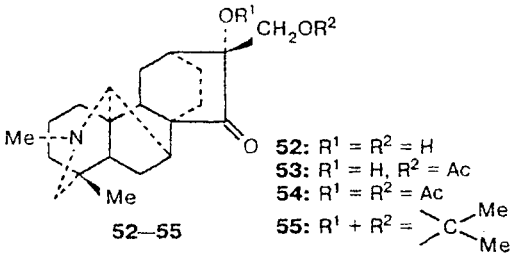
49: R = Me, M^+ 377 (20%) *m/z* 346 (100%)
50: R = H, M^+ 363 (31%) *m/z* 332 (100%)

subsequently to elimination of ring *D* fragments with some variations depending on the nature of the substituents in this ring.[36,37]



51, 56

51: R = H
56: R = Ac



52—55

52: $R^1 = R^2 = H$
53: $R^1 = H$, $R^2 = Ac$
54: $R^1 = R^2 = Ac$
55: $R^1 + R^2 =$

The most intense peak in the spectrum of dictisine is due to the molecular ion, while in the spectrum of its diacetate **56**, the most intense peak corresponds to the M^+-Ac ions. The main route of fragmentation of compound **54** involves consecutive elimination of CO and an acetoxyl radical from the C(17) atom.

The mass spectra of the majority of compounds of this group, like those of alkaloids of the songorine type, contain intense (often the most intense) molecular ion peaks; an exception is provided by compounds **45** and **46**, whose molecular ions are unstable owing to the presence of the carbonyl group and the double bond in the allylic position with respect to the bond being cleaved.

* * *

Analysis of the existing data on the mass spectrometry of diterpene alkaloids shows that each group of the compounds under consideration is characterized by its own peculiar decomposition pathways, which can change dramatically in some cases depending on the nature of the substituents in the molecule. Nevertheless, mass spectra provide important information on the type of diterpene alkaloid and the positions and the nature of the functional groups in the molecule.

The most significant feature of the mass spectra of all diterpene alkaloids is the presence of a peak of the ion resulting from abstraction of the substituent attached to the C(1) atom from the molecular ion. In the case of norditerpene alkaloids of the aconitine type (an oxygen-containing functional group at the C(8) atom) and of lycoctonine alkaloids (oxygen-containing functional groups at C(7) and C(8)), this peak is the most intense, except for those cases where the C(6) atom carries a methoxy group, and the C(7) and C(8) atoms carry an α-diol system. In the latter case, the intensity of this peak decreases, and the peak of the M^+-Me ion becomes the most intense. The presence of functional groups at the C(6), C(7), and C(8) atoms, as a rule, largely hampers fragmentation of norditerpene alkaloids and their derivatives by all routes and results in an intense peak of the M^+-Me ion.

Fragmentation of C_{18}-diterpene alkaloids containing an ester group at the C(4) atom, unlike that of compounds containing a similar functional group in any other position, involves elimination of a molecule of the ester-forming acid from the molecular ion as the prevailing process. In the remaining cases, the mass spectra of C_{18}- and C_{19}-diterpene alkaloids are similar.

The course of fragmentation in norditerpene alkaloids changes dramatically when a double bond is introduced in position 10(12) or 8(15). In this case, the main fragmentation pathway involves cleavage of the C(7)—C(17) bond followed by the abstraction of substituents from the C(6), C(7), and C(8) atoms in the case of $\Delta^{10(12)}$ derivatives or by the elimination of the substituent from the C(16) atom in the case of $\Delta^{8(15)}$ derivatives.

All of the diterpene alkaloids incorporating an oxygen bridge between the C(1) and C(19) atoms undergo typical fragmentation involving the elimination of an acrolein molecule from the molecular ion to give the M^+-56 ion. When a substituent is attached to the C(18) atom, it is subsequently eliminated.

The destruction of C_{20}-diterpene alkaloids under the action of electron impact, unlike that of norditerpene alkaloids, normally starts with cleavage of the C(7)—C(20) bond and elimination of fragments of rings *C* and *D*. These processes are intensified on going to dihydro-derivatives.

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Received February 10, 1997;
in revised form April 8, 1997