STRUCTURE OF ACONIFINE

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The structure of the new alkaloid aconifine, which has been isolated from the tubers and epigeal part of *Aconitum karakolicum* Rapcs. has been established on the basis of the results of chemical transformations and spectral characteristics. Some features of the selective acetylation of aconitine and aconine have been elucidated.

Aconitine, napelline, songorine, a base with mp 122-124°C, identified as isoboldine [1-3], and a new alkaloid with the composition $C_{34}H_{47}NO_{12}$ ($M^+ - OCH_3$ = 630.2904) having mp 195-197°C (acetone), which has been called aconifine [4], have been isolated previously from the tubers of *Aconitum karakolicum* Rapcs. collected in the gorge of the R. Tyup (Terskei Ala-Tau range, Kirg SSR). Isoboldine and aconifine were also isolated from epigeal part of *Aconitum karakolicum* [3].

The spectral characteristics of aconifine show great similarity with those of aconitine. The NMR spectrum of aconifine has signals due to N-ethyl, acetyl, benzoyl, and four methoxy groups. The IR spectrum of the alkaloid has the absorption bands of hydroxy groups (3590, 3520 cm^{-1}) and ester groups (1720, 1740 cm^{-1}), of an aromatic ring (1500, 1600 cm^{-1}) and of ethereal C–O bonds (1100 cm^{-1}). Acetylation with acetyl chloride formed tetraacetylaconifine (II). Consequently, aconifine has the developed formula $C_{19}H_{18}(N{-}C_2H_5)(OCH_3)_4(OH)_4(OCOCH_3)\cdot(OCOC_6H_5)$ and contains the largest number of oxygen substituents of all diterpene alkaloids with established structures.

The alkaline hydrolysis of aconifine led to benzoic acid and an amorphous amino alcohol—aconifidine (III).

It has been shown previously that under the conditions of mass spectrometry alkaloids containing an acetoxy group at C_8 and a benzoyloxy group at C_{14} readily eliminate an acetic acid molecule and the peak of the molecular ion is either absent or has a low intensity [5, 6]. In the mass spectrum of aconifine, the peak of the molecular ion is very small (0.3%), the maximum peak being that of the ion $M^+ - 91$, and the next in intensity being $M^+ - 109$, which, as in aconitine, is due to the successive elimination of an acetic acid molecule, a methoxyl radical, and a molecule of water at the expense of an acetoxy residue at C_8, a methoxy group at C_1, and a hydroxy group at C_3 [5]. Furthermore, the ratio of the $M - OR_1$, M^+, and $M^+ - 15$ peaks in the mass spectrum of aconifinidine show that the methoxy group at C_1 is α-oriented [7].

The acetylation of (I) with acetic anhydride in the presence of pyridine gave a monoacetate (IV) in the NMR spectrum of which, as in the spectra of the acetates of acomonine and of iliensine [8, 9], a one-proton quartet is observed at 4.91 ppm (J_1 = 10 Hz, J_2 = 7 Hz) showing that the hydroxy group at C_3 was acetylated. The signal of the methyl protons of the acetoxy group in aconifine appears at 1.26 ppm. This phenomenon is characteristic for alkaloids containing a benzoyloxy group at C_{14} and an acetoxy group at C_8, as is explained on the methyl protons of the acetoxy group [10-12]. The position of the benzoloxy group at C_{14} is confirmed by the presence in the NMR spectrum of aconifine of a one-proton doublet at 5.24 ppm (J = 5 Hz) due to the geminal β-C_{14} proton [10, 12, 13].

The vacuum pyrolysis of aconifine led to the formation of two main products, one of which underwent saponification when it was chromatographed on a column of alumina and consisted of pyroaconifidine (V). Its IR spectrum has the absorption band of a carbonyl group in a six-membered ring at 1690 cm^{-1}. It is known that the pyrolysis of alkaloids containing an acetoxy group at C_8 and a hydroxyl at C_{15} is accompanied by the elimination of a molecule of

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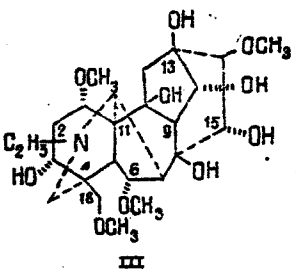
acetic acid with the formation of ketone [4, 15]. These facts confirm the presence in aconifine of an acetoxy group at C_8 and show the presence of hydroxy group at C_{15}, which by analogy with aconitine probably has the α-orientation [16]. The pyrolysis of (I) was accompanied by the liberation of benzoic acid, which is obviously connected with the more far-reaching breakdown of the molecule.

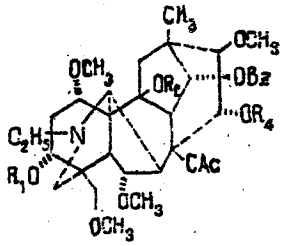
The oxidation of aconifine with potassium permanganate in aqueous acetone gave two products. The main product differed from the initial compound by 28 m.u. Its NMR spectrum showed the methyl signals of an acetoxy group (1.31 ppm, 3 H, singlet) and the signals of four methoxy groups (3.08, 3.21, 3.28, 3.69 ppm, 3 H each, singlets), and of five aromatic protons (7.44 and 7.97 ppm, total of 5 H, multiplets), but lacked the signal of the methyl protons of an N-ethyl group. These facts permit the conclusion that the compound obtained was N-deethylaconifine (VI). The second product possessed no basic properties and its molecular weight was 14 m.u. greater than that of aconifine. The IR spectrum of this compound had intense adsorption bands of ester and lactam carbonyls (1710 and 1650 cm^{-1}, respectively). Consequently, the second product was oxoaconifine (VII). Analogous products are formed in the case of aconitine, which is explained by the presence of an α-methoxy group at C_6 [17, 18].

The signal of the proton at C_{14} in aconifine is shifted downfield by 0.44 ppm as compared with the corresponding signal in the spectrum of aconitine. In a study of the NMR spectra of a number of diterpene alkaloids, it was shown [6, 19, 20] that such a shift is due to the descreening influence of a C_{10} hydroxy group on the β-C_{14} proton.

It was mentioned above that the signal of the C_{14} proton appears in the form of a doublet which shows the presence of a substituent at C_9 or C_{13}. In view of the fact that aconifine is not oxidized by periodic acid and, consequently, contains no free cis-diol system, and also of the great similarity of the chemistry and spectral characteristics of aconifine and aconitine, we may conclude that there is a hydroxyl at C_{13} and methoxy groups at C_{16} and C_{18}, and suggest structure (I) for aconifine.



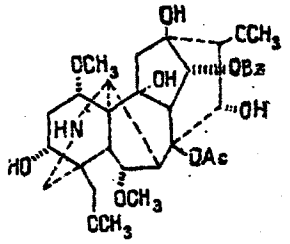
III



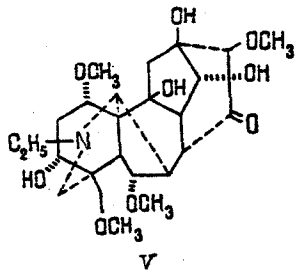
I. $R_1 = R_2 = R_3 = R_4 = H$

II. $R_1 = R_2 = R_3 = R_4 = COCH_3$

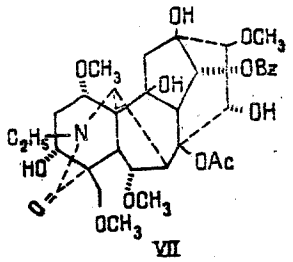
IV. $R_1 = COCH_3, R_2 = R_3 = R_4 = H$



VI



V



VII

This structure is confirmed by the results of study and comparison of the ^{13}C NMR spectra of aconifine and a number of alkaloids with closely related structures [21, 22]. The assignment of the signals were made on the basis of the ^{13}C NMR spectra obtained in deuterochloroform and deuteropyridine under the conditions of complete and incomplete (off-resonance) suppression of carbon-proton couplings and of the results of a comparative study of the signals in aconifine and aconitine and some other alkaloids of similar structure [21].

The ^{13}C NMR spectrum of aconifine in deuteropyridine contains 32 signals. If one bears in mind the fact that in a monosubstituted benzene ring there are two pairs of magnetically equivalent carbon atoms, it may be concluded that the spectrum clearly shows the signals of all the carbon atoms.

The off-resonance spectrum of aconifine contains seven singlets corresponding to seven quaternary carbon atoms. As compared with aconitine, in the signal of which there are six singlets, the spectrum of aconifine shows an additional weak-field singlet at 78.6 ppm due to the C_{10} carbon atom. The hydroxy group at C_{10} has a substantial influence on the chemical shifts of the neighboring carbon atoms relative to the spectrum of aconitine. Thus, the signal of the C_{11} carbon atom appears at 55.9, i.e., shifted downfield by 6.1 ppm as compared with aconitine.

The signal of the C_2 methylene group appears at 33.5 ppm, and the C_{12} signal has undergone considerable downfield shift through the β-hydroxy effect and is found at 48.9 ppm.

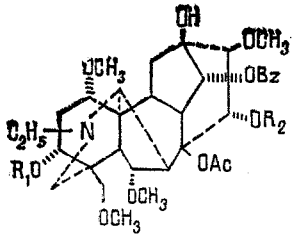
The C_9 tertiary carbon atom adjacent to the C_{10} hydroxy group also undergoes a β-hydroxy effect and is observed at 54.0 ppm, i.e., shifted downfield by 9.8 ppm.

The signals of the γ-carbon atoms C_1, C_5, and C_8 are shifted upfield by 3.6, 3.8, and 2.3 ppm, while the C_{13} signal is shifted downfield by 3.0 ppm.

It can be seen from the facts given above that on passing from deuterochloroform to deuteropyridine there are chemical shifts of the C_2, C_3, and C_4 carbon atoms similar to what takes place in aconine and pseudoaconine; these changes show that with a change in the solvent the conformation of ring A is transformed from boat to chair [23]:

Number	VIII ($CHCl_3$)	I ($CDCl_3$)	I (C_6D_5N)
1	83,4	79,8	80,4
2	36,0	33,5	35,9
3	70,4	71,6	68,4
4	43,2	43,1	43,9
5	46,6	42,8	42,9
6	82,3	83,6	84,3
7	44,8	44,7	45,5
8	92,0	89,7	90,5
9	44,2	54,0	55,0
10	40,8	78,6	78,5
11	49,8	55,9	56,1
12	34,0	48,9	49,4
13	74,0	77,0	75,6
14	78,9	77,3	77,4
15	78,9	78,7	79,8
16	90,1	90,1	91,7
17	60,1	61,2	61,7
18	75,6	74,9	73,5
19	48,8	47,7	49,0
N | CH_2	46,9	47,2	47,4
| CH_3	13,3	13,3	13,6
1′	55,7	55,4	55,5
6′	57,9	58,2	58,1
16′	60,7	61,2	61,4
18′	58,9	59,1	58,4
C=O	172,2	172,1	172,2
| CH_3	21,3	21,5	21,2
C=O	165,9	166,1	166,1
| C_6H_5	129,8 129,6 128,6 129,2	130,2 129,7 128,6 133,2	130,5 129,7 128 6 133,2

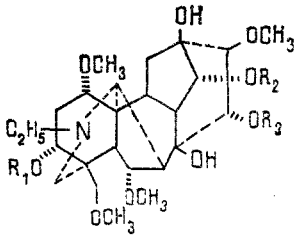
It was mentioned above that the acetylation of aconifine with acetic anhydride in the presence of pyridine formed a monoacetate at C_3 (IV), and the hydroxy group at C_{15} was not acetylated. It has been shown previously for the case of aconitine that it is not oxidized by chromium trioxide [16]. These facts induced us to study aconitine and aconine in acetylation reactions in more detail. On acetylation under mild conditions, aconitine, like aconifine, gives a monoacetate at C_3 (IX) in the NMR spectrum of which the additional signal of an acetoxy group appears at 2.03 ppm and the signal of a proton geminal to it at 4.85 ppm (quartet, J_1 = 10 Hz, J_2 = 7 Hz). It was possible to obtain aconitine diacetate (X) only on acetylation with acetyl chloride for 12 h.



VIII. $R_1 = R_2 = H$

IX. $R_1 = COCH_3$, $R_2 = H$

X. $R_1 = R_2 = COCH_3$



XI. $R_1 = R_2 = R_3 = H$

XII. $R_1 = H$, $R_2 = R_3 = COCH_3$

XIII. $R_1 = R_2 = R_3 = COCH_3$

The NMR spectrum of diacetylaconitine shows the signals of a N-ethyl group, three acetoxy groups, four methoxy groups, and a benzoyl group. The signal of the proton at C_3 appears in the form of a quartet at 4.92 ppm (J_1 = 10 Hz, H_2 = 7 Hz), and the signal of the β-C_{15} proton in the form of a doublet with a coupling constant of 5 Hz at 5.07 ppm. The observed coupling constant agrees well with that calculated for the C_{15}-β proton from a study of a Dreiding model.

The course of the reaction on the acetylation of aconine (XI) with acetic anhydride in the presence of pyridine is different. The acetylation of aconine for 15 minutes led to the formation of a mixture of products of which the main one was the diacetate of aconine at C_{14} and C_{15} (XII). In its NMR spectrum the signal of the proton geminal to the C_{14} acetoxy group appears at 4.60 ppm (1 H, doublet, J = 5 Hz) and that of the C_{15} proton appears at 5.16 ppm (1 H, doublet, J = 6 Hz). Consequently, in aconine the main direction of the reaction is connected with the acetylation of the hydroxy groups of ring D and not of the hydroxyl at C_3, as is observed in iliensine [9]. In view of the relative difficulty of acylating a hydroxyl at C_{14} [24], we may assume that intramolecular catalysis is involved in the acetylation of aconine [25, 26]. More prolonged acetylation forms aconine triacetate (XIII), in the NMR spectrum of which are observed the signals of the β-C_3 proton at 4.83 ppm (1 H, quartet, J_1 = 10 Hz, J_2 = 7 Hz), of the β-C_{14} proton at 4.57 ppm (1 H, doublet, J = 5 Hz), and of the β-C_{15} proton at 5.21 ppm (1 H, doublet, J = 6 Hz).

EXPERIMENTAL

Melting points are uncorrected. IR spectra were obtained on a UR-20 spectrophotometer, mass spectra on an MKh-1303 and MKh-1310 mass spectrometers fitted with a system for direct introduction into the ion source, PMR spectra on a JNM-H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard (values given in the δ scale), and ^{13}C NMR spectra on WP-80 (Bruker) and Varian-XL-100-15 spectrometers in deuterochloroform at 20 MHz and in deuteropyridine at 25.3 MHz, respectively, in the pulsed regime with subsequent Fourier transformation under conditions of complete and partial decoupling of the C–H interactions (off-resonance). The concentrations of the solutions were 0.2-0.25 M. Chemical shifts are given relative to TMS as internal standard. For chromatography we used KSK silical gel and alumina (activity grade II).

Aconifine (I). mp 195-197°C (acetone); hydrochloride with mp 183-184°C (acetone). $[\alpha]_D^{20}$ + 14.8° (CH_3OH). NMR spectrum (ppm): 0.96 (3 H, triplet, J = 6 Hz), 1.26 (3 H, singlet), 3.61 (3 H, singlet), 3.14 (6 H, singlet), 3.00 (3 H, singlet), 7.87 and 7.39 (5 H, multiplets), and 5.24 (1 H, doublet, J = 5 Hz).

Aconifine Tetraacetate (II). A solution of 80 mg of aconifine in 2 ml of acetyl chloride was kept at room temperature for 90 h. The acetyl chloride was evaporated off, the residue was dissolved in water, and the solution was made alkaline with sodium carbonate in the presence of ice and was extracted with ether. The ethereal solution was dried with sodium sulfate. After the solvent had been distilled off with the aid of acetone 37 mg of a powdered product was isolated. M^+ 829. IR spectrum: 1720, 1740 cm^{-1}.

The Amino Alcohol of Aconifine (III). A solution of 0.19 g of aconifine in 6 ml of 5% KOH in methanol was boiled for 1 h. The methanol was evaporated off, the residue was dissolved in cooled 2% sulfuric acid, the solution was extracted with ether three times, and the ethereal extract was dried over sodium sulfate. Removal of the solvent by distillation

yielded 15 mg of benzoic acid. The acid solution was made alkaline with sodium carbonate and evaporated to dryness, and the residue was shaken with chloroform several times with heating and the resulting solution was dried over sodium sulfate. After the solvent had been distilled off, 90 mg of pulverulent amino acid was isolated with the aid of acetone. Mass spectrum: M^+ 515 (2.3%), 500 (4.2%), 484 (100%), 468 (67%), 466 (30%), 450 (14.4%), 438 (4%), 436 (5%). NMR spectrum (ppm): 1.12 (3 H, triplet), 3.12 (3 H, singlet), 3.15 (3 H, singlet), 3.30 (3 H, singlet), 6.58 (3 H, singlet), 4.50 (1 H, doublet, J = 5 Hz).

Aconifine Monoacetate (IV). A solution of 90 mg of aconifine in 3 ml of acetic anhydride and 0.1 ml of pyridine was kept for 60 h. The reaction product was worked up as in the preparation of compound (II). With the aid of acetone, 70 mg of crystalline monoacetate was isolated with mp 211-213°C. $(M^+ - 60)$ 643. NMR spectrum (ppm): 1.07 (3 H, triplet, J = 6Hz), 1.38 (3 H, singlet), 2.01 (3 H, singlet), 3.10 (6 H, singlet), 3.21 (3 H, singlet), 3.69 (3 H, singlet), 4.91 (1 H, quartet, J_1 = 10 Hz, J_2 = 7 Hz), 5.36 (1 H, doublet, J = 5 Hz), 7.49 and 8.00 (5 H, multiplets).

Pyrolysis of Aconifine. Aconifine (0.3 g) was heated in vacuum at 195-200°C for 6 min. The walls of the vessel became coated with sublimed crystals of benzoic acid (15 mg). The reaction product was chromatographed on a column of alumina, and elution with benzene–methanol (50:1) yielded 0.11 g of the pulverulent product (V). M^+ 497. IR spectrum: 1690 cm^{-1}.

Marion Oxidation of Aconifine. A solution of 0.32 g of potassium permanganate in 80 ml of a 50% mixture of acetone and water was added to a solution of 0.3 g of aconifine in 40 ml of the same solvent and the mixture was shaken for 15 min. Then the excess of potassium permanganate was decomposed with sodium sulfite. The manganese dioxide that deposited was filtered off, and the acetone was distilled off on the water bath. The residual aqueous solution was acidified with 2% sulfuric acid, with cooling, and was extracted with ether. The extract was dried over sodium sulfate, and after the solvent had been distilled off, with the aid of acetone 20 mg of oxoaconifine (VI) was isolated with mp 290°C, $(M^+ - 60)$ 615. IR spectrum: 1710, 1650 cm^{-1}.

With cooling, the acid solution was made alkaline with sodium carbonate and was extracted with chloroform. The product obtained after the chloroform had been distilled off was chromatographed on a column of silica gel. Benzene–methanol (30:1) eluates yielded 80 g of pulverulent noraconifine (VI). $(M^+ - 60)$ 573. NMR spectrum (ppm): 1.31 (3 H, singlet), 3.08 (3 H, singlet), 3.20 (3 H, singlet), 3.27 (3 H, singlet), 3.69 (3 H, singlet), 5.30 (1 H, doublet, J = 5 Hz), 7.47 and 7.97 (5 H, multiplets).

Monoacetylaconitine (IX). A mixture of 0.3 g of aconitine with 6 ml of acetic anhydride and 0.3 ml of pyridine was kept at room temperature for 60 h. The acetic anhydride was evaporated off, the residue was dissolved in water, the solution was made alkaline with sodium carbonate, and the reaction product was extracted with ether. The residue obtained after the ether had been distilled off was treated with ether–acetone (10:1). This yielded 0.19 g of the crystalline monoacetate (IX) with mp 201-203°C, $(M^+ - 60)$ 627. NMR spectrum (ppm): 1.07 (3 H, triplet, J = 6 Hz), 1.38 (3 H, singlet), 2.01 (3 H, singlet), 3.10 (6 H, singlet), 3.25 (3 H, singlet), 3.69 (3 H, singlet), 4.85 (1 H, quartet, J_1 = 10 Hz, J_2 = 7 Hz), 5.36 (1 H, doublet, J = 5 Hz). IR spectrum: 1720 cm^{-1}.

Aconitine Diacetate (X). A mixture of 0.3 g of aconitine and 7 ml of acetyl chloride was kept at room temperature for 12 h. After elimination of the acetyl chloride the residue was dissolved in water, and the solution was made alkaline and was extracted with ether. After the solvent had been driven off, with the aid of acetone 0.16 g of diacetate was isolated with mp 157-159°C. M^+ 729. NMR spectrum (ppm): 1.07 (3 H, triplet, J = 6 Hz), 1.32 (3 H, singlet), 2.01 (3 H, singlet), 2.03 (3 H, singlet), 3.16 (6 H, singlet), 3.18 (3 H, singlet), 3.33 (3 H, singlet), 4.29 (1 H, doublet, J = 4 Hz), 4.92 (1 H, quartet, J_1 = 10 Hz, J_2 = 7 Hz), 5.07 (1 H, doublet, J = 5 Hz), 7.48 and 7.97 (5 H, multiplet).

Aconine Diacetate (XII). A mixture of 0.34 g of aconine with 5 ml of acetic anhydride and 0.2 ml of pyridine was kept at room temperature for 15 min. The acetic anhydride was evaporated off and the residue was worked up as in the preceding experiment. Treatment with ether–acetone (5:1) led to the separation of a crystalline product which, after recrystallization from ether–acetone, had mp 224-225°C. Yield 210 mg. M^+ 583. NMR spectrum (ppm): 1.10 (3 H, triplet, J = 6 Hz), 2.00 (3 H, singlet), 2.17 (3 H, singlet), 3.20 (3 H, singlet), 3.25 (3 H, singlet), 3.50 (3 H, singlet), 3.61 (3 H, singlet), 4.60 (1 H, doublet, J = 5 Hz), 5.16 (1 H, doublet, J = 6 Hz).

Aconine Triacetate (XII). A mixture of 0.3 g of aconine with 5 ml of acetic anhydride and 0.2 ml of pyridine was kept at room temperature for 8 h. The acetic anhydride was evaporated off, the residue was dissolved in water, and the solution was extracted with ether. The extract was dried over sodium sulfate and distilled. The product was chromatographed on a column of silica gel and from the benzene–methanol (100:1) eluates with the aid of hexane 210 mg of pulverulent aconine triacetate was isolated. M^+ 625. NMR spectrum (ppm): 1.09 (3 H, triplet, J = 6 Hz), 2.01 (6 H, singlet), 2.13 (3 H, singlet), 3.14 (3 H, singlet), 3.16 (3 H, singlet), 3.20 (3 H, singlet), 3.50 (3 H, singlet), 4.57 (1 H, doublet, J = 5 Hz), 4.83 (1 H, quartet, J_1 = 10 Hz, J_2 = 7 Hz), 5.18 (1 H, doublet, J = 6 Hz).

SUMMARY

The structure of the new alkaloid aconifine isolated from the tubers and epigeal part of *Aconitum karakolicum* Rapcs. has been established on the basis of the results of a study of the chemical transformations and spectral characteristics.

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