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CRYSTAL AND MOLECULAR STRUCTURE OF THE NEW DILACTONE ANABSIN

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A complete x-ray structureal study has been made of the dilactone anabsin. The crystals are monoclinic, $a = 9.863$ (4) Å, $b = 14.240$ (6) Å, c = A, c 11.149 (6) A, $\gamma = 103.61°$, $z = 2$, space group $P2_1$ (diffractometer, 2035 reflections, MLS in the anisotropic approximation, R β 0.65). The conformation of the molecule and the position of attachment of the monomeric parts of anabsin have been determined unambiguously. The length of the bonds and the magnitude of the valence angles are the usual ones. The five-membered rings A, C, D, and H have the envelope conformation, and the five-membered ring F a planar conformation. The seven-member ring G has the chair conformation and B a distorted twisted chair conformation. The linkages of rings A/B and G/H are trans, and of E/F cis.

The bislactone anabsin ($C_{30}H_{40}O_7$) isolated from *Artemisia absinthium* L., family Compositae, has been ascribed the structure (I) on the basis of chemical and spectral characteristics [1, 2]. In order to establish the linkage of the monomeric parts of anabsin and its spatial structure unambiguously, we have performed an x-ray structural study. Preliminary results of this study have been published previously [3].

The molecule of the diguaianolide anabsin the XY projection is shown in Fig. 1. The conformations of the rings can be judged unambiguously from the figures of Table 1, which gives the equations of the planes and the deviations of the atoms from the corresponding planes. It can be seen from this Table that the lactone ring A has the ^{22}E envelope conformation, the deviation of the C(22) atom being 0.54 A. The cycloheptane ring B (the C(16), C(20), C(21), C(22), C(23), C(24), and C(25) atoms) has a $^{22,21}C_{24}$ distorted twisted chair structure, the C(20), C(21), and C(24) atoms deviating in different directions from the plane by 1.22, 1.30, and −0.62 Å, respectively. The furan ring C has the ^{20}E envelope conformation, the C(20) atom deviating from the plane by 0.876 Å. The cyclopentane rings D and E also have envelope conformations, the deviations of the C(20) and C(16) from the corresponding planes being 0.977 and −0.893 Å. Ring F is planar. The cycloheptane ring G (the atoms C(1), C(5), C(6), C(7), C(8), C(9), and C(10)) is a $^{5,6}C_9$ chair, the deviations of the C(5), C(6), and C(9) atoms in different directions from the plane passing through the C(1), C(7), C(8), and C(10) atoms being 1.082, 1.107, and −0.663 Å, respectively. The lactone ring H has the ^{7}E envelope conformation, the deviation of the C(7) being −0.661 Å.

The linkages of rings A/B and G/H are trans, and of E/F cis.

The length of the bonds and the sizes of the valence angles are given in Tables 2 and 3. As can be seen from Table 2, the lengths of the C-C bonds in the rings range from 1.486 to 1.583 Å, but the mean value of 1.538 Å is close to the standard 1.541 Å [4]. The mean length of a O-C(sp^3) bond is 1.473 Å. In the γ-lactone ring H the C=O double bond is somewhat shortened: 1.176 Å in place of 1.21 Å [4]. The nature of the variation of the valence angles is readily traced from the figures of Table 3. In spite of the considerable variation, the values of the valence angles agree with those given for organic compounds [5]. The two molecules of methanol of crystallization are bound to the anabsin molecule by $O_{m1}...O(32)$ and $C_{m2}...O(35)$ hydrogen bonds with lengths of 2.76 Å and 2.77 Å, respectively. The O(35) oxygen atom also forms a so-called "bifurcated" hydrogen bond with the oxygen atom O(31) of the ether bridge with a length of 2.72 Å.

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TABLE 1. Equations Ax + By + Cz − D = 0 of the Planes and the Deviations of the Atoms from the Corresponding Planes, δ (Å)

Ring	Atom	A	B	C	D	δ
A	O (3)	−4,910	4,046	9,477	5,404	−0,026
	C (21)					0,014
	C (26)					−0,014
	C (27)					0,026
	C(22)*					−0,543
B	C (22)	−8,248	7,680	4,684	7,959	0,051
	C (23)					−0,059
	C (16)					0,052
	C (25)					0,059
	C(20)*					1,223
	C(2)*					1,300
	C(24)*					0,618
C	C (16)	5,210	7,546	5,771	9,618	0,027
	O (1)					0,045
	C (19)					−0,030
	C (25)					−0,043
	C(20)*					0,876
D	C (17)	−0,564	13,250	−3,638	9,998	0,108
	C (8)					−0,107
	C (19)					0,073
	C (16)					−0,075
	C(20)*					0,977
E	C (2)	−9,663	4,147	2,120	2,781	−0,066
	C (3)					0,065
	C (17)					0,045
	C (20)					−0,043
	C(16)*					−0,893
F	C (1)	4,844	7,138	−6,652	2,651	0,039
	C (2)					−0,042
	C (3)					0,031
	C (4)					−0,006
	C (5)					−0,022
						−0,026
G	C (7)	3,465	10,991	3,590	11,966	0,030
	C (8)					−0,029
	C (10)					
	C (1)					0,026
	C (5)*					1,082
	C (6)*					1,107
	C (9)*					−0,663
H	O (4)	0,135	13,721	1,135	9,632	−0,018
	C (6)					0,011
	C (11)					−0,011
	C (12)					0,018
	C (7)*					−0,661

*Atoms not included in the calculation of the equations of the planes.

Packing of the Molecules. The anabsin molecules are linked by intermolecular hydrogen bonds formed by the oxygen atoms of the hydroxy and carbonyl groups (O(31)...O(36), 2.83 Å) and form helices around a twofold screw axis (Fig. 2). There are somewhat shortened van der Waals contacts of 3.00 and 3.05 Å, respectively, between the oxygen atoms of a molecule of methanol O_{m1} and the C(27) and O(33) atoms of the anabsin molecule. The other contacts are normal.

EXPERIMENTAL

The anabsin crystals, grown from methanolic solution, proved to be the dimenthanol solvate $C_{30}H_{40}O_7 \cdot (CH_3OH)_2$.

The parameters of the elementary cell and the space group were determined from precession x-ray diagrams and were refined in a Syntex-$P2_1$ four-circle automatic diffractometer (Institute of Bioorganic Chemistry of the Academy of Sciences of the Uzbek SSR): a = 9.863(4) Å, b = 14.240(6) Å, c = 11.149(6) Å, γ = 103.61°, V = 1521.9 Å, ρ_{calc} = 1.26 g/cm^3, M = 576.68, z = 2, space group $P2_1$.

TABLE 2. Length of the Bonds in the Anabsin Structure, Å

Bond	r	Bond	r
O (1)—C (19)	1,472 (7)	O (1)—C (25)	1,475 (7)
O (2) C (10)	1,411 (6)	O (3) –C (21)	1,464 (6)
O (3)—C (27)	1,331 (6)	O (4)—C (6)	1,483 (7)
O (4)—C (12)	1,370 (7)	O (5) C (18)	1,404 (6)
O (6)– C (27)	1,216 (6)	O (7) –C (12)	1,176 (8)
C (1)– C (2)	1,566 (8)	C (1) C (5)	1,523 (8)
C (1)– C (10)	1,557 (8)	C (2)—C (3)	1,536 (8)
C (2)—C (17)	1,542 (8)	C (3) –C (4)	1,519 (8)
C (3)—C (20)	1,571 (8)	C (4) C (5)	1,334 (7)
C (4)—C (15)	1,487 (8)	C (5) C (6)	1,486 (8)
C (6)—C (7)	1,520 (8)	C (7) –C (8)	1,497 (7)
C (7)—C (11)	1,544 (8)	C (8)—C (9)	1,555 (8)
C (9)—C (10)	1,547 (7)	C (10) –C (14)	1,564 (8)
C (11)—C (12)	1,529 (7)	C (11) –C (13)	1,513 (8)
C (16)—C (17)	1,545 (8)	C (16)—C (20)	1,583 (8)
C (16)—C (25)	1,532 (8)	C (17) –C (18)	1,565 (8)
C (18)—C (19)	1,559 (8)	C (19) –C (20)	1,567 (8)
C (19)—C (30)	1,517 (8)	C (20)—C (21)	1,521 (7)
C (21)– C (22)	1,537 (8)	C (22)—C (23)	1,534 (8)
C (22)– C (26)	1,509 (8)	C (23)—C (24)	1,518 (7)
C (24)—C (25)	1,524 (8)	C (25)—C (29)	1,522 (7)
C (26)– C (28)	1,520 (7)		

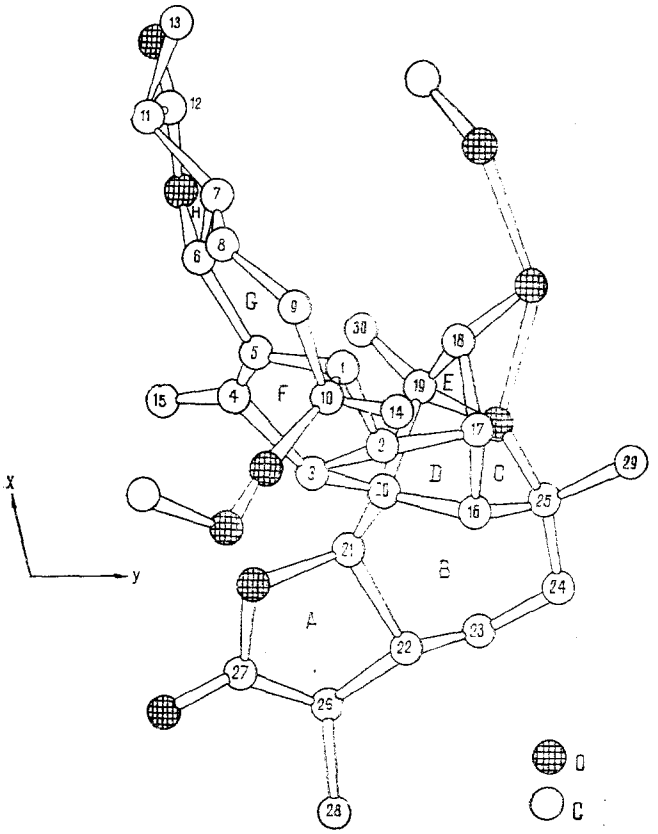

Fig. 1

A three-dimensional experimental set of intensities was measured on the same diffractometer by the $\theta/2\theta$ method using CuKα radiation and a nickel filter, $\sin\theta/\lambda \leqslant 0.55$, rate of scanning 10 deg/min, number of independent and nonzero reflections with $I > 2\sigma$, 2035.

The structure was determined by the direct method using the tangent formula according to the Rentgen-75 system of programmes [6]. An attempt at interpretation in the automatic regime, i.e., by screening the 1024 variants of the investigation of the 15 E-syntheses with

TABLE 3. Values of the Valence Angles in the Anabsin Structure

Angle	Degrees	Angle	Degrees
C (10) C (1) C (5)	114,62 (5)	C (17) C (18) O (5)	116,1 (5)
C (2) C (1) C (5)	102,3 (4)	C (17) C (18) C (19)	100,0 (4)
C (1) C (2) C (3)	107,4 (4)	O (5) C (8) C (19)	111,8 (5)
C (1) C (2) C (17)	102,1 (5)	C (18) C (19) C (20)	102,6 (5)
C (3) C (2) C (17)	116,2 (4)	C (18) C (19) O (1)	107,7 (5)
C (2) C (3) C (4)	104,9 (5)	C (20) C (19) O (1)	101,2 (5)
C (2) C (3) C (20)	105,0 (5)	C (18) C (19) C (30)	114,0 (5)
C (4) C (3) C (20)	120,7 (5)	O (1) C (19) C (30)	107,7 (5)
C (3) C (4) C (5)	111,0 (5)	C (20) C (19) C (30)	122,3 (5)
C (3) C (4) C (15)	123,2 (5)	C (16) C (20) C (19)	91,1 (4)
C (5) C (4) C (15)	125,7 (6)	C (16) C (20) C (21)	117,3 (5)
C (4) C (5) C (1)	114,0 (5)	C (16) C (20) C (3)	101,4 (4)
C (4) C (5) C (6)	122,7 (6)	C (19) C (20) C (21)	111,6 (5)
C (1) C (5) C (6)	123,3 (5)	C (19) C (20) C (3)	115,3 (5)
C (5) C (6) O (4)	110,6 (5)	C (3) C (20) C (21)	117,1 (4)
C (5) C (6) C (7)	117,7 (5)	C (20) C (21) O (3)	111,5 (5)
C (7) C (6) O (4)	102,6 (5)	C (20) C (2) C (22)	118,4 (5)
C (6) C (7) C (8)	113,6 (5)	C (22) C (21) O (3)	103,0 (4)
C (6) C (7) C (11)	100,0 (5)	C (21) C (22) C (23)	109,7 (5)
C (8) C (7) C (11)	117,9 (5)	C (7) C (11) C (12)	100,9 (6)
C (7) C (11) C (13)	118,0 (6)	C (21) C (22) C (26)	102,0 (5)
C (12) C (11) C (13)	113,5 (5)	C (23) C (22) C (26)	115,5 (5)
C (8) C (9) C (10)	118,4 (6)	C (22) C (23) C (24)	113,8 (5)
C (9) C (10) C (1)	113,7 (5)	C (23) C (24) C (25)	118,8 (6)
C (9) C (10) C (14)	104,0 (5)	C (24) C (25) O (1)	109,3 (4)
C (1) C (10) C (14)	109,2 (5)	C (24) C (25) C (16)	114,8 (5)
O (2) C (10) C (14)	105,6 (5)	C (24) C (25) C (29)	107,8 (6)
O (2) C (10) C (1)	111,3 (5)	O (1) C (25) C (16)	101,5 (5)
O (2) C (10) C (9)	112,5 (5)	O (1) C (25) C (29)	109,2 (5)
C (11) C (12) O (7)	129,2 (6)	C (16) C (25) C (29)	113,9 (5)
C (11) C (12) O (4)	108,9 (5)	C (19) O (1) C (25)	108,0 (4)
O (4) C (12) O (7)	121,4 (7)	C (21) O (3) C (27)	109,1 (5)
C (2) C (17) C (16)	100,8 (4)	O (3) C (27) O (6)	121,9 (6)
O (3) C (27) C (26)	111,6 (5)	O (6) C (27) C (26)	126,5 (6)
C (2) C (17) C (18)	107,6 (5)	C (22) C (26) C (27)	101,7 (5)
C (16) C (17) C (18)	103,8 (5)	C (27) C (26) C (28)	113,7 (6)
C (17) C (16) C (20)	93,7 (5)	C (22) C (26) C (28)	117,9 (7)
C (17) C (16) C (25)	113,3 (4)	C (20) C (16) C (25)	104,8 (5)
C (10) C (1) C (2)	112,3 (5)	C (7) C (8) C (9)	111,3 (6)

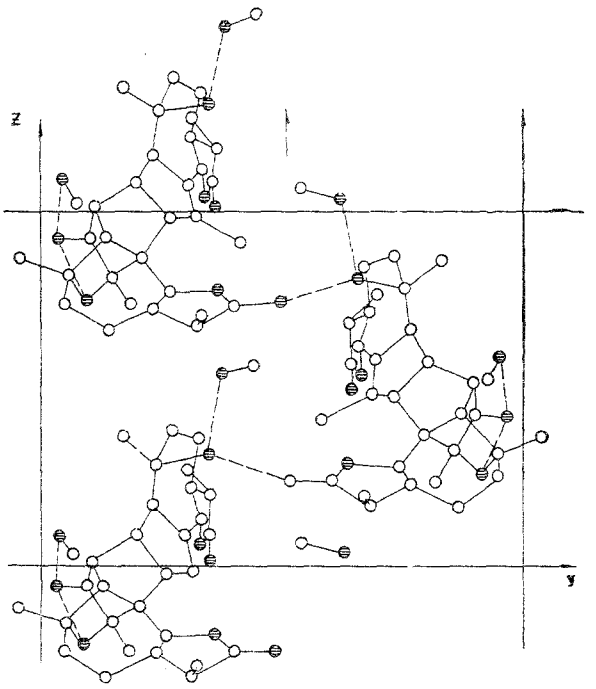

Fig. 2

TABLE 4. Coordinates of the Atoms and Their Anisotropic Thermal Factors × 10^4

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C (1)	3014 (6)	7766 (4)	6588 (5)	77	33	47	30	6	13
C (2)	1787 (6)	8024 (4)	5868 (6)	79	33	56	14	2	6
C (3)	1384 (6)	7272 (4)	4862 (5)	69	37	42	14	13	6
C (4)	2453 (5)	6661 (4)	4938 (5)	64	35	59	20	6	9
C (5)	3326 (5)	6940 (4)	5854 (5)	62	45	51	33	— 4	11
C (6)	4465 (5)	6457 (4)	6154 (5)	61	50	49	27	4	9
C (7)	5399 (6)	6848 (4)	7212 (6)	83	45	60	47	— 2	15
C (8)	4683 (7)	6651 (5)	8401 (6)	105	66	54	50	—56	—23
C (9)	3876 (7)	7435 (5)	8713 (6)	102	71	42	64	—36	—19
C (10)	2620 (6)	7510 (4)	7920 (6)	92	46	47	37	19	— 6
C (11)	6637 (7)	6385 (5)	6959 (6)	95	49	70	54	10	7
C (12)	6737 (6)	6473 (5)	5594 (7)	72	56	96	56	56	50
C (13)	8004 (7)	6799 (6)	7593 (8)	85	71	129	60	—38	—33
C (14)	2074 (8)	8351 (5)	8502 (6)	154	60	60	96	—15	—24
C (15)	2428 (7)	5819 (5)	4143 (6)	106	44	70	34	—38	—19
C (16)	915 (6)	8815 (4)	4264 (5)	103	27	51	28	—00	— 2
C (17)	2144 (6)	8980 (4)	5159 (6)	95	36	53	21	— 0	0
C (18)	3436 (6)	8967 (4)	4352 (6)	72	39	66	— 8	21	— 0
C (19)	2685 (6)	8486 (4)	3200 (5)	92	45	55	51	32	10
C (20)	1266 (6)	7877 (4)	3705 (5)	83	31	42	42	20	— 2
C (21)	321 (6)	7367 (4)	2707 (5)	71	39	44	22	— 0	16
C (22)	—1040 (6)	7680 (4)	2454 (6)	95	43	57	33	—13	18
C (23)	— 724 (8)	8617 (5)	1719 (7)	149	58	67	76	—41	37
C (24)	— 138 (6)	9517 (5)	2457 (6)	101	48	71	55	9	41
C (25)	1142 (7)	9548 (4)	3235 (5)	112	39	47	35	33	1
C (26)	—1905 (7)	6804 (5)	1824 (6)	108	62	55	53	—40	— 5
C (27)	—1381 (6)	6000 (4)	2397 (6)	77	41	57	— 7	—28	—20
C (28)	—3483 (8)	6648 (7)	1857 (8)	110	88	105	75	—45	—22
C (29)	1704 (8)	10588 (5)	3638 (7)	155	46	79	47	— 8	12
C (30)	3605 (7)	8054 (5)	2378 (7)	106	69	67	77	46	—13
O (1)	2215 (4)	9237 (3)	2519 (4)	103	46	56	56	30	20
O (2)	1503 (4)	6685 (3)	8008 (4)	92	62	58	41	22	17
O (3)	— 163 (4)	6331 (3)	2944 (4)	84	40	57	28	—15	—13
O (4)	5472 (4)	6549 (3)	5149 (4)	91	70	59	64	12	10
O (5)	4330 (5)	9870 (3)	4105 (5)	112	41	100	3	7	21
O (6)	—1961 (5)	5147 (3)	2394 (5)	118	47	98	9	—74	— 5
O (7)	7722 (5)	6566 (4)	4971 (5)	106	101	111	112	72	57
O(M1)*	590 (7)	6170 (5)	307 (5)	265	83	127	127	104	4
C(M1)	1182 (11)	5402 (6)	596 (8)	237	59	86	116	37	— 3
O(M2)	6216 (5)	9592 (4)	5842 (6)	120	97	114	66	—57	—79
C(M2)	7237 (9)	9223 (7)	5209 (9)	130	90	124	30	— 4	—69

*O(M1), C(M1), and C(M2) are the atoms of the solvate methanol molecules.

TABLE 5. Coordinates of the Hydrogen Atoms of the Anabsin Molecule × 10^3

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H (1)	391	834	671	H (20)	16	617	933
H (2)	397	590	839	H (21)	189	1,014	5
H (3)	626	566	724	H (22)	354	733	957
H (4)	578	756	705	H (23)	108	850	805
H (5)	220	578	1,124	H (24)	193	833	953
H (6)	101	749	207	H (25)	241	1,123	109
H (7)	285	897	847	H (26)	322	1,105	—56
H (8)	229	960	559	H (27)	—9	869	458
H (9)	—159	685	101	H (28)	—188	871	158
H (10)	136	618	854	H (29)	392	566	628
H (11)	92	786	635	H (30)	476	798	854
H (12)	—4	1,014	198	H (31)	28	483	1,117
H (13)	254	587	327	H (32)	89	1,083	414
H (14)	—105	952	311	H (33)	447	873	222
H (15)	181	517	449	H (34)	—408	598	144
H (16)	—369	730	166	H (35)	518	1,021	466
H(17)	52	689	500	H (36)	— 152	757	321
H(18)	—383	657	278	H (37)	534	678	906
H(19)	360	998	155	H (38)	304	789	150

the best S-estimates was unsuccessful. After several screenings of the coordinate and reference reflections it was possible to find the correct phase variant. For this purpose, of the 300 normalized amplitudes ($E \geqslant 1.4$) the following were selected as the coordinate and reference reflections:

Index of the reflection	Coordinate reflections	Reference reflections
h	$\bar{1}\ 0\ \bar{9}$	$0\ \bar{3}\ \bar{4}\ 3\ 4$
k	$1\ 3\ 3$	$1\ 4\ 5\ 6\ 8$
l	$1\ 0\ 0$	$0\ 1\ 7\ 5\ 4$

In the E-synthesis with the best R factor of 0.24 we found 30 out of the 37 nonhydrogen atoms of the molecule. By ascribing to these atoms the scattering power of carbon atoms we constructed a three-dimensional electron-density series (R = 0.39) in which all the atoms of the anabsin molecule appeared. After arranging the atoms according to varieties, the structure of the disguaianolide was refined by the method of successive approximations to an R-factor of 0.22. On analyzing the results of the subsequent F-synthesis, in addition to the atoms of the anabsin molecule, we found four peaks standing out with respect to the height of the electron density. These peaks, after the scattering power of carbon atoms had been ascribed to them, were included in the set of coordinates, and a three-dimensional series of electron density was constructed. In this F-synthesis, the two molecules of methanol clearly appeared and the divergence factor R was then 0.16. The structure was refined by the method of least squares in the block-diagonal variant, first in the isotropic and then in the anisotropic approximation, to an R-factor of 0.083. A Fourier difference synthesis showed the positions of 38 hydrogen atoms. The final R-factor, taking the hydrogen atoms into account, was 0.065. The coordinates and anisotropic thermal factors are given in Table 4, and the coordinates of the hydrogen atoms in Table 5.

The experimental figures on the Syntex diffractometer were obtained with the assistance of B. Ibragimov.

CONCLUSION

On the basis of the results of an x-ray structural investigation, the position of linkage of the two monomeric moieties of anabsin and its spatial structure has been determined.

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