REACTION OF C_{19}-DITERPENE ALKALOIDS WITH SODIUM IN LIQUID AMMONIA

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The reaction of C_{19}-diterpene alkaloids with sodium and liquid ammonia in the presence and in the absence of a proton donor – an alcohol – has been investigated. In the absence of the proton donor the hydroxy group is converted into a carbonyl group, which is characteristic only for C-6-hydroxy or -acetoxy derivatives.

One of the problems in the chemistry of the C_{19}-diterpene alkaloids is the selective demethylation of methoxy groups and the elimination of oxygen functions.

We have studied the reaction of C_{19}-diterpene alkaloids with sodium and liquid ammonia in the presence and in the absence of a proton donor – alcohol. When the reaction was performed with eldeline (I), eldelidine (II) and delcorine (III) in the absence of an alcohol, unexpected results were obtained. In addition to the corresponding deoxy products (IV) and (V), the corresponding 6-keto derivatives (VI)-(VII) were isolated as the main reaction products, and in the cases of eldeline and eldelidine the reaction took place monotypically and the yield of the 6-keto products reached 60%. When the reaction was performed in the presence of an alcohol the initial compounds were recovered almost completely and a mixture of reaction products was formed in insignificant amounts (1-2%).

As is well known, under the conditions of the Birch reaction radical anions are formed as intermediate products [1, 2]. In our case, when the reaction was performed in the absence of an alcohol the radical anion formed at the hydroxy or the acetoxy group in the C-6 position decomposed to the deoxy products (IV) and (V) and to the 6-keto products (VI) and (VII). In the presence of a proton donor – an alcohol – however, the intermediate radical anion was "quenched" by a proton.

An attempt to apply the reaction with sodium and liquid ammonia to condelphine (VIII), browniine (IX), lycoctonine (X), and deoxydelcorine (XI), having hydroxy and acetoxy groups in various positions, left the initial compounds unchanged in all cases. Thus, the reaction of diterpene alcohols with sodium and liquid ammonia that has been detected – the conversion of a hydroxy group into a carbonyl group – is apparently characteristic only for C-6-hydroxy or -acetoxy derivatives.

The performance of the reaction of eldelidine with lithium in liquid ammonia using ether as solvent gave a 6% yield of dehydroeldelidine and a 85% recovery of the initial product. The replacement in the last-mentioned reaction of the solvent ether by tertiary butyl alcohol led to a 94% recovery of eldelidine. It was impossible to isolate other reaction products (see scheme on following page).

EXPERIMENTAL

The homogeneity of the substances was checked chromatographically in a thin layer of alumina (for chromatography) in the ether–methanol (100:1), ether–methanol (50:1), chloroform, chloroform–methanol (100:1), and chloroform–methanol (50:1) systems and on type KSK silica gel in the chloroform–methanol (40:1) system. IR spectra were recorded on a UR-20 instrument (tablets with KBr), PMR spectra on a JNM-4 H-100/100 MHz spectrometer (δ, ppm, $CDCl_3$, HMDS), and mass spectra on a MKh-1310 instrument fitted with a system for direct introduction into the ion source.

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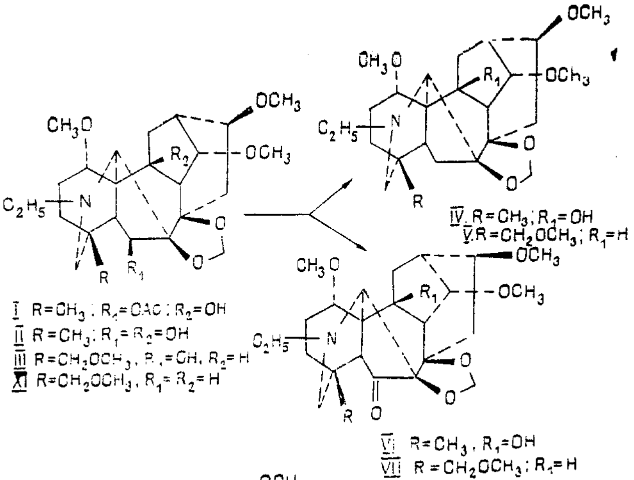


I $R=CH_3$; $R_1=OAc$; $R_2=OH$

II $R=CH_3$; $R_1=R_2=OH$

III $R=CH_2OCH_3$, $R_1=OH$, $R_2=H$

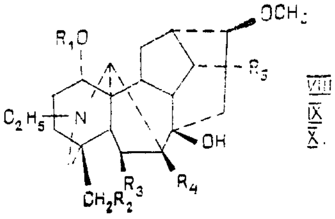
XI $R=CH_2OCH_3$, $R_1=R_2=H$

IV. $R=CH_3$; $R_1=OH$

V. $R=CH_2OCH_3$; $R_1=H$

VI $R=CH_3$, $R_1=OH$

VII $R=CH_2OCH_3$; $R_1=H$



VIII. $R_1=R_3=R_4=H$, $R_2=OCH_3$; $R_5=OAc$

IX $R_1=CH_3$; $R_2=R_3=OCH_3$; $R_4=R_5=OH$

X. $R_1=CH_3$; $R_2=R_4=OH$; $R_3=R_5=OCH_3$

General Procedure. With constant stirring, 0.1-0.2 g of a base in 50 ml of dry benzene was added dropwise to a solution of 1 g of sodium in 100 ml of liquid ammonia. (The solvents used were benzene, ether, and benzene + ether, and in all cases the result of the reaction was the same). The mixture was stirred for 6-7 h and was left overnight with free evaporation of the ammonia. The excess of sodium was decomposed with alcohol. The solvent was evaporated off and the residue was dissolved in 5% sulfuric acid. The acid solution was washed with chloroform and then, with cooling, was made alkaline with sodium carbonate and was extracted with chloroform. After the solvent had been distilled off, the reaction product was chromatographed on alumina or silica gel.

Reaction of Eldeline with Sodium in Liquid Ammonia. The reaction was performed by the procedure described above. The amount of eldeline taken was 0.2 g, and the reaction product was chromatographed on a column of deactivated alumina. Elution with hexane–ether (1:4) yielded 6-deoxyeldeline (IV) (~15%), $C_{25}H_{39}NO_6$, mp 160-162°C (ether); dehydroeldelidine (VI) (60%); and eldelidine (~3%). The dehydroeldelidine and the eldelidine were identified by direct comparison with authentic samples (mixed melting point, TLC, PMR, IR, and mass spectra).

PMR spectrum of (IV) (ppm): 0.85 (3 H, singlet, $C-CH_3$); 1.00 (3 H, triplet, $N-C_2H_5$); 3.17, 3.25, 3.47 (each 3 H, singlets, 3 OCH_3); 4.1 (1 H, triplet with J = 5 Hz, β-H at C-14); 4.80 and 4.85 (each 1 H, singlets, CH_2O_2). Mass spectrum: M^+ 449; $M^+ - 31$ (100%).

Reaction of Eldelidine with Sodium and Liquid Ammonia. The amount of eldelidine taken was 0.3 g, and the reaction product was chromatographed on a column of deactivated alumina. Elution with hexane–ether (1:4) yielded 6-deoxyeldelidine (~5%), dehydroeldelidine (60%), and eldelidine (~7%).

Reaction of Delcorine with Sodium in Liquid Ammonia. The amount of delcorine taken was 0.1 g and the reaction product was chromatographed on a column of deactivated alumina. On elution with hexane–ethyl acetate (4:1), delcorine (70%), deoxydelcorine (~2%), and dehydrodelcorine (~7%) were isolated. The delcorine, deoxydelcorine, and dehydrodelcorine were identified by direct comparison with authentic samples (mixed melting point; TLC; and PMR, IR, and mass spectra).

Reaction of Eldelidine with Lithium in Liquid Ammonia. 1) The reaction was performed by the procedure described above using ether as solvent. The reaction product was chromatographed on a column of deactivated alumina. On elution with ether–methanol (50:1), dehydroeldelidine (~6%) and eldelidine (85%) were isolated.

2): Tertiary butyl alcohol was used as solvent. The reaction product was chromatographed on a column of deactivated alumina. Elution with ether–methanol (50:1) yielded eldelidine (94%).

SUMMARY

The reaction of C_{19}-diterpene alkaloids (eldeline, eldelidine, delcorine, deoxydelcorine, condelphine, lycoctonine, and browniine) with sodium and liquid ammonia in the presence and in the absence of a hydrogen donor – an alcohol – has been studied. It has been established that the transformation of a hydroxy group into a carbonyl group in the absence of a proton donor is characteristic only for C-6-hydroxy or -acetoxy derivatives.

LITERATURE CITED

1. A. J. Birch and H. Smith, Quart. Rev., 12, 17 (1958).
2. E. M. Kaiser, Synthesis, 391 (1970).

SPECTRAL-FLUORESCENT PROPERTIES OF MAIZE GRAIN TRYPSIN INHIBITOR

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The trypsin inhibitor isolated from maize grain has been investigated by the methods of IR, UV, fluorescence, derivative, and differential spectroscopy. Its spectral characteristics have been determined and the influence of the temperature and of a detergent on the structure of the protein has been studied.

The investigation of spectral characteristics permits the structural features of protein inhibitors of proteinases to be revealed. The nature of absorption in the ultraviolet region of trypsin inhibitors isolated from various plant sources is determined by the ratio of aromatic amino acid residues [1, 2]. Information on the parameters of the UV absorption of a trypsin inhibitor from maize grain has been limited to a determination of its extinction coefficient [3, 4]. Investigations performed by the methods of IR spectrophotometry [5], derivative [6, 7] and differential [7] spectroscopy, and fluorescence [2, 8] are permitting the elucidation of features of the structural organization of plant trypsin inhibitors, but for the inhibitor protein isolated from maize grain the spectral characteristics have not been determined in spite of differences, in comparison with other proteinase inhibitors, in the formation of the secondary structure with a predominance of α-helical sections above the β-structure that have been reported [9].

A comparative investigation of trypsin inhibitors of an initial and a mutant maize that we had carried out previously [10] showed differences in their component compositions.

In view of this, in the present work we have investigated the spectral and fluorescent characteristics of a trypsin inhibitor isolated from the initial maize (line A 204 +++) and that from a maize mutant with respect to the opaque-2 gene (line A 204 o2o2o2).

The IR spectra (cm^{-1}) of the trypsin inhibitor from the grain of the maizes with different genotypes were similar and were typical for proteins:

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