SUMMARY

Twelve alkaloids have been isolated from the epigeal part of wild *Glaucium corniculatum* (L.) J. Rudolf, one of them — norbracteolin — proving to be new.

Dehydrocorydine, predicentrine, glaufidine, thalicmidine, reticulin, and stylopine α-methohydroxide have been isolated from this species for the first time.

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CRYSTALLINE AND MOLECULAR STRUCTURES OF THE ALKALOID DELCOSINE

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The molecular and crystalline structures of the diterpene alkaloid delcosine (iliensine) have been investigated by x-ray structural analysis. It has been confirmed that the OH group in ring A is located at C(1) and has the α orientation. The rings in the molecule have the following conformations: A, B, and D — boat; C and F — envelope; E — chain. The ring linkages are: A/B — trans; A/E — cis; B/C — cis; B/D — cis; B/F — cis. The conformations and linkages of the rings are identical with those observed in lycoctonine.

In order to determine fully and unambiguously the spatial structure of the diterpene alkaloid delcosine (iliensine) (I) isolated from the plant *Delphinium biternatum* Huth., belonging to the family Ranunculaceae [1], we have performed an x-ray structural analysis.

The structure of the molecule of (I) projected onto the (010) crystallographic plane is shown in Fig. 1. The shapes and conformations of the rings can be judged from the figures of Table 1, which gives the coefficient of the equations of the main planes and the deviations of the atoms from them. The cyclohexane ring A (the C(1)C(2)C(3)C(4)C(5)C(11) atoms) has the boat conformation (the C(1), C(3), C(4), and C(11) atoms lie in one plane with an accuracy of 0.07 Å), and ring D (the C(8)C(9)C(13)C(14)C(15)C(16) atoms) also has the boat shape but with a slight flattening on the side of the C(16) atom. The seven-membered ring B (the C(5)C(6)C(7)C(8)C(9)C(10)C(11) atoms) has the boat conformation (with an accuracy of 0.05 Å); the departure of the C(5), C(6), and C(9) atoms from the plane of the other four amounts to 1.25, 1.45, and 0.50 Å, respectively (see Table 1). The five-membered ring C (the C(9)C(10)C(12)C(13)C(14) atoms) and F (the C(5)C(6)C(7)C(11)C(17) atoms) have the envelope conformation, but in ring F this form is somewhat distorted. The heterocycle E (the C(4)C(5)C(11)C(17)N(18)C(19) atoms) has the chair conformation. Ring linkages are as follows: A/B — trans; A/E — cis; B/C — cis; B/D — cis; B/F — cis. The conformations of the rings and also their linkages agree completely with those observed in hydroxymethyllycoctine hydriodide [2]. The hydroxy group in ring A is present in position 1 and is α-oriented, which confirms

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TABLE 1. Coefficients of the Equations Ax + By + Cz = D of the Main Planes of the Fragments of the Molecule (I) and the Deviation (δ) of the Atoms from the Planes

Plane	Atom	δ, Å	*A*	*B*	*C*	*D*
A	C(1)	−0,07	0,75	14,59	7,47	11,59
	C(3)	0,07				
	C(4)	−0,07				
	C(11)	0,07				
	C(2)*	0,62				
	C(5)*	0,64				
B	C(7)	0,05	−3,73	13,92	3,34	6,42
	C(8)	−0,04				
	C(10)	0,04				
	C(11)	−0,05				
	C(5)*	1,25				
	C(6)*	1,45				
	C(9)*	0,50				
	C(17)*	−0,87				
C	C(9)	0,60	3,65	11,28	9,59	11,70
	C(10)	−0,01				
	C(12)	0,01				
	C(13)	0,00				
	C(14)*	0,76				
D	C(8)	0,01	−1,81	−1,30	17,04	7,37
	C(9)	−0,01				
	C(13)	0,01				
	C(15)	−0,01				
	C(14)*	0,87				
	C(16)*	0,28				
F	C(5)	−0,06	4,62	3,81	13,59	13,58
	C(6)	−0,09				
	C(7)	0,09				
	C(17)	−0,06				
	C(11)*	0,80				
E	C(5)	−0,02	7,52	2,59	−4,08	2,68
	C(4)	0,02				
	C(17)	0,02				
	N(18)	−0,02				
	C(11)*	0,93				
	C(19)*	−0,58				

the results of previous work [3, 4]. The orientations of the other substituents are as follows: The CH_2OCH_3 group in position 4 is β, the OCH_3 groups in positions 6 and 15 are β, the OH's in positions 7 and 8 are β, and the OH at C(14) is α-oriented.

The lengths of the bonds and the values of the valence angles are given in Table 2. These magnitudes were determined with an error not greater than 0.012 Å and 0.67°, respectively. The lengths of ordinary C_{sp^3}—C_{sp^3} bonds range between 1.48 and 1.58 Å, but within the 3σ limits they can be harmonized with the generally accepted value of 1.54 Å. The scatter in the lengths of the heterobonds is small, and their values are close to the standard values [5]. The considerable variation in the angles from 96.3 to 117.7° at the tetrahedral carbon atom bonds is connected with the stress present in the bridge fragments of the molecule [6, 7].

The mutual positions of the hydroxy and ester groups favor the formation of intramolecular H-bonds of the O—H...O and O—H...N type as can be seen from the following distances: O(20)...N(18) 2.67 Å; O(24)...O(27) 2.68 Å; and O(26)...O(27) 2.67 Å.

The packing of the molecules of (I) is shown in Fig. 2 in projection on the plane of the b, c axes. The O(20)H and O(28)H hydroxy groups participate in the intermolecular H-bonds. The molecules transformed by twofold screw axes are connected by intermolecular H-bonds and form an infinite chain directed along the c crystallographic axis.

EXPERIMENTAL

The delcosine crystals were grown from methanol solution. The space group and the parameters of the elementary cell were determined from rotation and Weissenberg x-ray patterns and were refined on a Syntex $P2_1$ diffractometer (Institute of Bioorganic Chemistry, Academy of Sciences of the Uzbek SSR) using Mo K_α radiation: a = 7.836(5), b = 16.207(9), c = 17.577(9); d_{calc} = 1.356 g/cm³; space group P $2_12_12_1$, z = 4. A three-dimensional set of

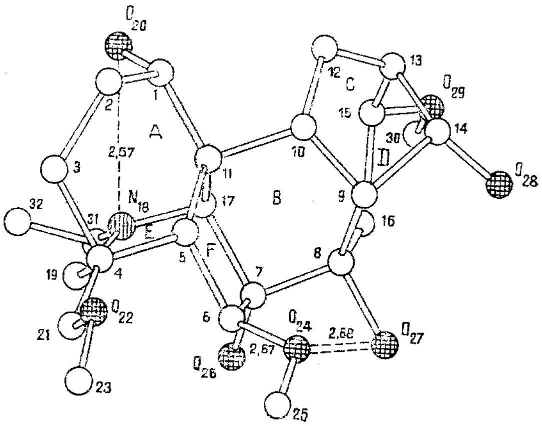

Fig. 1. Structure of the delcosine molecule.

TABLE 2. Interatomic Distances (r, Å) and Valence Angles (ω, deg)

Distance	r	Distance	r	Angle	ω	Angle	ω
C(1)—C(2)	1,54	C(9)—C(10)	1,54	2—1—11	111,6	4—21—22	107,4
C(1)—C(11)	1,54	C(9)—C(14)	1,53	2—1—20	109,1	8—9—10	112,3
C(1)—O(20)	1,45	C(10)—C(11)	1,55	11—1—20	114,7	8—9—14	109,7
C(2)—C(3)	1,48	C(10)—C(12)	1,53	1—2—3	112,0	10—9—14	101,7
C(3)—C(4)	1,54	C(11)—C(17)	1,54	2—3—4	113,7	9—10—11	117,7
C(4)—C(5)	1,54	C(12)—C(13)	1,54	3—4—5	111,4	9—10—12	105,2
C(4)—C(19)	1,55	C(13)—C(14)	1,51	3—4—19	112,3	11—10—12	111,2
C(4)—C(21)	1,54	C(13)—C(15)	1,52	3—4—21	109,6	1—11—5	112,3
C(5)—C(6)	1,55	C(14)—O(28)	1,41	5—4—19	106,0	1—11—10	107,5
C(5)—C(11)	1,56	C(15)—C(16)	1,58	5—4—21	111,8	1—11—17	115,1
C(6)—C(7)	1,57	C(15)—O(29)	1,43	19—4—21	105,6	5—11—10	115,2
C(6)—O(24)	1,43	C(17)—N(18)	1,46	4—5—6	111,1	5—11—17	96,3
C(7)—C(8)	1,54	N(18)—C(19)	1,44	4—5—11	110,2	10—11—17	110,4
C(7)—C(17)	1,55	N(18)—C(31)	1,45	6—5—11	103,9	10—12—13	105,8
C(7)—O(26)	1,40	C(21)—O(22)	1,41	5—6—7	104,9	12—13—14	101,5
C(8)—C(9)	1,55	O(22)—C(23)	1,42	5—6—24	116,1	12—13—15	110,9
C(8)—C(16)	1,52	O(24)—C(25)	1,43	7—6—24	112,3	14—13—15	112,6
C(8)—O(27)	1,44	O(29)—C(30)	1,39	6—7—8	112,6	9—14—13	101,5
		C(31)—C(32)	1,50	6—7—17	101,6	9—14—28	112,6
				6—7—26	111,0	13—14—28	116,8
				8—7—17	110,9	13—15—16	113,3
				8—7—26	110,3	13—15—29	107,8
				17—7—26	110,2	16—15—29	109,2
				7—8—9	109,9	7—17—11	100,7
				7—8—16	110,9	7—17—18	118,5
				7—8—27	105,1	11—17—18	110,6
				9—8—16	114,9	17—18—19	113,8
				9—8—27	112,7	17—18—31	114,4
				16—8—27	102,7	19—18—31	114.4
				4—19—18	113,2	21—22—23	111.3
				6—24—25	112,4	15—29—30	113.6
						18—31—32	113.1

intensities was obtained on the diffractometer mentioned, about 2000 independent reflections being measured. The calculations were carried out with the 1640 structural factors exceeding 2σ.

The structure was interpreted by the direct method using the Rentgen-75 program [8] in the automatic regime: From 310 values of E $\geqslant$1.24 were composed 4650 ternary products, the reference group consisting of eight reflections. An E-series was constructed from the best variant of the signs and in this 28 out of the 32 nonhydrogen atoms were found (R factor 0.25). For a more accurate localization of the atoms and to find the lacking atoms several ρ(xyz) syntheses were calculated. Then the structure was refined by the method of least squares (MLS) on the isotropic approximation to R = 0.14. In the following stage the position parameters of all the atoms were refined in the full-matrix anisotropic approximation to R = 0.104. In the final stage, difference electron-density (ED) syntheses were calculated by the method of least squares in order to find the coordinates of the hydrogen atoms. Out of the 39 hydrogen atoms, 19 were localized. The coordinates of the C, O, and N atoms and

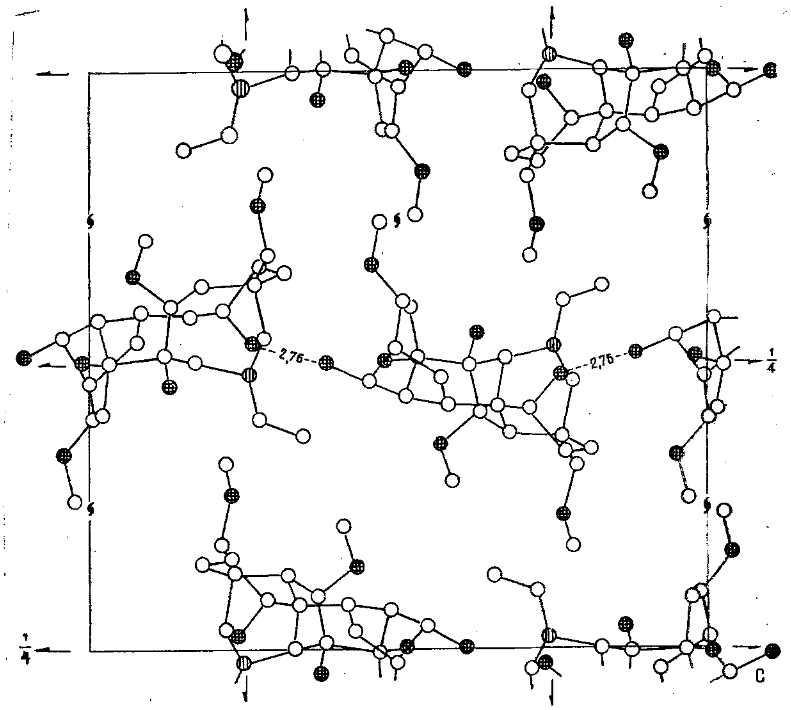

Fig. 2. Packing of the molecules of (I).

TABLE 3. Coordinates ($\times 10^4$) of the C, O, and N Atoms and Coordinates ($\times 10^3$) of the H Atoms Found from the Difference ED Synthesis

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
C (1)	2993 (11)	4136 (6)	7231 (5)	H (1)	179	404	698
C (2)	3289 (12)	3384 (6)	7754 (5)	H (2)	318	283	744
C (3)	4889 (13)	3459 (5)	8195 (5)	H (2)′	247	347	817
C (4)	6443 (11)	3717 (5)	7709 (5)	H (3)	499	283	848
C (5)	6031 (10)	3684 (5)	6856 (4)	H (3)′	479	397	864
C (6)	7511 (12)	4051 (5)	6377 (4)	H (5)	569	311	663
C (7)	6927 (9)	4951 (5)	6183 (4)	H (6)	826	432	684
C (8)	6278 (10)	5035 (5)	5362 (4)	H (10)	315	350	598
C (9)	4970 (11)	4339 (6)	5185 (4)	H (12)	112	447	562
C (10)	3753 (11)	4178 (5)	5854 (5)	H (12)′	203	503	626
C (11)	4484 (10)	4259 (4)	6672 (4)	H (13)	167	552	477
C (12)	2249 (12)	4768 (6)	5731 (5)	H (14)	277	418	449
C (13)	2664 (11)	5249 (5)	4998 (4)	H (15)	345	633	571
C (14)	3734 (12)	4628 (6)	4567 (5)	H (16)	583	603	469
C (15)	3634 (11)	6033 (6)	5177 (4)	H (17)	469	550	656
C (16)	5639 (10)	5907 (5)	5209 (4)	H (19)	845	474	781
C (17)	5458 (9)	5084 (4)	6760 (4)	H (20)	369	511	781
N (18)	5890 (8)	5227 (3)	7556 (3)	H (26)	835	600	580
C (19)	7018 (12)	4616 (5)	7875 (5)	H (27)	787	433	485
O (20)	2592 (8)	4852 (3)	7695 (3)	H (31)	733	637	753
C (21)	7989 (11)	3169 (5)	7913 (4)				
O (22)	7571 (8)	2349 (3)	7710 (3)				
C (23)	8962 (12)	1808 (5)	7836 (5)				
O (24)	7987 (7)	3594 (3)	5712 (3)				
C (25)	8980 (14)	2881 (6)	5891 (6)				
O (26)	8239 (7)	5516 (3)	6320 (3)				
O (27)	7780 (6)	4987 (3)	4895 (3)				
O (28)	4582 (8)	4915 (4)	3911 (3)				
O (29)	3236 (7)	6624 (3)	4601 (3)				
C (30)	3826 (14)	7415 (5)	4763 (5)				
C (31)	6357 (12)	6070 (5)	7728 (5)				
C (32)	5955 (23)	6313 (6)	8530 (5)				

the coordinates of the hydrogen atoms found from the difference ED synthesis are given in Table 3.

M. R. Yagudaev participated in a discussion of the results obtained.

SUMMARY

The spatial structure of the diterpene alkaloid delcosine (iliensine) has been determined by x-ray structural analysis and it has been confirmed unambiguously that the OH group in ring A is present at C(1) and has the α orientation.

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STRUCTURE OF THE PRODUCTS OF THE METABOLISM OF DEOXYPEGANINE AND OF DEOXYVASICINONE

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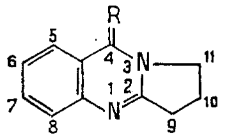
The structures of the main components of the total metabolites of the anticholinesterase drug deoxypeganine (DOP) and its analog deoxyvasicinone (DOV) in the rat organism have been studied. The structures of two metabolites of DOP and DOV — 11α-hydroxydeoxyvasicinone and 2-(β-ethoxycarbonyl)ethyl-4-quinazoline — have been determined by the PMR method. On the basis of their structures and the results of measurements of the elementary compositions of ions, the fragmentation of the compounds has been elucidated. A minor component of the total metabolites has been isolated by chromato-mass spectrometry and for it the structure of 6-methoxydidehydrovasicinone is proposed. A scheme of the metabolism of DOP and DOV has been put forward.

Over a number of years, we have been studying the metabolites, excreted with the urine of animals, of the hydrochloride of deoxypeganine (DOP, I) and its derivative deoxyvasicinone (DOV, II) [1], which possess cholinotropic activity. It has been shown that the biotransformation of DOP takes place through a stage of the formation of DOV [2].



I. $R = H_2$ Deoxypeganine

II. $R = O$. Deoxyvasicinone

Mass spectrograms of the combined free metabolites of DOP and DOV are similar in the region of the spectrum above m/z 185 (Fig. 1, Ia and IIa). Even greater similarity is observed between the spectrum of the total combined metabolites of (I) and (II) (Fig. 1, Ib, IIb). A quantitative determination of the sums of the free metabolites of these drugs showed that their amounts of biotransformation products were of the same order of magnitude, but DOP (I) was subjected to metabolic transformation to a far smaller degree than DOV (II) [2]. In view of this, the main material used for isolating the pure components and demonstrating their structures was the sum of the metabolites of DOV. As the result of a preliminary separation of the sum of the free metabolites of (II) on a column of alumina, in addition to the

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