Resonance electron capture mass spectra of some diterpenoid alkaloids

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Formation of negative ions from molecules of some diterpenoid alkaloids under conditions of resonance electron capture was studied. Ions formed by capturing low-energy electrons in the lowest unoccupied molecular orbital similar to the π*-C=O or π*-Ph—CO_2 orbitals contribute predominantly to the mass spectra.

Key words: diterpenoid alkaloids, resonance electron capture, negative molecular ion.

Electron impact induced fragmentation of alkaloids of various structure has been well studied. Both common (typical of most compounds) trends in the formation of positive ions and specific (characteristic of particular types of molecules) features of this process have been established.[1] At the same time no studies on the resonance electron capture (REC) by alkaloids have been reported so far.

This class of compounds is also of interest from the standpoint of development of the REC technique, since fragmentation of negative molecular ions (NMI) strongly depends on the nature of the molecular orbitals involved in resonance. This is typical of most relatively simple molecules.[2—6] As to complex compounds including alkaloids, the situation is much more complicated because the molecular structures contain functional groups that weakly interact with one another.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-III 300 spectrometer with $SiMe_4$ as an internal reference. IR spectra were recorded on a Specord M-80 spectrophotometer in Nujol. Mass spectra and the ionization efficiency curves for negative ions (NI) were obtained on a MI-1201 mass spectrometer adapted for detecting NI under conditions of resonance electron capture. The electron energy scale was calibrated against the maximum efficiency of SF_6 ionization to generate SF_6^- ions and NH_3 ionization to generate NH_2^- ions. The halfwidth of the electron energy distribution was 0.3—0.4 eV, the electron current was 0.5 μA; the resonance maxima were determined with an error of ±0.1 eV.

Anhydrolycaconitine (**1**) and lappaconitine (**2**) were isolated from a mixture of alkaloids obtained by extraction of the roots of *Aconitum septentrionale* K. with aqueous acetone. Anhydrolycoctonine (**3**) was obtained by alkaline hydrolysis of compound **1**.[7] Methyllycaconitine (**4**), elasine (**5**), and deltaline (**6**) were isolated from roots of *Delphinium elatum* L.[8] The physicochemical characteristics of compounds **1**—**6** were identical to those reported in the literature.[7—11] 16-Demethoxy-19-oxosecolycoctonine (**7**) was obtained[12—13] by alkaline hydrolysis of **4** to lycoctonine (**8**),[14] which was then oxidized into a 19-oxo derivative[15] (**9**) with $KMnO_4$. The remaining stages of the synthetic procedure are described below.

19-Oxosecomethanollycoctonine (11). 19-Oxolycoctonine (**9**, 2.2 g) and HIO_4 (2 g) were dissolved in 125 mL of water. The mixture was allowed to stand for 360 h, made alkaline with Na_2CO_3 until pH 9, and extracted with 1,2-dichloroethane (DCE). Evaporation of the solvent gave 1.87 g of a mixture of 19-oxosecolycoctonine (**10**) and 19-oxosecodemethanollycoctonine (**11**). To a solution of the mixture of **10** and **11** (a total of 1.87 g) in EtOH (30 mL), 130 mL of 30% H_2SO_4 was added with stirring. After 2 h the mixture was dissolved with water (150 mL), made alkaline with Na_2CO_3 until pH 9, and extracted with DCE. The solvent was evaporated to give 1.79 g (87%) of 19-oxosecodemethanollycoctonine (**11**). IR spectrum, ν/cm^{-1}: 1640, 1720, 1730 (C=O). Mass spectrum, *m/z*: 447 $[M]^+$. ^{1}H NMR ($CDCl_3$, *J*/Hz), δ: 1.08 (t, 3 H, $C\underline{H}_3CH_2N$, *J* = 7.0); 3.01, 3.25, 3.54 (all s, 9 H, 3 OMe); 6.06 (d, 1 H, C(15), *J* = 9.5); 6.94 (t, 1 H, C(16), *J* = 9.5). ^{13}C NMR ($CDCl_3$), δ: 79.9 (d, C(1)); 24.2 (t, C(2)); 28.9 (t, C(3)); 46.5 (s, C(4)); 48.1 (d, C(5)); 74.9 (d, C(6)); 206.6 (s, C(7)); 198.7 (s, C(8)); 57.5 (d, C(9)); 38.3 (d, C(10)); 46.6 (s, C(11)); 29.4 (t, C(12)); 40.3 (d, C(13)); 89.0 (d, C(14)); 130.8 (d, C(15)); 147.6 (d, C(16)); 67.6 (d, C(17)); 67.0 (t, C(18)); 172.2 (s, C(19)); 12.2 (q, $\underline{C}H_3CH_2N$); 41.5 (t, $CH_3\underline{C}H_2N$); 54.6 (q, C(1)O$\underline{C}H_3$); 59.8 (q, C(6)O$\underline{C}H_3$); 53.7 (q, C(14)O$\underline{C}H_3$).

16-Demethoxy-19-oxosecolycoctonine (7). 19-Oxosecodemethanollycoctonine (**11**, 0.91 g) dissolved in EtOH (20 mL) was hydrogenated in the presence of Pd/C (60 mg). The reaction mixture was filtered and the solvent was evaporated to give 0.89 g (97%) of 16-demethoxy-19-oxosecolycoctonine (**7**). IR spectrum, ν/cm^{-1}: 1650, 1690, 1780 (C=O). Mass spectrum, *m/z*: 449 $[M]^+$. ^{1}H NMR ($CDCl_3$, *J*/Hz), δ: 1.06 (t, 3 H, $\underline{C}H_3CH_2N$, *J* = 7.0); 3.02, 3.25, 3.51 (all s, 9 H, 3 OMe). ^{13}C NMR ($CDCl_3$), δ: 79.9 (d, C(1)); 26.4 (t, C(2)); 26.4 (t, C(3)); 46.6 (s, C(4)); 47.5 (d, C(5)); 73.7 (d, C(6)); 206.1 (s, C(7)); 208.5 (s, C(8)); 56.8 (d, C(9)); 34.2 (d, C(10)); 46.9 (s, C(11)); 30.4 (t, C(12)); 41.9 (d, C(13)); 86.8 (d, C(14)); 35.8

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1768—1770, August, 2003.

1066-5285/03/5208-1864 $25.00

(t, C(15)); 25.2 (t, C(16)); 67.7 (d, C(17)); 66.4 (t, C(18)); 169.5 (s, C(19)); 12.3 (q, $\underline{C}H_3CH_2N$); 41.4 (t, $CH_3\underline{C}H_2N$); 52.1 (q, C(1)O$\underline{Me}$); 59.8 (q, C(6)O$\underline{C}H_3$); 54.2 (q, C(14)O$\underline{C}H_3$).

Results and Discussion

Saturated hydrocarbons form almost no NI under the REC conditions (cross-section for the formation of NI is less than 10^{-22} cm^2). Only as the multiple bonds and functional groups appear in the molecular structure, the cross-section sharply increases and sometimes is as large as ~10^{-14} cm^2.[4]

The alkaloid molecules studied in this work represent systems of largely separated different functional groups capable of bearing negative charge (C=O, OH, OMe, and $PhCO_2$ groups). Therefore one would expect a number of resonance states suitable for the formation of NI. However, the data in Table 1 show that most NI are formed in the low-energy region and are probably due to capture of an electron in the lowest unoccupied MO (LUMO). Indeed, studies of the acetaldehyde, acetone, and ketal molecules at low electron energies (0.8—1.2 eV) revealed the "shape resonances" associated with electron capture in the π*-MO.[3,16] According to MNDO/d calcu-

Scheme 1

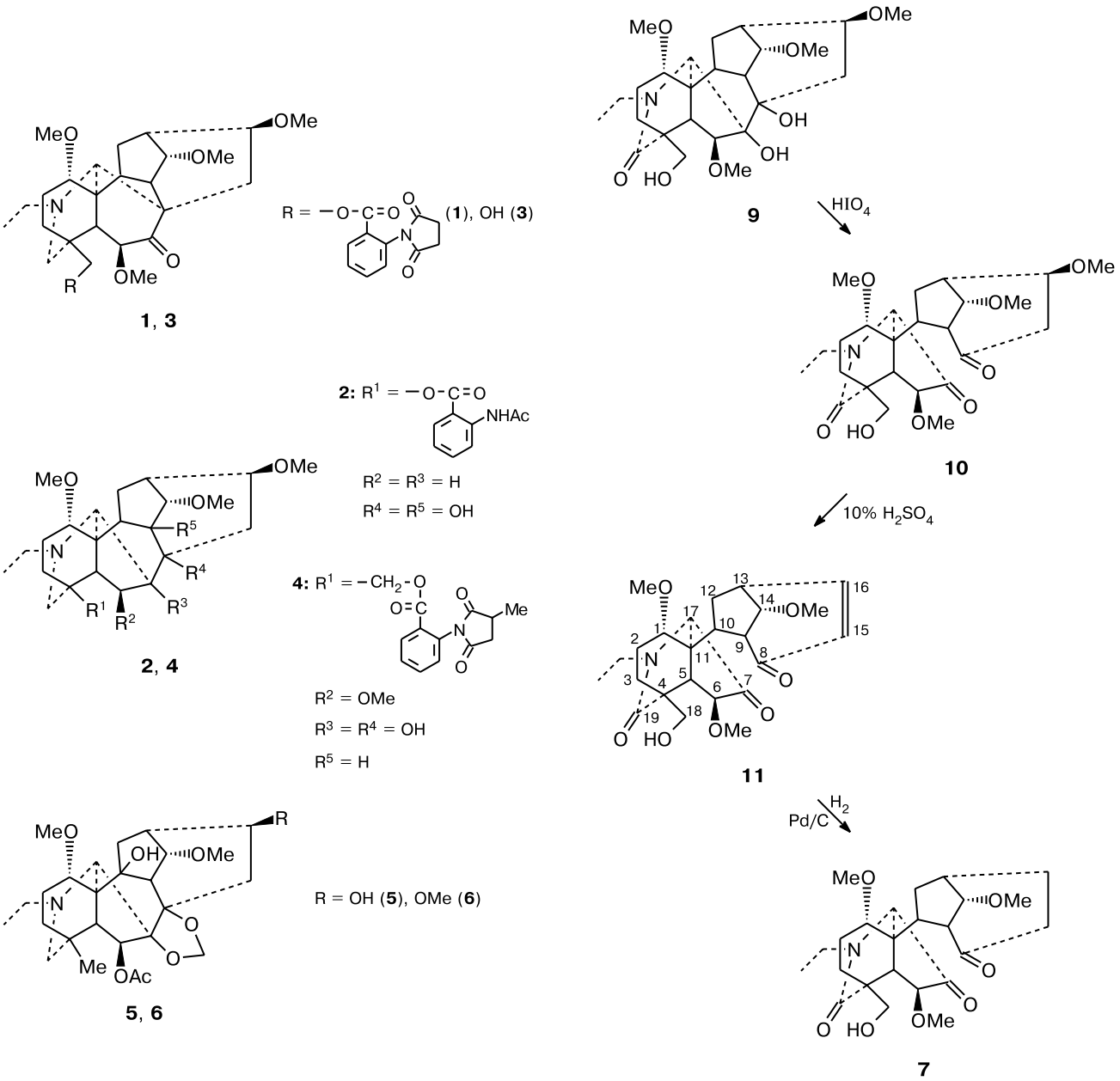
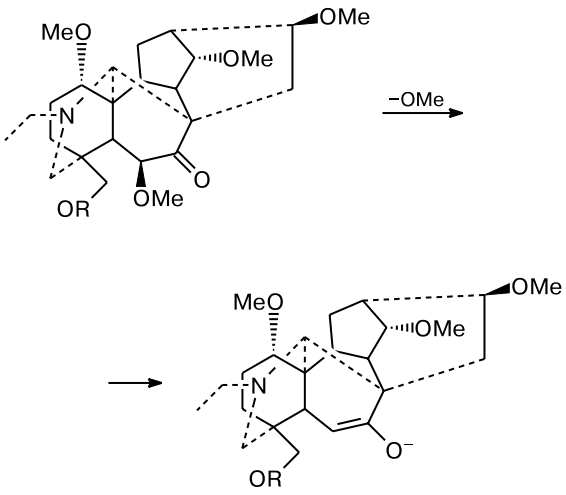


Table 1. Mass spectra of negative ions of diterpenoid alkaloids **1**—**7**

Compound	*m*/z (*I*(%))/*E*(eV)
1	649 $[M - H]^-$ (<0.1)/8.3; 619 $[M - OMe]^-$ **(100)/0.7**, (1.2)/4, (1)/8; 218 $[OCOPhN(COCH_2)_2]^-$ (0.4)/0.6, (0.2)/8.4; 202 $[COPhN(COCH_2)_2]^-$ (6)/7.5, (5.4)/8; 98 $[N(COCH_2)_2]^-$ (1)/3.3
2	178 $[OCOPhNHCOMe]^-$ **(100)/0.5**, (<0.1)/4.2, (<0.1)/8.5; 162 $[COPhNHCOMe]^-$ (<0.1)/1.1; 134 $[PhNHCOMe]^-$ (<0.1)/5.4, (<0.1)/6.4, (<0.1)/7.7; 41 $[HC_2O]^-$ (<0.1)/5.8
3	448 $[M - H]^-$ (12)/2.1, (26.7)/6.3, (20)/7.7; 418 $[M - OMe]^-$ **(100)/0.6**, (36.7)/5.2, (33)/5.8, (23)/6.9
4	651 $[M - OMe]^-$ (<0.8)/0.7, (0.6)/1.8, (0.4)/3.6, (0.6)/5.8; 232 $[OCOPhN(CO)_2C_3H_6]^-$ **(100)/0.6**, (7)/8.7; 188 $[PhN(CO)_2C_3H_6]^-$ (0.8)/0.6, (3.1)/6.3, (0.4)/10.6; 160 $[(PhNCOC_3H_6]^-$ (1)/4, (0.6)/4.6, (1.6)/6; 120 $[OCOC_6H_4]^-$ (0.8)/5.5; 112 $[N(CO)_2C_3H_6)]^-$ (1.1)/6.8; 43 $[C_2H_3O]^-$ (0.2)/6.4; 42 $[NCO]^-$ (0.7)/2.3, (0.6)/7.2, (0.6)/8.1
5	492 $[M - H]^-$ (1.9)/2.3, (2.0)/3.3; 475 $[M - H_2O]^-$ (3.1)/2.6; 463 $[M - OCH_2]^-$ (2.5)/2.6, (0.5)/3.3; 450 $[M - COMe]^-$ (4.1)/2.1; 434 $[M - OCOMe]^-$ (1.0)/3.0; 59 $[OCOMe]^-$ **(100)/2.5**
6	506 $[M - H]^-$ (0.9)/1.9, (0.8)/2.3, (0.3)/3.5; 489 $[M - H_2O]^-$ (<0.1)/2.6; 477$[M - OCH_2]^-$ (1.4)/2.1, (0.3)/3.5; 464 $[M - COMe]^-$ (6)/2.1; 448 $[M - OCOMe]^-$ (1.2)/2.7; 59 $[OCOMe]^-$ **(100)/2.6**
7	448 $[M - H]^-$ (1.8)/1.1; 418 $[M - OMe]^-$ **(100)/0.2**, (15)/4, (2)/8.1

lations,* the OMe and C=O groups at the C(6) and C(7) atoms of molecules **1**, **3**, and **7** contribute predominantly to the corresponding LUMOs. Therefore, the peak of the $[M-OMe]^-$ ion is the most intense peak in the mass spectra of these compounds (see Table 1). This ion is stabilized due to the formation of a double bond and to localization of the negative charge on the O atom (Schemes 1 and 2).

Scheme 2



As to compounds **2** and **4** whose molecules contain no neighboring C=O and OMe groups, the peaks of these ions are of low intensity; in this case, the peaks of the $[R^1]^-$ and $[R^1CH_2]^-$, respectively, are the most intense. According to quantum-chemical calculations, these fragments make the major contribution to the LUMO.

Analogously, the LUMOs of molecules **5** and **6** are determined by the contribution of the OAc group and the peak of the $[OCOMe]^-$ ion has the highest intensity.

Thus, the formation of NI from the alkaloid molecules studied in this work is due to capture of an electron in the LUMO similar in character to the π*-orbital of the C=O group at the C(7) atom in molecules **1**, **3**, and **7**, π*-orbital of the C=O group in the OAc moiety in molecules **5** and **6**, and π*-orbital of the Ph-CO_2 fragment in molecules **2** and **4**.

This work was carried out with the financial support of the Foundation for Support of Leading Scientists and Scientific Schools (Grant No. 00-15-97325)

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* All calculations were carried out using the GAUSSIAN program[17] with the standard core criteria and basis sets implemented in this program.

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Received March 24, 2003