molecular interaction of thio (sulfoxy) and urea groups separated by a saturated chain of six carbon atoms as a consequence of the existence of the molecules under investigation in a folded conformation has been established.

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STRUCTURE OF TERDELINE

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A new alkaloid which has been called terdeline has been isolated from the epigeal part of Delphinium ternatum. Its structure has been demonstrated on the basis of spectral characteristics and the preparation of a demethylene derivative, and also by direct passage from eldelidine to terdeline.

We have previously reported the isolation from Delphinium ternatum of a base $C_{27}H_{43}NO_7$ (I) with mp 116-118°C (ether—hexane), which proved to be new and eas called terdeline [1].

The PMR spectrum of the alkaloid has the signals of C-methyl and N-ethyl groups and of five methoxy groups and a methylenedioxy group. When terdeline was heated in 10% sulfuric acid, product (II) was obtained the PMR spectrum of which lacked the signal of a methylenedioxy group and contained the signals of five methoxy groups. The IR spectrum and the deuteration of the base showed the absence of hydroxy groups form (I). The following developed formula may be given for terdeline:

$$C_{17}H_{18}(C—CH_3)\ (N—C_2H_5)\ (CH_2O_2)\ (OCH_3)_5$$

The mass spectrum of (I) was characteristic for the spectra of diterpene bases with the lycoctonine skeleton, and the maximum peak, corresponding to $M^+ - 31$ ion, showed the presence of a methoxy group at C-1 [2]. The ^{13}C NMR spectrum of terdeline with complete decoupling from protons consists of 26 isolated signals, and only one of them, at 50.3 ppm, corresponds to two carbon atoms (C-9 and $-CH_2-CH_3$) the values of the chemical shifts of

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TABLE 1. Chemical Shifts of the Signals of the Carbon Atoms and Their Assignment in the ^{13}C NMR Spectra of Terdeline (I), Dictyocarpinine (III), Eldelidine (IV), Delcorine (V), Deoxydelcorine (VI), and Deoxylycoctonine (VII) (δ, ppm; $CDCl_3$; 0 – TMS)

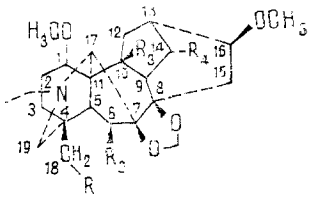
C-atom	I	III [3]	IV [3]	V [3]	VI [4]	VII [5]
1	77,7	79,9	80,2	83,1	83,1	82,8
2	27,2	26,4	27,0	26,4	26,6	26,8
3	36,8*	36,9	38,7	31,8	32,2	37,3
4	33,0	33,9	33,6	38,1	38,1	34,1
5	44,3	51,9	51,0	52,6	44,5	43,4
6	90,3	77,3	77,4	78,9	32,2	91,5
7	91,9	93,4	92,4	92,7	90,5	88,6
8	82,8	82,8	83,5	83,9	81,7	77,6
9	50,3	51,6	51,5	48,1	47,8	55,2
10	88,5	80,5	82,4	40,3	43,6	46,2
11	57,6	55,4	56,2	50,2	50,8	49,3
12	36,6*	36,7	36,8	28,1	28,0	28,9
13	38,1	36,5	37,6	37,9	38,3	38,2
14	81,7	72,6	81,6	82,5	83,5	84,5
15	35,3	33,2	34,3	33,3	33,1	33,8**
16	82,7	81,2	81,6	81,8	81,9	84,1
17	63,1	64,0	63,2	63,9	61,8	64,3
18	26,3	25,4	25,6	78,9	79,0	26,8
19	57,1	57,2	57,3	53,7	52,6	56,8
$N-CH_2$	50,3	50,5	50,4	50,7	50,4	50,9
CH_3	13,8	14,0	13,9	14,0	13,8	14,0
$O-CH_2-O$	94,0	93,4	93,3	92,9	93,3	—
1′	54,9	55,6	55,5	55,5	55,4	55,6**
6′	58,5	—	—	—	—	58,2**
10′	52,0	—	—	—	—	—
14′	57,8	—	57,9	57,8	57,6	57,7**
16′	56,0	56,3	56,2	56,3	56,1	56,2
18′	—	—	—	59,6	59,3	—

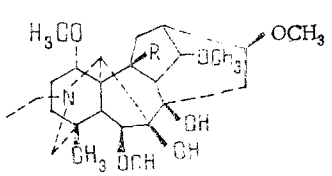
* The mutaually opposite assignment is possible.
** In this case the assignment has been reconsidered in comparison with the initial assignment in [5].

which proved to be identical. The assignment of the signals of the carbon atoms was made by a comparative analysis of the spectral characteristics of (I) obtained under the conditions of complete and partial decoupling from the protons with those of diterpene alkaloids: dictyocarpinine (III), eldelidine (IV), delcorine (V) [3], deoxydelcorine (VI) [4], and deoxylycoctonine (VII) [5]. The results of the assignment and the values of the chemical shifts of the carbon atoms of terdeline are given in Table 1.

As can be seen from Table 1, the introduction of an oxygen substituent into the C-10 position leads to an upfield shift of the C-1 signal by approximately 3-5 ppm (I, III, IV). The replacement of a methoxymethyl group at C-4 by a methyl group causes an appreciable downfield shift of the C-3 and C-19 signals and, conversely, an upfield shift of the C-4 signal (I, III, IV, VII). The presence of a methoxy group at C-6 has no appreciable influence on the C-5 chemical shift (I, VI, VII), while a hydroxy group in the same position causes a considerable downfield shift of the C-5 signal (III, IV, V). The expected downfield shift takes place when a hydroxy group at C-10 (III, IV) is replaced by a methoxy group (I). The presence of an oxygen substituent at C-10 leads to a substantial downfield shift of the C-11 and C-12 signals (I, III, IV).

The facts given above permit structure (I) to be proposed for terdeline.





I. $R_1 = H$; $R_2 = R_3 = R_4 = OCH_3$
III. $R_1 = H$; $R_2 = R_3 = R_4 = OH$
IV. $R_1 = H$; $R_2 = R_3 = OH$; $R_4 = OCH_3$
V. $R_1 = R_4 = OCH_3$; $R_2 = OH$; $R_3 = H$
VI. $R_1 = R_4 = OCH_3$; $R_2 = R_3 = H$
VIII. $R_1 = H$; $R_2 = R_4 = OCH_3$; $R_3 = OH$

II. $R = OCH_3$
VII. $R = H$

To confirm this hypothesis, we methylated eldelidine (IV) with methyl iodide in the presence of dioxane and of N,N-dimethylformamide (DMFA). In the case of dioxane, ~90% of 6-O-methyleldelidine (VIII) and ~5% of 6,10-di-O-methyleldelidine (I) were formed. An increase in the time of methylation did not lead to a change in the ratio of products formed. When DMFA was used, ~87% of (I) and ~7% of (VIII) were formed. The 6,10-di-O-methyleldelidine was identical with terdeline in all respects (mixed melting points, TLC, and IR spectra). Thus, terdeline is the first diterpene alkaloid with a methoxy group at C-10.

EXPERIMENTAL

The homogeneity of the substances was checked by chromatography in a thin layer of alumina (for chromatography) in the hexane–ether, (1:1), ether, and ether–methanol (100:1) systems and with the use of 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 JNM-4H-100/100 MHZ instrument (δ, ppm; $CDCl_3$; HMDS), ^{13}C NMR spectra on a CFT-20 spectrometer (Varian), in $CDCl_3$ with TMS as internal standard, and mass spectra on an MKh-1310 instrument fitted with a system for direct introduction into the ion source.

For the Isolation and Separation of the Total Alkaloids, see [6].

Terdeline (I). After being dried in vacuum, the substance melted at 116-118°C. IR spectrum: 1100 cm^{-1} (simple C–O bonds). PMR spectrum: 0.89 (3H, s, $C-CH_3$), 1.07 (3H, t, $N-CH_2-CH_3$), 3.18, 3.29, 3.31, 3.41, (5 OCH_3), 5.07 (2H, s, $O-CH_2-O$). Mass spectrum: m/z (%): M^+ 493(2), M^+-15(6), M^+-29(8), M^+-30(32), M^+-31(100), M^+-45(10), M^+-47 (9).

Demethyleneterdeline (II). A mixture of 0.11 g of terdeline and 15 ml of 10% sulfuric acid was heated in the steam bath for 18 h. With cooling, the reaction mixture was made alkaline with sodium carbonate and was extracted with ether. The residue after the evaporation of the solvent was chromatographed on alumina (deactivated). The reaction product was eluted with a mixture of hexane and ether. Hexane–ether (1:2) yielded the chromatographically homogeneous product (II). PMR spectrum, ppm: 0.91 (3H, s, $C-CH_3$), 0.99 (3H, t, J = 7 Гe, $N-CH_2-CH_3$), 3.18; 3.27; 3.32; 3.37; 3.39 (3 H each, s, 5 OCH_3), Mass spectrum: M^+ 481.

Methylation of Eldelidine in Dioxane. A. A mixture of 0.05 g of the base, 5 ml of dioxane, 2.5 ml of methyl iodide, and 0.06 g of sodium hydride was boiled 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 solution was washed with ether and, with cooling, was made alkaline with sodium carbonate and was extracted with ether. The residue after the solvent had been distilled off was chromatographed on alumina. The reaction product was eluted with mixtures of hexane, ether, and chloroform. Hexane–ether (1:5) yielded 2 mg of 6,10-di-O-methyleldelidine (I) with mp 116-118°C (hexane–ether), and ether–chloroform (1:1) gave 45 mg of 6-O-methyleldelidine (VIII) with mp 132-134°C (hexane–ether).

B. A mixture of 0.05 g of the base, 5 ml of dioxane, 2.5 ml of methyl iodide, and 0.06 g of sodium hydride was boiled for 18 h. The reaction products were worked up and isolated by the procedure described above. This gave ~3 mg of (I) and ~45 mg of (VIII).

Methylation of Eldelidine in DMFA. A mixture of 0.05 g of the base, 10 ml of DMFA, 2.5 ml of methyl iodide, and 0.06 g of sodium hydride was boiled for 8 h. The reaction products were worked up and isolated by the procedure described. This gave ~43 mg of (I) and ~3 of (VIII).

SUMMARY

A new alkaloid, which has been called terdeline, has been isolated from the epigeal part of Delphinium ternatum. Its structure has been demonstrated on the basis of the results of a study of spectral characteristics, the production of demethyleneterdeline, and a passage from eldelidine to terdeline.

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PROTEIN CONTENT, ACTIVITY AND AMINO ACID COMPOSITION OF PROTEINASE INHIBITORS OF SEEDS OF SOME VARIETIES OF PEA AND THEIR HYBRIDS

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The results are given of a study of the quantitative content of protein in the seeds of some pea varieties and mutants, the activity of the total inhibitor proteins, and correlations of their activity with the protein content of the seeds and the amino acid compositions of the proteinase inhibitors. Considerable differences have been found in the amounts of a number of amino acids of the protein inhibitors of parental varieties and mutants of the pea, the amounts of serine, glutamic acid, alanine, and valine correlating positively with the inhibitor activity.

Considerable amounts of proteins capable of acting as effective inhibitors of proteolytic enzymes of living organisms — trypsin and chymotrypsin — have been found in the seeds of legumes (soybean, pea, bean, lupin, etc.) [1-4].

Various functions are ascribed to proteinase inhibitors in plants. It is considered that they may play the role of reserve proteins or regulators of the activity of proteolytic processes preventing the premature breakdown of the reserve proteins [5]. Proteins inhibiting trypsin and chymotrypsin are capable of suppressing the activity of the proteases of a number of harmful insects and phytopathogenic microorganisms thereby protecting plants from damage [6]. In addition, these proteins find use in the elucidation of the mechanism of the action of specific enzymes [7] and in practical medicine [8].

At the same time, it is considered that the presence of inhibitors in a grain, particularly when they have a high activity, considerably lowers their nutrient value and impairs the technological properties of the proteins of cultivated plants [9]. Therefore, in the selection of agricultural crops directed to increasing protein content one of the criteria of the quality of the seeds is the amount and activity of proteins that are proteinase inhibitors.

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