FEATURES OF THE SPLITTING OUT OF A METHYL RADICAL FROM LYCOCTONINE ALKALOIDS UNDER ELECTRON IMPACT

M. S. Yunusov, Ya. V. Rashkes,
B. T. Salimov, É. F. Ametova,
G. V. Fridlyanskii

UDC 543.51+547.944/945

The mass spectra of 53 alkaloids and their derivatives are considered. It is known that the presence of a $C_6(OCH_3)$–$C_7(OH)$–$C_8(OH)$ grouping in C_{19}-diterpene alkaloids leads to a high intensity of the $(M - 15)^+$ ions at the expense of the $C_6(OCH_3)$ group and considerably suppresses the competing processes of forming the $[M - OH(OCH_3)]^+$ ions in the alkaloids and the $(M - 56)^+$ ions in the anhydroxy bases. When the above-mentioned grouping is absent, the $(M - 15)^+$ ions are formed mainly by the splitting out of a CH_3 from a N-ethyl group.

Usually, a skeleton of the lycoctonine type in C_{19}-diterpene alkaloids does not undergo far-reaching decomposition under electron impact. Stabilization of the fragments sets in, as a rule, as the result of single-stage processes, the main ones of which are the ejection of a methyl radical or of a OR radical from the C_1 atom [1].

While the position of detachment of a OR group is known in the majority cases [1, 2], the processes forming the $(M - CH_3)^+$ ions are unclear. In an earlier publication [1], comparing the spectra of C_{19}-diterpene alkaloids and some of their derivatives, we showed the Pelletier's idea of the formation of $(M - CH_3)^+$ ions through the detachement of CH_3 from a N-ethyl group [3] cannot be extended to alkaloids of the lycoctonine type, since in the spectrum of N-methylde-N-ethyllycoctonine and that of de-N-ethyllycoctonine the peak of this ion has the same intensity as in the spectrum of lycoctonine itself. It was also concluded that the substituents at C_1, C_{16}, and C_{18} did not participate in this process. After some years, Waller [4], studying the mass spectra of delcosine and its monoacetate, and also that of delsoline, suggested a scheme for the formation of $(M - CH_3)^+$ ions by the detachment of CH_3 from the methoxy group at C_6 after the initial cleavage of the C_1–C_{11} bond. We recorded cases of a considerable rise in the peaks of the $(M - CH_3)^+$ ions in the spectra of the 7-OCH_3 derivatives of the bases [5].

On comparing the mass spectra of a large number of C_{19}-diterpene alkaloids, we directed our attention to the fact that they may bear a considerable amount of structural information thanks to the characteristic redistribution of the intensities of the peaks of the M^+, $(M - CH_3)^+$, and $(M - OR)^+$ ions, the ratio of which is determined by the number, nature, and positions of the OR groups in the alkaloid. Furthermore, we set ourselves the aim of elucidating the origin of the $(M - 15)^+$ ion in the C_{19}-diterpene alkaloids having a lycoctonine skeleton by comparing the mass spectra at our disposal, and also those taken from the literature and studying the spectra of deuterium analogs. The spectra considered relate to the following five groups of compounds. Two groups contain a hydroxyl at C_1 and differ by the fact that the first has OH groups at C_7 and C_8 and the second only at C_8. Two other groups have the same characterizing feature but a methoxyl at C_1. The fifth group consists of the 1-methoxy-7,8-methylenedioxy-substituted bases.

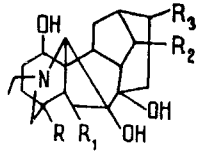
Table 1-5 give the relative intensities of the peaks of the M^+, $(M - CH_3)^+$, and $[M - OH(OCH_3)]^+$ ions in the spectra of the five groups mentioned. These figures reflect one of the most important features of the spectra of the lycoctonine bases – competition between two main pathways for their breakdown. On passing from 1-hydroxy to 1-methoxy- derivatives the contribution of the processes involving the ejection of a radical from C_1 increases, and

---

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii. No. 4, pp. 525-536, July-August, 1985. Original article submitted June 22, 1983.

 0009-3130/85/2104-0492$09.50

TABLE 1. Intensities of the Main Fragments in Main Spectra of Gq-Diterpene Alkaloids

Compound		Relative intensity, %					
		M^+ (m/z)	$(M-15)^+$	$(M-OH)^+$	$(M-56)^+$	$(M-87)^+$	$\frac{(M-OH)^+}{(M-15)^+}$
Dihydromonticoline (I)	R=OH, R_1=H, R_2=OCH_3, R_3=OCH_3	24(409)	70	100	9	–	1,4
Cardiopetalidine (II) [8]	R=CH_3, R_1=R_3=H, R_2=OH	27(363)	74	100			1,4
Umbrosine (III)	R=CH_2OCH_3, R_1=H, R_2=R_3=OCH_3	35(437)	54	100	2	11	1,9
Delphinifoline (IV) [9]	R=CH_2OCH_3, R_1=R_2=OH, R_3=OCH_3	50(439)	62	100			1,6
Delcosine (V)	R=CH_2OCH_3, R_1=R_3=OCH_3, R_2=OH	14,7(453)	100	36,3	1,5	4	0,4
Delsoline (VI)	R_2=CH_2OCH_3, R_1=R_2=R_3=OCH_3	25(467)	100	52,5	1,5	6	0,5
Dehydrodelcosine (VII)	R=CH_2OCH_3, R_1=OCH_3, R_2=O, R_3=OCH_3	18,6(451)	100	28,5			0,3

that of the $(M - CH_3)^+$ ions decreases. As can be seen from the corresponding columns of Tables 1-4, the ratio of the intensities of the peaks of these ions then decreases by an order of magnitude (for example, compare such pairs of compounds as isotalitisidine—talatisamine, delcosine—browniine, dihydromonticoline—demethyldeoxydelcorine, etc.). The quantitative difference compel us to consider the 1-hydroxy- and 1-methoxy-derivatives separately but permit the revelation of common laws within these groups. Thus, the maximum intensity of the peaks of the $(M - CH_3)^+$ ions is observed in the 7,8-dihydroxy-6-methoxy compounds (Tables 1 and 3). In the spectra of 7,8-dihydroxy bases not containing a 6-methoxy group this magnitude decreases. The peaks of the $(M - CH_3)^+$ ions are weakest in the spectra of the 8-hydroxy derivatives (Tables 2 and 4). The presence of a methoxy group at C_6 in the 7,8-methylenedioxy derivatives (Table 5) also causes a small increase in the height of the peaks of the $(M - CH_3)^+$ ions (6-O-methyldelcorine, 6-O-methyleldelidine).

In the absence of an oxygen function at C_7, a methoxyl at C_6 does not appreciably increase the contribution of the $(M - CH_3)^+$ ions to the total ion current, as can be seen with neoline (Table 2) and aconine (Table 4) as examples. The rule observed confirms a point of view put forward by Waller et al. [4] for the alkaloids delcosine and decoline according to which CH_3 is detached from the methoxy group at C_6 but throws doubt upon the mechanism proposed by the same authors for the formation of the $(M - CH_3)^+$ ion without taking the influence of a 7-hydroxy group into account.

A consideration of the spectra of the 6- and 18-OCD_3 analogs of delphatine (XX, XXI) confirmed that in the 7,8-dihydroxy-6-methoxy compounds the main source of splitting out of a CH_3 radical is the methoxyl at C_6. The height of the peak of the $(M - CD_3)^+$ ion in the spectrum of the C_6-OCD_3 analog (XX) is 79% of the sum of the heights of the $(M - CH_3)^+$ and $(m\text{-}CD_3)^+$ peaks. In the spectrum of the isomer with the OCD_3 group at C_{18} (XXI), however, the $(M - CD_3)^+$ ions are absent. Thus, in the case of delphatine about 1/5 of the $(M - CH_3)^+$ ions are formed from other sources.

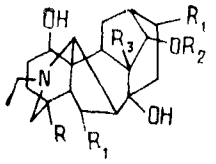
A comparison of the spectra of compounds containing no $C_6(OCH_3)$—$C_7(OH)$—C_8 (OH) chain (talitisamine (XXVIII), aconoridine (XXX) and is dimethyl ether (XXXII), 14-trideuteromethylaconoridine (XXXI), and the [D_6]dimethyl ether of aconoridine (XXXIII) shows that the participation of the methoxyls at C_{14} and C_{18} is not important in the formation of the $(M - CH_3)^+$ ions.

The increase in the heights of the peaks of the $(M - CH_3)^+$ ions on passing to the 7,8-dihydroxy bases (I-IV) and (XXV-XXVII) in comparison with the 8-monools (VIII-XVI) and (XXVIII_ XXXIV) may indicate either an increase in the contribution of the initial source of detachment of CH_3 or the appearance of a new fragmentation pathway. We may note that in this case methoxy groups at C_{14} and C_{18} make no appreciable contribution to the formation of the $(M - CH^3)^+$ ions, as is shown by a comparison of the spectra of umbrosine (III) and delphinifoline (IV), and of dihydromonticoline (I) and cardiopetalidine (II). An analogous conclusion concerning an OCH_3 group at C_{15} can be drawn by comparing the spectra of the methylenedioxy derivatives deoxydelcorine (XXXV) and corumdephine (XXXVI).

Summarizing all the material presented, it may be concluded that in the absence of a methoxy at C_6 not one of the methoxy groups usually present in the lycoctonine alkaloids (apart from the above-mentioned C_7—OCH_3) takes upon itself the role of the main source of the methyl radical split out. At the same time, the sharp changes in the contributions of the competing processes with a change in the substituents at C_1 and C_7 forced us to check whether the process of ejection of CH_3 from the N-ethyl group did not increase in the absence of a methoxyl at C_6 or of a C_7—OH group. For this purpose it was necessary to analyze the spectrum of a compound without an ethyl substituent on the nitrogen atom. For the expected changes to be appreciable we had to use compounds with OH groups at C_1, since in their spectra the peaks of the $(M - CH_3)^+$ ions have a high intensity. In the case of de-N-ethylneoline, this peak amounted to 5% in relation to the maximum peak of the $(M - OH)^+$ ion, while in neoline (XII) it amounted to 35%. It follows from this that in compounds where the methoxyl at C_6 is not the main source of $(M - CH_3)^+$ ions, this role is taken upon itself mainly by the N-ethyl group. In the case of the 1-methoxy derivatives, the contribution of this process is many times smaller. It becomes still less significant in 7,8-dihydroxy-6-methoxy bases of the lycoctonine type, which explains the reason for the coincidence of the contributions of the $(M - CH_3)^+$ ions in the case of lycoctonine and of de-N-ethyllycoctonine [1].

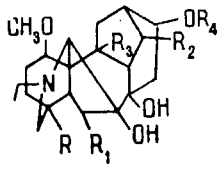
Developing the idea of the influence of competition between two main fragmentation pathways of the diterpene bases, it may be assumed that in the absence of a substituent at C_1 in

TABLE 2

Compound		Relative intensity, %					
		$M^+(m/z)$	$(M-15)^+$	$(M-OH)^+$	$(M-56)^+$	$(M-87)^+$	$\frac{(M-OH)^+}{(M-15)^+}$
Karakoline (VIII)	$R=CH_3$, $R_1=R_2=R_3=H$, $R_4=OCH_3$	28(377)	24	100	6	—	4,1
Karakolidine (IX)	$R=CH_3$, $R_1=R_2=R_3=H$, $R_4=OCH_3$, $C_{10}-OH$	23(393)	22	100	8	—	4,5
Cardiopetaline (X) [8]	$R=CH_3$, $R_1=R_2=R_3=R_4=H$	18(347)	27	100			3,7
Dihydromonticamine (XI)	$R=OH$, $R_1=R_2=R_3=H$, $R_2=CH_3$, $R_4=OCH_3$	13(393)	28	100	11	—	3,5
Neoline (XII)	$R=CH_2OCH_3$, $R_1=OCH_3$, $R_2=R_3=H$, $R_4=OCH_3$	32(437)	35	100	8	10	2,8
Lappacnidine (XIII)	$R=R_3=OH$, $R_1=H$, $R_2=CH_3$, $R_4=OCH_3$	25(409)	36	100	14	—	2,7
Talatisidine (XIV)*	$R=CH_2OCH_3$, $R_1=R_2=R_3=H$, $R_4=OCH_3$	100(407)	93	57	—	—	0,61
Isotalatisidine (XV)	$R=CH_2OCH_3$, $R_1=R_2=R_3=H$, $R_4=OCH_3$	34(407)	30	100	2	13	3,3
Condelphine (XVI)	$R=CH_2OCH_3$, $R_1=R_3=H$, $R_2=COCH_3$	29(449)	28	100	2	14	3,6

*Apart from talatisidine (C_1-β-OH), all the alkaloids listed have C_1-α-OH.

TABLE 3

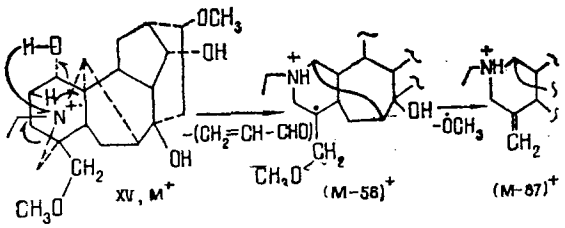
Compound		Relative intensity, %			
		M^+(m/z)	$(M-15)^+$	$(M-OCH_3)^+$	$\frac{(M-OCH_3)^+}{(M-15)^+}$
Lycoctonine (XVII)	R=CH_2OH, R_1=R_2=OCH_3, R_3=H, R_4=CH_3	4,5(467)	26	100	3,8
Browniine (XVIII)	R=CH_2OCH_3, R_1=OCH_3, R_2=OH, R_3=H, R_4=CH_3	7,0(467)	28	100	3,6
Delphatine (XIX)	R=CH_2OCH_3, R_1=R_2=OCH_3, R_3=H, R_4=CH_3	6,0(481)	23	100	5,0
[D_3]Delphatine (XX)	R=CH_2OCH_3, R_1=OCD_3, R_2=OCH_3, R_3=H, R_4=CH_3	8,0(484)	6$(M-CH_3)^+$ 23$(M-CD_3)^+$	100	3,5
[D_3]Dephatine (XXI)	R=CH_2OCD_3, R_1=R_2=OCH_3, R_3=H, R_4=CH_3	7,0(484)	22$(M-CH_3)^+$	100	4,5
Delectinine (XXII)	R=CH_2OH, R_1=OCH_3, R_2=OH, R_3=H, R_4=CH_3	8,8(453)	49	100	2,0
Delbiterine (XXIII)	R=CH_2OCH_3, R_1=R_2=OCH_3, R_3=R_4=H	9,3(467)	28	100	3,6
Dehydrobrowniine (XXIV)	R=CH_2OCH_3, R_1=OCH_3, R_2=O, R_3=H, R_4=CH_3	9,0(465)	37	100	2,7
Demethylenedeoxydelcorine (XXV)	R=CH_2OCH_3, R_1=R_3=H, R_2=OCH_3, R_4=CH_3	5,0(451)	6	100	16,6
Demethyleneeldelidine (XXVI)	R=CH_3, R_1=R_3=OH, R_2=OCH_3, R_4=CH_3	6,6(453)	5	100	22,7
Demethylenedelcorine (XXVII)	R=CH_2OCH_3, R_1=OH, R_2=OCH_3, R_3=H, R_4=CH_3	9,2(467)	4	100	27,0

1-deoxycondelphine the 100% peak of the $(M - CH_3)^+$ ion also arises as a result of the fragmentation of the N-ethyl group [12].

As is known [1], the peak of the $(M - 15)^+$ ion in the spectra of the 19-oxo compounds containing a methoxy group at C_6 or C_{18} is the maximum peak. A comparison of the spectra of the C_6–OCD_3 and C_{18}–OCD_3 deuterium analogs of the 19-oxo alkaloid delphatine (XX, XXI) shows that when these two groups are present simultaneously about 3/4 of the $(M - 15)^+$ ions are formed through the attachment of CH_3 from C_6–OCH_3, and approximately 1/5 by the splitting out of a methyl radical from C_{18}–OCH_3. Where there is no methoxyl substituent at C_6 (comparison of the spectra of the 19-oxo derivatives (XXXI and XXXIII) and [14-OCD_3]talatisamine), the $(M - 15)^+$ ion is formed to the extent of 99% by the detachment of CH_3 from C_{18}–OCH_3. The simultaneous absence of methoxy groups at C_6 and C_{18} leads to a sharp fall in the intensity of the peak of the $(M - 15)^+$ ion in oxolappaconine [6] and oxoaconosine.

The dependence of the intensity of the peak of the $(M - CH_3)^+$ ion on the presence of the $C_6(OCH_3)$–$C_7(OH)$–$C_8(OH)$ grouping can also be traced in the internal ethers of α-carbinolamines (Table 6). In the spectra of the anhydrohydroxy products of delsoline (L), delcosine (LI), nordelcosine (LII), and 18-hydroxy-14-O-methylgadesine (LIII) the peak of the $(M - CH_3)^+$ ion has the maximum intensity, and there is also an intense peak of the $(M - 33)^+$ ion the appearance of which is due to the subsequent elimination of a molecule of water. The absence of the above-mentioned grouping leads to a sharp decrease in the intensities of the peaks of the $(M - 15)^+$ and $(M - 33)^+$ ions, and the peaks of the $(M - 56)^+$ ions (XLV-XLVII) or the $(M - 31)^+$ ions (XLVIII-XLIX) formed by the ejection of an acrolein molecule of a methoxy radical become the maximum peaks [6]. The processes of ejection of a methoxy radical competes with the ejection of an acrolein moelcule in compounds having a C_4-methoxymethylene chain (XLV, XLVIII, XLIX). An increase in the contribution of the $(M - 31)^+$ ions to the total ion current is also observed on passing from the anhydrohydroxy bases (XLIX and LI) to their nor-analogs (XLVIII and LII).

The formation of the peaks of $(M - 56)^+$ ions of medium intensity is also observed in the spectra of alkaloids with a 1-α-hydroxy group. The appearance of these ions is connected with the intial migration of the hydrogen atom of the α-hydroxy group at C_1 to the nitrogen atom and the subsequent elimination of an acrolein molecule, which is characteristic of the anhydroxy bases [6];



This scheme is confirmed, in the first place, by the fact that the amounts of isotopic label in the polyisotope peaks of the M^+ and $(M - 56)^+$ ions in the spectra of the OD analogs of these bases coincide. In the second place, in the spectrum of a 1-β-OH- base – talatisidine (XIV) – there is no $(M - 56)^+$ ion.

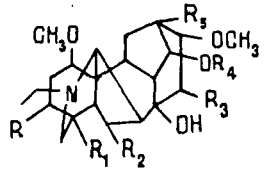
The intensity of the peaks of the $(M - 56)^+$ ions for the 1-α-hydroxy bases also depends on the presence of the $C_6(OCH_3)$–$C_7(OH)$–$C_8(OH)$ grouping. Its presence (VI, V) lowers the intensity of this peak, which becomes considerably more appreciable in compounds where this grouping is absent (Tables 1 and 2). However, in some cases the intensity of the peak of the $(M - 56)^+$ ion falls (XVI, III, XV), since it decomposes further with the elimination of a methoxy radical from the methoxymethyl residue at C_4 and with the formation of the $(M - 87)^+$ ion. This fragmentation pathway is confirmed by the fact that in compounds (I, VIII, IX, XI, and XIII) having no methoxymethyl chain, the peak of a $(M - 87)^+$ ion is absent.

EXPERIMENTAL

The review mass spectra of the compounds given in Tables 1-6 were taken on a MKh 1303 mass spectrometer (direct intoduction) at temperatures of 100-120°C. The ionizing voltage was 40 V and the cathode emission current 50 μA. The O–D analogs were obtained by dissolving the samples in CD_3OD and eliminating the solvent in the lock of the mass spectrometer.

The homogeneity of the substances was checked by chromatography in a thin layer of type

TABLE 4

Compound		Relative intendity, %			
		M+(m/z)	(M−15)+	(M−OCH_3)+	$\frac{(M-OCH_3)^+}{(M-15)^+}$
Talatisamine (XXVIII)	R=R_2=R_3=R_4=R_5=H, R_1=CH_2OCH_3	3(421)	2,0	100	67
Aconine (XXIX)	R=R_3=R_5=OH, R_1=CH_2OCH_3, R_4=H, R=OCH_3	1(499)	3,2	100	31
Aconoridine (XXX)	R=R_2=R_3=R_4=R_5=H, R_1=CH_2OH	4(407)	3,2	100	31
14-Trideuteromethylaconoridine (XXXI)	R=R_2=R_3=R_5=H, R_1=CH_2OH, R_4=CD_3	3(424)	2,0	100	50
Methyl ether of aconoridine (XXXII)	R=R_2=R_3=R_5=H, R_1=CH_2OCH_3, R_4=CH_3	2(435)	3,1	100	32
[D_6]Dimethyl ether of aconorodine (XXXIII)	R=R_2=R_3=R_5=H, R_1=CH_2OCD_3, R_4=CD_3	3(441)	3,0	100	42
Aconosine (XXXIV)	R=R_1=R_2=R_3=R_4=R_5=H	1(377)	2,4	100	

KSK silica gel in the benzene–methanol (4:1) and chloroform–methanol (20:1) systems and in a thin layer of alumina of "for chromatography" grade in the chloroform–methanol (50:1) system.

Deuteromethylation of Delcorine. A mixture of 0.3 g of delcorine, 15 ml of dioxane, 2.5 ml of deuteromethyl iodide, and 0.25 g of soidum hydride was boiled with stirring for 8 h. The sodium hydride was separated off and the filtrate was evaporated to dryness. The residue was dissolved in 5% sulfuric acid, the acid solution was washed with ether and was then made alkaline with sodium carbonate, and the reaction product was extracted with ether. After the solvent had been distilled off, 0.31 g of chromatographically homogeneous [6-OCD_3]delcorine was obtained.

Hydrolysis of [6-OCD_3]Delcorine. A solution of 0.31 g of deuteromethyldecorine in 15 ml of 10% sulfuric acid was boiled for 10 h. After being cooled to room temperature, the acid solution was washed with ether, and it was then made alkaline with sodium carbonate and was extracted with ether. The etheral extracts were dried over sodium sulfate. The residue after the elimination of the ether was dissolved in ethanol and the solution was acidified with 10% ethanolic hydrochloric acid. The perchlorate of the deuterium analog of delphatine (XX) separated out in an amount of 0.21 g.

Permanganate Oxidation of the Deuterium Analog of Delphatine (XX). A solution of 0.1 g of potassium permanganate in 100 ml of 50% aqueous acetone was added to a solution of 0.1 g of the deuterium analog of delphatine in 7 ml of 80% aqueous acetone. The reaction mixture was shaken for 10 min. The excess of potassium permanganate was decomposed with sodium sulfate. The residue was separated off and, after the acetone had been distilled off, the filtrate was acidified with 5% sulfuric acid and extracted with chloroform. The chloroform extracts were separated, and the residue was treated with hexane. The hexane-soluble fraction gave 0.037 g of the chromatographically homogeneous 19-oxo derivative of the deuterium analog of delphatine (XX).

Deuteromethylation of Lycoctonine. A mixture of 2.0 g of lycoctonine, 20 ml of dioxane, 8 ml of deuteromethyl iodide, and 0.2 g of sodium hydride was boiled with stirring for 8 h. The reaction mixture was filtered, the filtrate was evaporated, and the residue was treated by a similar method to that for the preparation of (XX). This gave 0.41 g of the perchlorate of the 18-OCD_3 analog of delphatine (XXI) with mp 202-203°C (decom.).

Permanganate Oxidation of the Deuterium Analog of Delphatine (XXI). A solution of 0.25 g of potassium permanganate in 200 ml of 50% aqueous acetone was added to a solution of 0.25 g of (XXI) in 15 ml of 80% aqueous acetone. The reaction mixture was shaken for 10 min. Then it was worked up by the method described for the preparation of (XX). This gave 0.17 g of the 19-oxo derivative of the deuterium analog of delphatine (XXI).

Deuteromethylation of Oxotalatisamine. A mixture of 0.05 g of oxotalatisamine (XI), 15 ml of dioxane, 0.5 ml of deuteromethyl iodide, and 50 mg of sodium hydride was boiled with stirring for 8 h. The reaction mixture was worked up by the method described for the preparation of [6-OCD_3]delcorine. This gave 0.051 g of chromatographically homogeneous [14-OCD_3]-19-oxotalatisamine.

Deuteromethylation of Aconoridine. A mixture of 0.03 g of aconoridine, 15 ml of dioxane, 0.5 ml of deuteromethyl iodide, and 0.05 g of soidum hydride was boiled with stirring for 8 h. The sodium hydride was separated off, and the filtrate was worked up by the method described for the preparation of [6-OCD_3]delcorine. This gave 0.03 g of a product consisting of mono-and dideuteromethylaconoridines (XXXI and XXXIII, respectively).

Permanganate Oxidation of Products of the Deuteromethylation of Aconoridine. A solution of 0.025 g of potassium permanganate in 20 ml of 50% aqueous acetone was added to a solution of 0.025 g of the mixture of mono- and dideuteromethylaconoridines in 5 ml of 80% aqueous acetone. The reaction mixture was shaken for 10 min and was then worked up by the method described for the preparation of (XX). This gave 0.01 g of a mixture of 19-oxo derivatives of [14-OCD_3]- and [14,18-OCD_3]- mono- and dideuteromethyl ethers.

Preparation of N-norneoline. A solution of 0.05 g of neoline in 5 ml of acetone was mixed with a solution of 0.05 g of $KMnO_4$ in 15 ml of water. The mixture was shaken at room temperature for 5 min, and then sodium sulfide was added. The manganese dioxide that had precipitated was separated off and the acetone was evaporated off on the water bath. The residual aqueous solution was acidified with 5% sulfuric acid and was washed with ether and,

TABLE 5

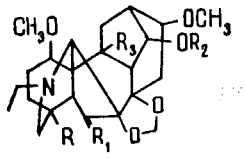
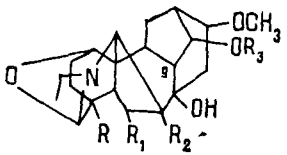
Compound		Relative intensity, %			
		$M^+(m/z)$	$(M-15)^+$	$(M-OCH_3)^+$	$\frac{(M-OCH_3)^+}{(M-15)^+}$
Deoxydelcorine (XXXV)	$R=CH_2OCH_3$, $R_1=H_2$, $R_2=CH_3$, $R_3=H$	4,3(463)	4,7	100	21,2
Corumdephine (XXXVI)	$R=CH_2OCH_3$, $R_1=H_2$, $R_2=CH_3$, $R_3=H$, $C_{15}-OH$	5,0(449)	4,0	100	25,0
Delcorine (XXXVII)	$R=CH_2OCH_3$, $R_1=H$, OH, $R_2=CH_3$, $R=H$	7,2(479)	3,6	100	27,9
Dehydrodelcorine (XXXVIII)	$R=CH_2OCH_3$, $R_1=O$, $R_2=CH_3$, $R_3=H$	3,3(477)	3,3	100	30,3
Delcoridine (XXXIX)	$R=CH_2OCH_3$, $R_1=H$,OH, $R_2=R_3=H$	7,5(465)	4,0	100	25,0
Ilidine (XL)	$R=CH_2OCH_3$, $R_1=O$, $R_2=R_3=H$	6,0(463)	3,0	100	33,3
Eldelidine (XLI)	$R=R_2=CH_3$, $R_1=H$, OH, $R_3=OH$	3,6(465)	2,2	100	45,4
Dictyocarpinine (XLII)	$R=CH_3$, $R_1=H$, OH,$R_2=H$, $R_3=OH$	22,8(451)	5,7	100	17,5
6-Methyldelcorine (XLIII)	$R=CH_2OCH_3$, $R_1=H$, OCH_3, $R_2=CH_3$, $R_3=H$	6,3(493)	12,7	100	7,8
6-Methyleldelidine (XLIV)	$R=R_2=CH_3$, $R_1=H$, OCH_3, $R_3=OH$	6,2(479)	8,0	100	12,5

TABLE 6

Compound		Relative intensity, %				
		M+(m/z)	(M−15)+	(M−31)+	(M−33)+	(M−56)+
Anhydrohydroxyumrosine (XLV)	R=CH_2OCH_3,R_1=H,R_2=OH,R_3=CH_3	8(435)	15	33	2	100
Anhydrohydroxydihydromonticoline (XLVI)	R=R_2=OH,R_1=H,R_3=CH_3	5(407)	9	2	1	100
Anhydrohydroxylappaconidine (XLVII)	R=OH,R_1=R_2=H,R_3=CH_3,C_9—OH	12(407)	13	4	4	100
Anhydrohydroxynorisotalatisidine (XLVIII)	R=CH_2OCH_3,R_1=R_2=R_3=H,>NH	11(377)	3	100	1	8
Anhydrohydroxyisotalatisidine (XLIX)	R=CH_2OCH_3,R_1=R_2=R_3=H	17(405)		100		73
Anhydrohydroxydelcosine (L)	R=CH_2OCH_3,R_1=OCH_3,R_2=OH,R_3=CH_3	9(465)	100	9	35	9
Anhydrohydroxydelcosine (LI)	R=CH_2OCH_3,R_1=OCH_3,R_2=OH,R_3=H	5(449)	100	6	31	4
Noranhydrohydroxydelcosine (LII)	R=CH_2OCH_3,R_1=OCH_3,R_2=OH,R_3=H,>NH	5(421)	100	27	55	3
18-Hydroxy-14-O-methylgadesine (LIII) [10].	R=CH_2OH,R_1=OCH_3,R_2=OH,R_3=CH_3	10(451)	100		40	6

after it had been made alkaline with sodium carbonate, the reaction product was extracted first with ether and then with chloroform. The ethereal fraction yielded the initial neoline and the chloroform fraction yielded amorphous N-norneoline.

SUMMARY

The presence of a $C_6(OCH_3)$–$C_7(OH)$–$C_8(OH)$ chain in the molecule of a C_{19} diterpene base leads a high intensity of the peak of $(M - 15)^+$ ion at the expense of the $C_6(OCH_3)$ group and considerably suppresses the competing processes of the formation of the $[M - OH(OCH_3)]^+$ ions in the case of the alkaloids and of the $(M-56)^+$ ions in the case of the anydroxy bases. Where either of these two elements of this chain is absent, the $(M - 15)^+$ ions are formed mainly by the detachment of CH_3 grom the N-ethyl group. A scheme of the origin of the $(M - 56)^+$ ions in the case of the 1-α-hydroxy bases has been substantiated.

LITERATURE CITED

1. M. S. Yunusov, Ya. V. Rashkes, V. A. Tel'nov, and S. Yu. Yunusov, Khim. Prir. Soedin., 515 (1969).
2. M. N. Sultankhodzhaev, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prir. Soedin., 481 (1975).
3. S. W. Pelletier and R. Aneja, Tetrahedron Lett., 557 (1967).
4. G. R. Waller, S. D. Sastry, and K. F. Kinneberg, Proc. Oklahoma Acad Sci., 53, 92 (1973).
5. M. S. Yunusov, V. E. Nezhevenko, and S. Yu. Yunusov, Khim. Prir. Soedin., 770 (1975).
6. V. A. Tel'nov, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prir. Soedin., 583 (1970).
7. M. S. Yunusov, Ya. V. Rashkes, and S. Yu. Yunusov, Khim. Prir. Soedin., 85 (1972).
8. A. G. Gonzalez, G. de la Fuente, M. Reina, V. Zabel, and W. H. Watson, Tetrahedron Lett., 1155 (1980).
9. V. N. Aiyar, P. W. Codling, K. A. Kerr, M. N. Benn, and A. J. Jones, Tetrahedron Lett., 483 (1981).
10. A. G. Gonzalez, G. de la Fuente, O. Munguia, Tetrahderon Lett., 4843 (1981).
11. M. S. Yunusov and S. Yu. Yunusov, Khim. Prir. Soedin., 90 (1970).
12. Ya. V. Rashkes and M. S. Yunusov, Khim. Prir. Soedin., 481 (1984).

ALKALOIDS OF Nitraria schoberi. STRUCTURE OF NITRARAINE

A. A. Ibragimov and S. Yu. Yunusov

UDC 547.944/945

The dehydration of nitraraine leads to the formation of 1-(2',6'-dimethylbenzyl)-β-carboline, together with other products. Several isomeric 1-(dimethylbenzyl)-β-carbolines have been synthesized for comparison. The products of acylation, hydrogenation, and oxidation of the alkaloid nitraraine have been studied. The results obtained have shown its structure as (±)-16-hydroxymethylyohimb-16-ene.

Continuing a study of the alkaloids of the epigeal part of Nitraria schoberi L., growing in the Kyzyl-Kum, from the combined mother liquors of the fractions with pH 6.5-3 [1] we have isolated a white crystalline base with the composition $C_{20}H_{24}N_2O$ (M^+ 308.18886), mp 208-281°C $[\alpha]_D \pm 0°$ (Py, *c* 1) , which we have called nitraraine (I). The UV spectrum of the alkaloid showed absorption maxima at 227, 284, and 292 nm (log ε 4.56, 3.87, 3.79), which are characteristic for the chromophoric group of compounds of the β-carboline series.

The IR spectrum of (I) contained absorption bands due to the vibrations of the following bonds: ano-disubstituted benzene ring (740 cm^{-1}), C–O in primary alcohols (1020 cm^{-1}), a substituted indole nucleus (1450, 1470, 1570, 1630 cm^{-1}), saturated C–H (2850, 2920 cm^{-1}),

---

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent.

Translated from Khimiya Prirodnykh Soedinenii. No. 4, pp. 536-544, July-August, 1985. Original article submitted September 18, 1984.

0009-3130/85/21040502$09.50