THERMAL DECOMPOSITION OF 10,11-METHYLENEDIOXY-3,4,12-TRIMETHOXY-7,8,13,13a-TETRAHYDRO-5H-ISOINDOLO[1,2-*b*][3]BENZAZEPINE METHOHYDROXIDE*

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Thermal decomposition of 10,11-methylenedioxy-3,4,12-trimethoxy-7,8,13,13a-tetrahydro-5*H*-isoindolo[1,2-*b*] [3]benzazepine (*V*) resulted in three desbases, the structures of which (*VII*, *XV*, and *XVIII*) were deduced mainly from spectroscopic evidence. The structure of the most polar desbase *VII* was further supported by its conversion to 1-methoxyallocryptopine (*XI*). The mechanism of formation of these compounds is discussed.

In previous communications[1,2] we described the formation of 10,11-methylenedioxy-3,4,12-trimethoxy-7,8-dihydro-5*H*-isoindolo[1,2-*b*] [3]benzazepin-5-one (*I*) by thermal decomposition of methohydroxide of narceine imide (*II*). The most important compound for arriving at its structure was 13,13a-dihydro-5-deoxo derivative *III* which was prepared from *I* by stepwise hydrogenation and reduction with lithium aluminium hydride. The structure of this derivative followed from its mass spectrum which could be compared with that of the so-called "Schöpf-Schweickert amine *VI*" (ref.[3-5]) (*IV*). Recently, it was also confirmed by a synthesis[5]. In the present communication we describe the thermal decomposition of the methohydroxide of 10,11-methylenedioxy-3,4,12-trimethoxy-7,8,13,13a-tetrahydro-5*H*-isoindolo[1,2-*b*][3]benzazepine (*V*) which provided supplementary chemical evidence of the correctness of the previously deduced[1,2] structure *III*.

The methohydroxide *V*, prepared from methiodide *VI* by means of moist silver oxide, was decomposed by heating to 180°C in the presence of barium hydroxide[6]. The reaction mixture was shown to consist of three basic components which were isolated in a pure state by repeated chromatography on a column of alumina. All the three compounds were found to be isomeric with the formula $C_{22}H_{25}NO_5$. Since hydroxide *V* can give rise only to two normal degradation products of the above elementary composition, one of the isolated compounds must have a rearranged skeleton. The structures of all the three desbases were derived mainly from the interpretation of their NMR spectra and confirmed by conversion to other derivatives or by comparison with an authentic sample.

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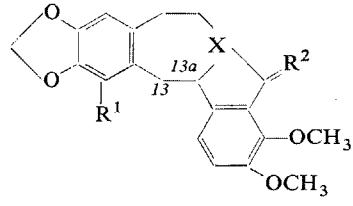
Some 25% of the reaction mixture was formed by the most polar desbase with a m.p. of 119–121°C. Its NMR spectrum contained singlets of three methoxy groups (3·70, 3·73 and 3·93 p.p.m. in the δ scale), one N-methyl group (2·43), one methylenedioxygroup (5·75) and one isolated aromatic proton (6·08 p.p.m.). A two-proton singlet at 3·60 p.p.m. and an unresolved four-proton multiplet at about 2·46 p.p.m. could be ascribed to the Ar—$C\underline{H}_2$—N—$C\underline{H}_2$—$C\underline{H}_2$—Ar group. In the region of aromatic and conjugated olefinic protons an AB quartet of two vicinal protons was found (6·80 d, 6·35 d, J = 12·0 Hz) and a two-proton singlet at 6·64 p.p.m. In view of the high value of the coupling constant, the AB quartet was ascribed to the protons of the (Z)-1,2-disubstituted double bond in the Ar—CH=CH—Ar system (ref.[7]), and the singlet to two aromatic protons in *ortho* position. These spectral properties were compatible only with the structure of 7-methyl-2,3-methylenedioxy--1,9,10-trimethoxy-5,6,7,8-tetrahydrodibenz[*c*,*g*]azecine (*VII*). In agreement with the suggested structure, the UV spectrum of azecine *VII* in methanol showed a maximum at 290 nm (log ε 3·79) which agreed well with spectral maximum[7] of demethoxyazecine *IX* (λ_{max} in 96% ethanol: 294 nm (log ε 3·84) and differed from the spectrum[8,9] of anhydromethyltetrahydroberberine A (ref.[10]) (*IX*, *trans* double bond) with (*E*)-configuration.

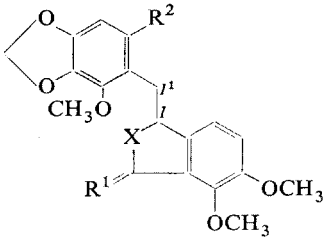


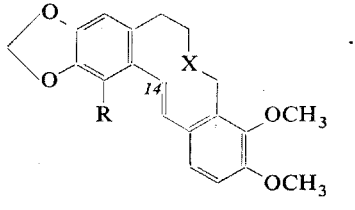
I, $R^1 = OCH_3$, $R^2 = O$, X = N, 13,13a double bond
III, $R^1 = OCH_3$, $R^2 = H_2$, X = N
IV, $R^1 = H$, $R^2 = H_2$, X = N
V, $R^1 = OCH_3$, $R^2 = H_2$, $X = \overset{(+)}{N}(CH_3)OH^{(-)}$
VI, $R^1 = OCH_3$, $R^2 = H_2$, $X = \overset{(+)}{N}(CH_3)I^{(-)}$

The correctness of these conclusions was checked by converting azecine *VII* into 1-methoxyallocryptopine (*XI*) using the method developed for the synthesis of alkaloids of the protopine type by Haworth and Perkin[11–13]. Whereas the conversion of *VII* to the corresponding N-oxide *XII* proceeded smoothly and quantitatively, the rearrangement of this oxide by heating with concentrated hydrochloric acid and acetic acid resulted in the desired keto base *XI*, as in the case[7] of *IX*, only in a very low yield. The structure of this compound was demonstrated spectroscopically. The UV spectrum of base *XI*, characterized by a single maximum at 283 nm (log ε 3·60)

was almost identical with the spectrum[14] of allocryptopine (*XIII*, λ_{max} 285 nm (log ε 3·80)) or coulteropine[15] (*XIV*, λ_{max} 286 nm (log ε 3·85)). In the IR spectrum of *XI* there was an intense band of the carbonyl group shifted characteristically, due to a transannular interaction with the nitrogen atom[16–19] toward 1 680 cm^{-1} (with allocryptopine[14] *XIII* the ν(C=O) is found at 1 668 cm^{-1}, with coulteropine[15] *XIV* at 1 675 cm^{-1}). Likewise, the mass spectrum of the base *XI* had a typical pattern of the spectra of the protopine group of alkaloids [20]. As expected, in addition to a number of peaks identical with those in the allocryptopine spectrum[20] (*XIII*) (*e.g.* a principal peak at *m/e* 164, further 149, 206), it contained also, in agreement with methoxy substitution at $C_{(1)}$, peaks shifted by 30 mass units toward higher values on the mass scale (*e.g.* *m/e* 383 (M^+), 193 and others). Mass spectrometry with double focussing revealed further that the elemental composition of the above ionic species agrees with the structures previously suggested[20]. The structure of *XI* and hence also of *VII* can thus be taken for proved.

The principal component of the mixture of desbases (some 68%) was oily and could not be induced to crystallize. Its NMR spectrum exhibited as expected the singlet of three OCH_3 groups (3·88, 3·79 and 3·75), one NCH_3 group (2·40), one methylenedioxy group (5·90) and one aromatic proton (6·75) along with a typical AB quartet of two vicinal aromatic protons (6·65 d, 6·45 d, J = 9·0 Hz). The complex signals between 5·07–7·10 corresponded to the vinyl group bound to an aromatic ring $Ar—CH_A=CH_B—H_C$ ($\underline{H}_A$ 7·10 dd, $\underline{H}_B$ 5·07 dd, $\underline{H}_C$ 5·40 dd, J_{AB} = 11·0 Hz, J_{AC} = 17·0 Hz, J_{BC} = 1·5 Hz). The NMR spectrum further contained a two-proton doublet centered at 3·02 p.p.m. (J = 6·5 Hz) resulting from an interaction with the vicinal methine proton, whose signal at about 4·00 p.p.m. was partly overlapped by the signal of the methoxy group (A_2X system). This indicated the presence of





II, R^1 = O, R^2 = $(CH_2)_2\overset{(+)}{N}(CH_3)_3OH^{(-)}$, X = NH, 1,$1^1$ double bond

VII, R = OCH_3, X = N—CH_3, *cis*-double bond

IX, R = H, X = N—CH_3, *cis*-double bond

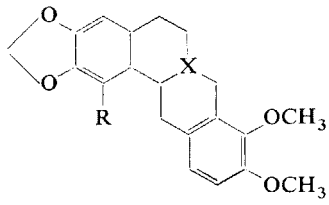
XII, R = OCH_3, X = CH_3N—O, *cis*-double bond

XV, R^1 = H_2, R^2 = CH=CH_2, X = NCH_3

XVI, R^1 = H_2, R^2 = CH_2CH_3, X = NCH_3

XVII, R^1 = H_2, R^2 = CH_2CH_3, X = $\overset{(+)}{N}(CH_3)_2I^{(-)}$

XXI, R^1 = H_2, R^2 = CH=CH_2, X = $\overset{(+)}{N}(CH_3)_2I^{(-)}$

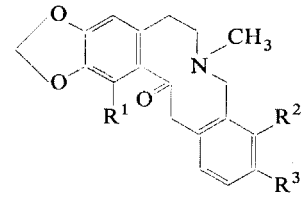


VIII, R = OCH_3, X = $\overset{(+)}{N}(CH_3)Cl^{(-)}$

X, R = H, X = $\overset{(+)}{N}(CH_3)A^{(-)}$

XIX, R = OCH_3, X = $\overset{(+)}{N}(CH_3)OH^{(-)}$

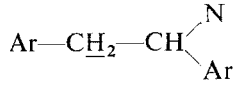
XX, R = OCH_3, X = $\overset{(+)}{N}(CH_3)I^{(-)}$



XI, $R^1 = R^2 = R^3 = OCH_3$

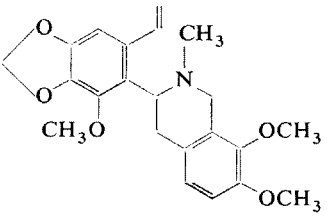
XIII, R^1 = H, $R^2 = R^3 = OCH_3$

XIV, $R^1 = OCH_3$, $R^2R^3 = O—CH_2—O$



grouping in the molecule. The magnetic equivalence of the two protons of the methylene group, following apparently from the free rotation about the C—C bond indicated, together with other evidence, the isoindoline structure *XV* for the principal degradation product. The signals of methylene protons of the N—CH$_2$—Ar group were overlapped by the signals of methoxy groups. In agreement with this structure, the desbase *XV* can be hydrogenated on Adam's catalyst in methanol to the crystalline dihydro derivative *XVI*, the NMR spectrum of which does not show the vinyl group signals any more while new signals of ethyl group appear (0·90 t, 2·15 q, J = 7·0 Hz). The same characteristic was retained also by its methiodide *XVII*.

The NMR spectrum of the third component which was present in the mixture by some 6%, contained, as in the case of desbase *XV*, the signals of three methoxy groups (3·88, 3 H; 3·84, 6 H), one methylenedioxy group (5·91) and one N-methyl group (2·20), together with signals of aromatic protons (6·82, 1 H, and 6·74, 2 *o*-H) and vinyl groups in the system of Ar—CH_A=CH_B—H_C (7·84 dd, H_A; 5·09 dd, H_B; 5·41 dd, H_C; J_{AB} = 11·0 Hz, J_{AC} = 17·0 Hz, J_{BC} = 1·5 Hz). In contrast with the above discussed spectrum of base *XV*, there was here, instead of the two-proton doublet at 3·02 p.p.m., a two-proton multiplet between 2·70–3·50 p.p.m. (the AB part of the ABX system), belonging to two magnetically nonequivalent protons at a ring carbon atom situated vicinally to another carbon carrying a phenyl group and a nitrogen-containing substituent. Another difference was found in the region of the medium magnetic fields where the AB quartet was situated at 3·68 (d) and 4·25 (d) p.p.m. with the same interaction constant J = 16 Hz which could be ascribed according to Chen and MacLean[21] to a pseudoaxial and a pseudoequatorial proton in the grouping N—CH$_2$—Ar in a six-membered ring. On the basis of these facts we ascribed to this desbase the structure of 1-methoxycanadinemethine (*XVIII*).



XVIII

The correctness of this asignment was confirmed by a direct comparison with an authentic sample which was obtained in a 90% yield by thermal decomposition of 1-methoxy-7-methylcanadinium hydroxide (*XIX*) carried out under conditions analogous to those with hydroxide *V*. In this experiment, the presence of dibenzazecine *VII* (some 8%) was also detected while the presence of the isoindoline desbase *XV* could not be demonstrated. On the other hand, thermal decomposition of 1-methoxycanadine methiodide (*XX*) in the presence of sodium hydroxide took place, as was described earlier[8] only under formation of methine *XVIII*.

On the basis of this finding it is assumed that during thermal decomposition of the starting quaternary hydroxide *V* the formation of methine *XV* is accompanied by an independent formation of azecine *VII* which, as described by Pyman[10] for the tetrahydroprotoberberine series and by Sotelo and Giacopello[22] for the tetrahydropseudoprotoberberine series, is cyclized not to the starting hydroxide *V* but rather to the isomeric methohydroxide of 1-methoxycanadine (*XIX*), the sole generator of 1-methoxycanadinemethine (*XVIII*).

EXPERIMENTAL

The melting points were determined on a Boetius micro block and have not been corrected. The UV spectra were determined on a Specord UV-VIS spectrometer (Jena, GDR), the IR spectra on a UR 10 spectrophotometer (Jena, GDR), the NMR spectra on a ZKR 60 (Jena, GDR). The chemical shifts are expressed in the δ-scale (p.p.m.). The mass spectra were measured on a high-resolution double-focussing mass spectrometer MS 902 (AEI, Great Britain), at the energy of ionizing electrons of 70 eV. The purity and homogeneity of all the products was checked chromatographically on a thin layer of alumina without binder in benzene–ethanol 94 : 6, 96 : 4, 98 : 2 and 100 : 0, or on layers of silica gel G with binder in toluene–acetone–ethanol–concentrated ammonia (50 : 50 : 7·5 : 2·5); detection was done in UV light or with Dragendorff's reagent.

Thermal Decomposition of Methohydroxide *V*

An aqueous suspension of silver oxide (from 2 g silver nitrate) was added to a solution of 2·56 g 10,11-methylenedioxy-3,4,12-trimethoxy-7,8,13,13a-tetrahydro-5*H*-isoindolo[1,2-*b*][3]benzazepine methiodide[2] (*VI*) in 750 ml water and the mixture was shaken for 2·5 h in the dark, the precipitate was filtered off, washed with water, the filtrate was combined with 5 ml saturated solution of barium hydroxide and evaporated under nitrogen. The residue was heated for 30 min

to 180°C, the product was extracted with benzene and, after washing with water and drying with anhydrous sodium sulfate, benzene was removed by distillation. The residue (1·78 g) was chromatographed (chromatography No 1) on a column of 60 g neutral alumina (activity II according to Brockmann), 30 ml fractions being collected. Fractions 1—13 (benzene) 302 mg, a mixture of bases *XV* and *XVIII*; fractions 14—19 (benzene–chloroform 98 : 2) 167 mg desbase *XV*; fractions 20—22 (benzene–chloroform 98 : 2) and 23—25 (benzene–chloroform 1 : 1) 1·23 g, a mixture of desbases *VII* and *XV*.

Pooled fractions 20—25 were rechromatographed (chromatography No 2) on a column of 40 g neutral alumina (activity II—III), 20 ml fractions being taken. Fractions 1—2 (benzene) 558 mg desbase *XV*; fractions 6—7 (benzene), 8—11 (benzene–chloroform 9 : 1) and 12—13 (benzene–chloroform 1 : 1) 338 mg desbase *VII*. Pooled fractions 1—13 from chromatography No 1 were separated (chromatography No 3) on a column of 15 g alumina (activity exactly II), 15 ml fractions being collected. Fractions 1—11 (benzene), 12—22 (benzene–chloroform 99 : 1) and 23—25 (benzene–chloroform 95 : 5) 72 mg desbase *XVIII*, fractions 26—29 (benzene–chloroform 95 : 5) 69 mg, a mixture of desbases *XV* and *XVIII*; fractions 30—33 (benzene–chloroform 95 : 5) 131 mg desbase *XV*.

7-*Methyl*-2,5-*methylenedioxy*-1,9,10-*trimethoxy*- 5,6,7,8-*tetrahydrodibenz*[c, g]*azecine* (VII), m.p. 119—121°C (methanol). For $C_{22}H_{25}NO_5$ (383·4) calculated: 68·91% C, 6·57% H, 3·65% N; found: 68·64% C, 6·51% H, 3·79% N. IR spectrum (chloroform): 1610 cm^{-1} (aromatic vibrations).

4,5-*Dimethoxy*-2-*methyl*-1-[(2′-*methoxy*-3′,4′-*methylenedioxy*-6′-*vinyl*)*benzyl*]*isoindoline* (XV). A brownish sirup unstable in air, characterized by its NMR spectrum and by derivatives *XXI*, *XVI* and *XVII*. The methiodide *XXI* was prepared by two-hours heating of a mixture of 100 mg of desbase *XV* and 0·5 ml methyl iodide in 4 ml benzene to 40—50°C (yield 32 mg); m.p. 212 to 216°C (decomp.) (acetone). UV spectrum in methanol: λ_{max} 222 nm (log ε 4·70), 274 (3·90). IR spectrum in Nujol: 1604, 1498 cm^{-1} (aromatic vibrations). NMR spectrum in CD_3OD: 6·83 (d), 6·18 (d), J = 9·0 Hz (2 *o*-H aromatic, ABq); 6·69 (s) (1 H aromatic); H_A 6·60 (dd), H_B 5·00 (dd), H_C 5·38 (dd), J_{AB} = 11·0 Hz, J_{AC} = 16·0 Hz, J_{BC} = 1·5 Hz (Ar—CH_A=CH_B—H_C); 5·90 (s) (OCH_2O); c. 4·90 (m) (overlapped by H_2O) (Ar—CH_2—CH(N)(Ar)); 3·85 (s), 3·84 (s), 3·77 (s) (3 OCH_3); 3·40 (s), 3·25 (s) ($>N^+(CH_3)_2$).

7,8-*Dimethoxy*-2-*methyl*-3-[(2′-*methoxy*-3′,4′-*methylenedioxy*-6′-*vinyl*)*phenyl*]-1,2,3,4-*tetrahydroisoquinoline* (XVIII), m.p. 117·5—121°C (methanol) (ref.[8] reports m.p. 113—114°C from ethylacetate). For $C_{22}H_{25}NO_5$ (383·4) calculated: 68·91% C, 6·57% H, 3·65% N; found: 68·81% C, 6·55% H, 3·84% N. UV spectrum in methanol: λ_{max} nm (log ε) 224 (4·52), 272 (3·93). IR spectrum in chloroform: 1601, 1492 cm^{-1} (aromatic vibrations).

4,5-*Dimethoxy*-2-*methyl*-1-[(2′-*methoxy*-3′,4′-*methylenedioxy*-6′-*ethyl*)*benzyl*]*isoindoline* (*XVI*). A solution of 243 mg desbase *XV* in 5 ml methanol was hydrogenated over 20 mg Adam's catalyst under normal pressure. After hydrogen consumption corresponding to one double bond the catalyst was filtered off and the solution evaporated *in vacuo*. The residue was recrystallized from a mixture of acetone–light petroleum, m.p. 172—177°C. NMR spectrum in $CDCl_3$: 6·66 (d), 6·12 (d), J = 9·0 Hz (2 *o*-H aromatic ABq); 6·35 (s) (1 H aromatic); 5·85 (s) (OCH_2O); 3·72 (s), 3·81 (s), 3·91 (s) (3 OCH_3); 0·90 (t) (Ar—CH_2—CH_3); 2·15 (q) (Ar—CH_2—CH_3), J = 7·0 Hz.

Methiodide XVII. A solution of 127 mg dihydro compound *XVI* in 2 ml benzene was heated for 2 h with 0·5 ml methyl iodide to 45—55°C. The crystals (65 mg) melted at 218—220·5°C (decomp.) (acetone). For $C_{23}H_{30}INO_5$ (527·4) calculated: 52·38% C, 5·73% H, 2·66% N; found: 52·24% C, 5·66% H, 2·55% N. UV spectrum in methanol: λ_{max} 285 nm (log ε 3·86). IR spectrum

in Nujol: 1612 cm^{-1} (aromatic vibrations). NMR spectrum in CD_3OD: 6·82 (d), 6·10 (d), $J = 9·0$ Hz (2 *o*-H aromatic); 6·37 (s) (1 H aromatic); 5·85 (s) (OCH_2O); 5·18 (d), 4·85 (d), $J = 15·0$ Hz (Ar—CH_2—N); 3·75 (s), 3·82 (s), 3·90 (s) (3 OCH_3); 3·42 (s), 3·26 (s) ($>N^+(CH_3)_2$); 2·11 (q) (Ar—CH_2—CH_3), 0·94 (t) (Ar—CH_2—CH_3). $J = 7·0$ Hz.

1-Methoxyallocryptopine (*XI*)

Perbenzoic acid (35 mg) in 1 ml chloroform was added to a solution of 75 mg desbase *VII* in 1 ml chloroform and the mixture was left to stand for 7 days at +5°C. After dilution with 8 ml chloroform the solution was washed three times with 5 ml 5% aqueous solution of sodium hydroxide, the aqueous extracts were washed with chloroform, the pooled chloroform fractions were washed with water, dried with anhydrous sodium sulfate and freed of the solvent by distillation: the yield was 102 mg N-oxide *XII*, m.p. 100—105°C which was processed further without purification.

A mixture of 102 mg oxide *XII*, 1·7 ml glacial acetic acid and 1·35 ml concentrated hydrochloric acid was refluxed for 1 h on a boiling-water bath. After evaporation *in vacuo* the residue was dissolved in 5 ml water, the solution was extracted twice with 5 ml benzene, the aqueous layer was filtered while hot with charcoal, cooled and made alkaline with 5% sodium hydroxide. The precipitate was extracted with 15 ml benzene, dried with anhydrous sodium sulfate and the benzene was evaporated. The yield was 20 mg of a product which was further separated on a thin layer of silica gel G in toluene–acetone–ethanol–concentrated ammonia (50 : 50 : 7·5 : 2·5). Detection was done in UV light. The least polar zone yielded 4·2 mg 1-methoxyallocryptopine, m.p. 125 to 129°C (methanol). Mass spectrum (double focussing) showed the following principal peaks (%, measured, calculated, composition): 10, 399·1682, 399·1682, $C_{22}H_{25}NO_6$ (M^+); 12, 383·1721, 383·1733, $C_{22}H_{25}NO_5$; 8, 368·1493, 368·1498, $C_{21}H_{22}NO_5$; 4, 355·1197, 355·1182, $C_{20}H_{17}O_6$; 5, 341·1028, 341·1025, $C_{19}H_{17}O_6$; 6, 325·1081, 325·1076, $C_{19}H_{17}O_5$; 9, 313·1078, 313·1076, $C_{18}H_{17}O_5$; 10, 297·1129, 297·1127, $C_{18}H_{17}O_4$; 9, 282·0886, 282·0892, $C_{17}H_{14}O_4$; 5, 282·1485, 282·1494, $C_{18}H_{20}NO_2$; 9, 232·0971, 232·0974, $C_{13}H_{14}NO_3$; 8, 220·0970, 220·0974, $C_{12}H_{14}NO_3$; 16, 206·1178, 206·1181, $C_{12}H_{16}NO_2$; 16, 193·0494, 193·0501, $C_{10}H_9O_4$; 100, 164·0837, 164·0837, $C_{10}H_{12}O_2$; 16, 149·0603, 149·0602, $C_9H_9O_2$.

Thermal Decomposition of 1-Methoxycanadine Methohydroxide (*XIX*)

A suspension of freshly precipitated moist silver oxide (from 1 g silver nitrate) was added to an aqueous solution of 1·18 g 1-methoxycanadine methiodide (*XX*), prepared from α-narcotinediol according to ref.[8] (m.p. 244—246°C, decomp.) and the mixture was shaken in a dark bottle for 3 h. The sediment was filtered off, the clear filtrate was combined with 6 ml saturated aqueous solution of barium hydroxide and water was distilled off in nitrogen atmosphere. The residue was heated for 30 min to 190—200°C. After cooling, the residue was extracted with benzene, the benzene fractions were washed with water and, after drying with anhydrous sodium sulfate, benzene was distilled off. The residue (800 mg) contained (according to thin-layer chromatography) two components and was then chromatographed on a column of alumina (activity II—III) in benzene. Pooling of the individual fractions yielded 395 mg desbase *XVIII*, m.p. 115—119°C, without depression when mixed with desbase *XVIII* isolated from the cleavage of methohydroxide *V*. For $C_{22}H_{25}NO_5$ (383·4) calculated: 68·91% C, 6·57% H, 3·65% N; found: 68·87% C, 6·72% H, 3·75% N. The spectral properties, as well as the mobilities on thin layers, were identical for the two compounds. Further fractions yielded a noncrystalline component containing (according to thin-layer chromatography) mostly desbase *VII* and traces of desbase *XVIII*.

The elemental analyses were carried out at the Analytical department of this Institute by Mr J. Kominek, the UV and IR spectra were recorded by Mrs I. Rudolská and Mrs J. Krumphanzlová. The mass spectra were measured by Dr M. Ryska, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague.

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