STRUCTURE TYPES OF DIHYDROERGOTOXINE MESYLATES+

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Three new crystal structures of dihydroergopeptines: dihydro-α-ergokryptine mesylate monohydrate acetone solvate (**1**), dihydro-α-ergokryptine mesylate monohydrate nitromethane solvate (**2**), and dihydroergocornine mesylate monohydrate methanol solvate (**3**) have been determined by X-ray single crystal diffraction. These structures were compared with published structures of dihydro-α-ergokryptine mesylate monohydrate ethanol solvate (**4**), dihydro-β-ergokryptine mesylate monohydrate methanol solvate (**5**), and dihydroergocristine mesylate monohydrate (**6**).

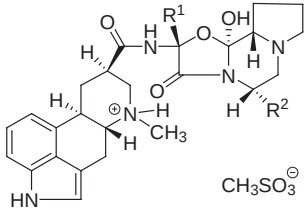
Keywords: Indole alkaloids; Ergot alkaloids; X-Ray diffraction; Crystal structures; Molecular packing; Hydrogen bonds; Polymorphism.

Ergot alkaloids are pharmacologically active metabolites produced by parasitic fungi of the genus Claviceps. These substances have been known since the Middle Ages[2]. They have various medical applications[3], due to the fact, that their chemical structure is closely related to the structures of natural neurotransmitters[4] (dopamine, adrenaline, serotonine). Ergot alkaloids of the dihydroergotoxine group are traditionally used in the treatment of elderly patients suffering from organic brain psychosyndrome, a condition characterized by impairment of cognitive functions with confusion and decreases in mental alertness[5]. Nowadays, the original use of a mixture of all

+ 24th paper on structure and polymorphism of ergot derivatives. For preceding paper of the series, see ref.[1]

four alkaloids, called dihydroergotoxine (dihydroergocristine, dihydro-α-ergokryptine, dihydro-β-ergokryptine, and dihydroergocornine) is gradually replaced by the use of single dihydroergopeptine alkaloids[6–8]. Recently, dihydro-α-ergokryptine was found to show also a neuroprotective activity and positive effect on erythrocyte fluidity under ischemic conditions[9–11].

Polymorphism is widespread in pharmaceuticals. Because polymorphs have different physical properties it is often advantageous to choose the proper polymorph for desired pharmaceutical application. The number of polymorphs can be determined by X-ray powder (different powder patterns) and single crystal X-ray studies (different unit cell parameters). Since various crystalline forms can differ in their pharmacokinetic profile (dissolution rate), bioavailability, chemical stability or physical stability[12], we report here on the existence of various crystalline forms of dihydroergotoxine mesylates and their comparison with the previously reported structures.



1, $R^1 = CH(CH_3)_2$, $R^2 = CH_2CH(CH_3)_2$, monohydrate acetone solvate
2, $R^1 = CH(CH_3)_2$, $R^2 = CH_2CH(CH_3)_2$, monohydrate nitromethane solvate
3, $R^1 = R^2 = CH(CH_3)_2$, monohydrate methanol solvate
4, $R^1 = CH(CH_3)_2$, $R^2 = CH_2CH(CH_3)_2$, monohydrate ethanol solvate
5, $R^1 = CH(CH_3)_2$, $R^2 = -C(H)(CH_3)-CH_2CH_3$, monohydrate methanol solvate
6, $R^1 = CH(CH_3)_2$, $R^2 = CH_2C_6H_5$, monohydrate

EXPERIMENTAL

Preparation of the Crystals

Dihydro-α-ergokryptine mesylate and dihydroergocornine mesylate are the products of IVAX CR Co. Dihydro-α-ergokryptine mesylate (500 mg) was dissolved in acetone (10 ml) and cube shaped colourless crystals of dihydro-α-ergokryptine mesylate monohydrate acetone solvate (**1**) were formed by partial evaporation of acetone during one day. Dihydro-α-ergokryptine mesylate (600 mg) was dissolved in nitromethane (80 ml) and cube shaped crystals of dihydro-α-ergokryptine mesylate monohydrate nitromethane solvate (**2**) were also obtained by partial evaporation of nitromethane within two weeks. Dihydroergocornine mesylate (200 mg) was dissolved in methanol (3 ml) and than ethyl acetate (5 ml) was

added to the solution with stirring. Cube shaped crystals of dihydroergocornine mesylate monohydrate methanol solvate (**3**) were obtained by partial evaporation of methanol in air.

Crystal Structure Determination

Data collection and refinement parameters are listed in Table I, final positions and thermal parameters will be deposited in CSD (ref.[13]). Program CRYSTALS[14] was used for refinement. The ORTEP program[15] was used for visualisation and PARST[16] was used for further calculations. The value of Flack enantiopole parameter[17] proved the expected absolute configurations. For peptide-like numbering[3] of the atoms, see Figs 1 and 2.

TABLE I
Data collection and refinement parameters

Parameter	**1**	**2**	**3**
Crystal dimensions, mm	0.5 × 0.5 × 0.8	0.6 × 0.5 × 0.4	0.3 × 0.2 × 0.5
Diffractometer used	Enraf–Nonius CAD4	Nonius KappaCCD	Nonius KappaCCD
Radiation used λ, Å	1.5418	0.71073	0.71073
Temperature, K	293	150	150
Range of *h*	0→16	–17→16	–14→14
k	0→16	–17→17	–19→19
l	–25→25	–27→26	–26→25
Total number of reflections measured	8 168	27 417	25 492
θ range, °	2.08–69.93	1.02–27.48	1.99–27.11
No. of independent reflections	5 681	8 579	3 617
Percentage of decomposition, %	22	0	0
Criterion of observed reflections		$I > 1.96(I_0)$	
Function minimised		$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
Weighting scheme		Chebychev polynomial (ref.[21])	
Parameters refined	470	702	656
Values of *R*	0.099	0.036	0.052
R_w	0.108	0.036	0.044
S	1.053	1.089	1.032
Flack factor (ref.[17])	0.03(4)	0.01(4)	0.1(1)
Ratio of the maximum least-squares shift to e.s.d. in the 1st cycle	0.002	0.0007	0.0006
Maximum and minimum heights in final Δρ map, e Å^{-3}	–1.20, 0.85	–0.70, 0.65	–0.44, 0.59

Crystal data for dihydro-α-ergokryptine mesylate monohydrate acetone solvate (**1**). $C_{32}H_{44}N_5O_5^+ \cdot CH_3O_3S^- \cdot H_2O \cdot C_3H_6O$ (M_r = 749.918), orthorhombic system, space group $P2_12_12_1$ (No. 19)[18], a = 13.473(1) Å, b = 13.787(1) Å, c = 21.2831(8) Å, Z = 4, V = 3 953.4(4) Å^3, D_c = 1.2599 g cm^{-3}, μ(CuKα) = 12.291 cm^{-1}. The structure was solved by direct methods (SIR92[19]) and anisotropically refined by full matrix least-squares on F (Table I). Hydrogen atoms linked to carbon atoms were located from expected geometry and the other (H1, H2, H3, H4, H5, H6) were found from the difference Fourier electron density map and were not refined.

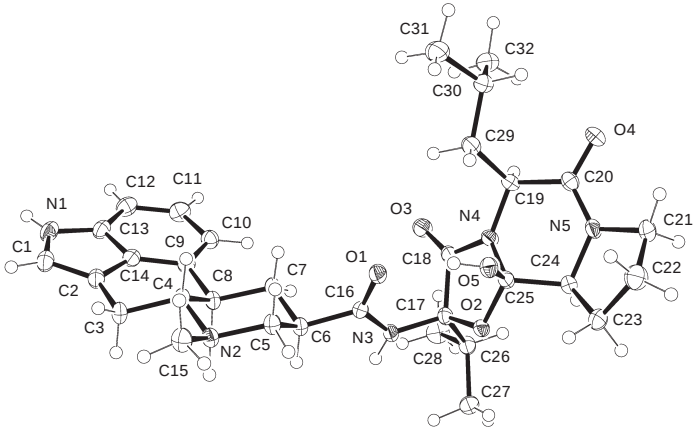


FIG. 1
ORTEP[15] view of dihydro-α-ergokryptine cation of **2**, showing the numbering scheme. Thermal ellipsoids are drawn at 50% probability. The representative example of the structure type II

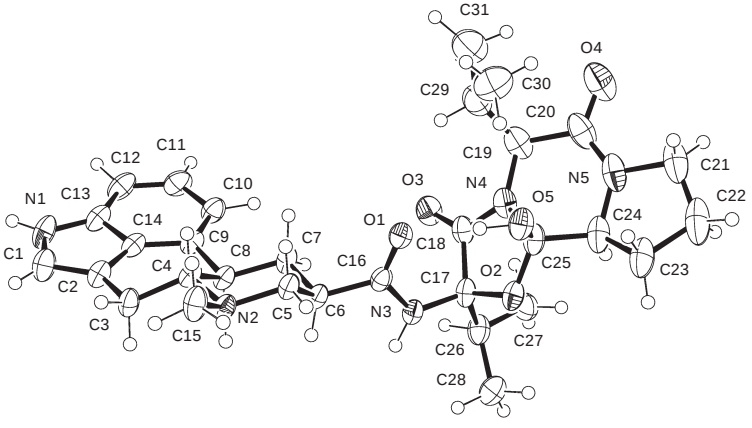


FIG. 2
ORTEP[15] view of dihydroergocornine cation of **3**, showing the numbering scheme. Thermal ellipsoids are drawn at 50% probability. The representative example of the structure type I

Crystal data for dihydro-α-ergokryptine mesylate monohydrate nitromethane solvate (**2**). $C_{32}H_{44}N_5O_5^+ \cdot CH_3O_3S^- \cdot H_2O \cdot CH_3NO_2$ (M_r = 752.878), orthorhombic system, space group $P2_12_12_1$ (No. 19)[18], a = 13.2880(2) Å, b = 13.2940(2) Å, c = 21.2020(2) Å, Z = 4, V = 3 745.35(9) Å^3, D_c = 1.3352 g cm^{-3}, μ(MoKα) = 1.528 cm^{-1}. The structure was solved by direct methods (SHELXS[20]) and anisotropically refined by full matrix least-squares on F (Table I). Hydrogen atoms were found from the difference Fourier electron density map. Positions and isotropic thermal parameters of hydrogen atoms were refined (Fig. 1).

Crystal data for dihydroergocornine mesylate monohydrate methanol solvate (**3**). $C_{31}H_{42}N_5O_5^+ \cdot CH_3O_3S^- \cdot H_2O \cdot 4/3(CH_3OH)$ (M_r = 720.172), orthorhombic system, space group $P2_12_12_1$ (No. 19)[18], a = 11.6750(2) Å, b = 15.3410(2) Å, c = 20.6350(3) Å, Z = 4, V = 3 695.9(1) Å^3, D_c = 1.2943 g cm^{-3}, μ(MoKα) = 1.494 cm^{-1}. The structure was solved by direct methods (SIR92[19]) and anisotropically refined by full matrix least-squares on F (Table I). Hydrogen atoms were found from the difference Fourier electron density map. Positions and isotropic thermal parameters of hydrogen atoms were refined. Only hydrogen atoms linked to the carbon atoms of methanol were located from the expected geometry and their thermal parameters were fixed. A second molecule of methanol with 1/3 occupation was revealed from the difference Fourier electron density map (Fig. 2).

CCDC 175764 for (**1**), CCDC 175765 for (**2**), CCDC 175766 for (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Dihydroergopeptine mesylates crystallize usually in form of various solvates or hydrates. It was found that small polar solvents, *e.g.*, methanol, ethanol, with various dihydroergotoxines can form structures of the same structure type[23] and thus the determined structures **1–3** are just representative examples of these structure types. Three other structures of dihydroergotoxine mesylates have been reported recently[22,23]: dihydro-α-ergokryptine mesylate monohydrate ethanol solvate (**4**), dihydro-β-ergokryptine mesylate monohydrate methanol solvate (**5**), and dihydroergocristine mesylate monohydrate (**6**). Solvates of dihydroergotoxine mesylates are prone to desolvatation and sometimes even a decrease in the alcohol content in the mother liquor causes decomposition of the crystals. Hence, the diffractometric measurements were carried out at 150 K except for **1**. A survey of the X-ray data of the studied structures is listed in Tables I and II.

Three structure types of dihydroergotoxine mesylates are described. Structural parameters of dihydroergocornine monohydrate methanol solvate (**3**) are close to the recently published[22] structures of dihydro-α-ergokryptine monohydrate ethanol solvate (**4**) and dihydro-β-ergokryptine monohydrate methanol solvate (**5**), which forms structure type I. The structure of di-

hydroergocornine (**3**) is not isostructural with those of **4** and **5**, because there is one deviation in the structure of dihydroergocornine (**3**). It is the second molecule of methanol with 1/3 occupation situated between two terminal chains of amino acids forming the cyclol moiety (see Fig. 3a). This is probably caused by constitution of the side chains of leucine and isoleucine in studied molecules of dihydroergokryptines occupy larger volume than the side chain of valine in the molecule of dihydroergocornine. As a result, there is not enough space for another molecule of the solvent in structures of dihydroergokryptines. Whereas dihydro-α-ergokryptine, dihydro-β-ergokryptine, and dihydroergocornine possess nearly identical conformations in the solid state and crystallize in the same structure types.

On the other hand, the structures of dihydro-α-ergokryptine solvates **1** and **2** are nearly isostructural and create the new structure type II (see Fig. 3b). The molecular structures of **1** and **2** are very similar as well as the hydrogen-bond networks, the positions of the molecules and also of the solvents mutually correspond.

The different steric hindrance of phenylalanine in dihydroergocristine mesylate monohydrate[22] (**6**) (the only structure of this compound described so far) causes its slightly different conformation. Thus its structure is the first representant of structure type III of dihydroergotoxines mesylates.

Hydrogen-bond network is similar for all studied dihydroergopeptines mesylates (Table III). Three possible donors and three possible acceptors of the hydrogen bonds were found in molecule of dihydroergotoxines. The "obligatory" intramolecular hydrogen bond O5–H···O1 between the

TABLE II
Structural parameters of dihydroergotoxine mesylates

Compound	Structural type	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3	*Z*	Space group
1	II	13.473(1)	13.787(1)	21.283(1)	3 953.4(4)	4	$P2_12_12_1$
2	II	13.2880(2)	13.2940(2)	21.2020(2)	3 745.35(9)	4	$P2_12_12_1$
3	I	11.6750(2)	15.3410(2)	20.6350(3)	3 695.9(1)	4	$P2_12_12_1$
4	I	11.756(1)	15.573(1)	21.009(4)	3 846.3(8)	4	$P2_12_12_1$
5	I	11.730(5)	15.490(1)	20.520(2)	3 728(2)	4	$P2_12_12_1$
6	III	12.736(2)	39.089(5)	7.130(1)	3 549.6(9)	4	$P2_12_12$

hydroxy group and the amide carbonyl oxygen O1 was found in all structures of ergopeptines[22–27] (except ergopeptams[27]).

The position of mesylate anion is fixed in the structure. Positions of the mesylate anions in structures **1–5** were compared (see Fig. 4). There was just one considerable difference between the orientations of the mesylate anions, namely in the structure of types I and II these anions point in mutually opposite directions. Since mesylate anion is linked in the crystal structure through hydrogen bonds to the molecule of dihydroergotoxine, the orientation of the molecule is different. In the presence of both the mesylate anion and a molecule of water, one can find four more characteristic hydrogen bonds in the crystal structures of dihydroergotoxine mesylates monohydrates. This concerns three intermolecular hydrogen bonds formed in such a way, that the mesylate anion is connected to the

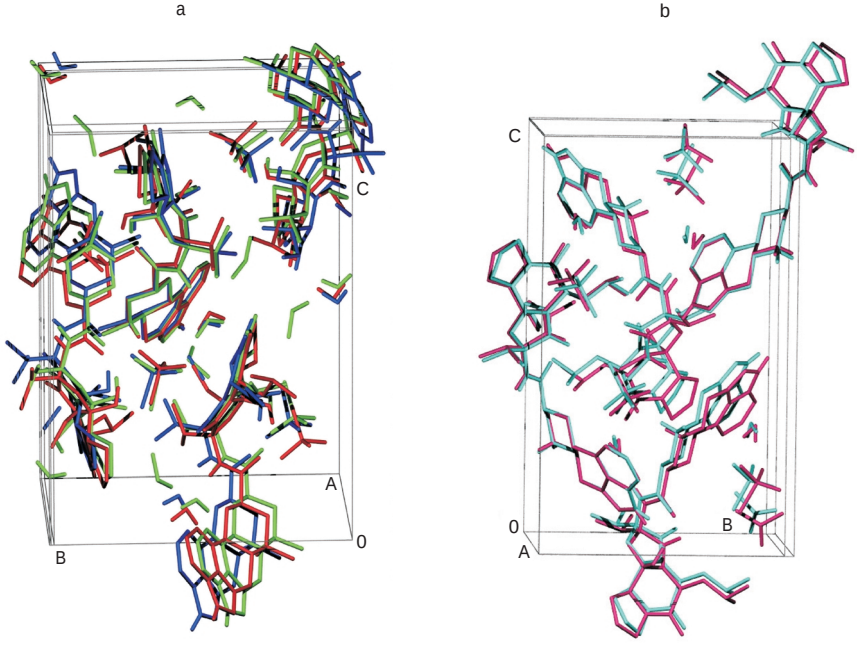


FIG. 3

a Structure type I. Dihydroergocornine mesylate monohydrate methanol solvate (**3**), green line, dihydro-α-ergokryptine mesylate monohydrate ethanol solvate (**4**), red line, and dihydro-β-ergokryptine mesylate monohydrate methanol solvate (**5**), blue line, viewing the $0 \rightarrow x$ direction. b Structure type II. Dihydro-α-ergokryptine mesylate monohydrate acetone solvate (**1**), light blue line, dihydro-α-ergokryptine mesylate monohydrate nitromethane solvate (**2**), pink line, viewing the $x \rightarrow 0$ direction

TABLE III

Hydrogen bonds in structures of dihydroergotoxine mesylates monohydrates (for other hydrogen bonds formed by solvent molecules, which are not included here see Table IV)

Parameter		Symmetry operation	D···A, Å	D–H···A, Å	D–H···A, °
O5–H···O1	**1**	*x*, *y*, *z*	2.804(5)	1.942(5)	157.3(4)
	2	*x*, *y*, *z*	2.776(1)	2.00(2)	153(2)
	3	*x*, *y*, *z*	2.782(3)	1.90(4)	163(4)
	4	*x*, *y*, *z*	2.829(3)	2.075(3)	146.1(3)
	5	*x*, *y*, *z*	2.845(3)	1.95(4)	167(3)
	6	*x*, *y*, *z*	2.662(6)	1.821(4)	131(9)
O9–H···O6	**1**	*x*, *y*, *z*	2.844(6)	2.022(6)	144.9(5)
	2	*x*, *y*, *z*	2.832(2)	2.02(3)	172(3)
	3	*x*, *y*, *z*	2.800(5)	1.86(4)	168(4)
	4(O100–H···O82)[a]	*x*, *y*, *z*	2.865(5)	1.950(5)	164.1(3)
	5(O100–H···O82)[a]	*x*, *y*, *z*	2.827(4)	2.07(6)	175(6)
	6(O91···O61)[a,b,c]	*x*, *y*, *z*	2.9257(2)	–	–
	6(O92···O62)[a,b,c]	*x*, *y*, *z*	3.2168(4)	–	–
N2–H···O8	**1**	*x*, *y*, *z*	2.758(8)	1.906(8)	144.7(5)
	2	*x*, *y*, *z*	2.740(2)	1.83(2)	162(2)
	3	*x*, *y*, *z*	2.883(4)	2.16(2)	166(2)
	4(N2–H···O81)[a]	*x*, *y*, *z*	2.812(4)	1.946(4)	169.5(3)
	5(N2–H···O81)[a]	*x*, *y*, *z*	2.866(4)	2.03(3)	176(3)
	6(N2–H···O81)[a,c]	*x*, *y*, *z*	2.72(2)	1.848(4)	149(6)
	6(N2–H···O82)[a,c]	*x*, *y*, *z*	2.80(2)	1.819(4)	160(6)
N3–H···O9	**1**	*x*, *y*, *z*	2.992(6)	2.132(6)	163.9(5)
	2	*x*, *y*, *z*	2.982(2)	2.10(2)	170(2)
	3	*x*, *y*, *z*	2.878(4)	1.92(4)	173(4)
	4(N3–H···O100)[a]	*x*, *y*, *z*	2.958(4)	2.181(4)	174.7(3)
	5(N3–H···O100)[a]	*x*, *y*, *z*	2.899(4)	2.14(3)	161(3)
	6(N3H···O91)[a,c]	*x*, *y*, *z*	3.085(9)		159(6)
	6N3–H···O92)[a,c]	*x*, *y*, *z*	3.032(9)	2.181(4)	139(5)
O9H···O4	**1**	–*x*+1/2, –*y*+1, *z*+1/2	2.860(6)	2.139(6)	144.7(5)
	2	–*x*–1/2, *y*, *z*–1/2	2.835(2)	2.02(3)	160(3)
	3	*x*+1/2, –*y*+1, *z*–1/2	2.812(4)	1.99(6)	162(5)
	4(O100–H···O4)[a]	–*x*+1/2, –*y*+1, *z*+1/2	2.862(5)	1.922(5)	173.4(4)
	5(O100–H···O4)[a]	*x*+1/2, –*y*+1, *z*–1/2	2.812(4)	1.95(5)	170(5)
N1–H···O3	**6**(N1–H···O3)	*x*–1, *y*, *z*+1	2.934(7)	2.108(4)	130(7)

[a] In loterature another atom numbering was used. [b] Hydrogen atom was not located, but the distance predicts hydrogen bond. [c] Disordered mesylate into two positions.

TABLE IV
Hydrogen bonds formed by solvent molecules in structures of dihydroergotoxine mesylates

Compound	Solvent	D–H···A	Symmetry operation	D···A Å	D–H···A Å	D–H···A °
1	acetone	N1–H···O10	$-x+1/2, -y, z+1/2$	2.940(8)	2.125(8)	152.6(6)
2	nitromethane	N1H···O11	$-x-1/2, -y+1, z-1/2$	3.127(2)	2.33(2)	168(2)
3	methanol	O10–H···O3	x, y, z	2.868(4)	2.03(5)	138(4)
		N1–H···O10	$-x+1/2, -y+1, z-1/2$	2.965(5)	2.21(4)	143(4)
4	ethanol	N1–H···O91	$-x+1/2, -y+1, z-1/2$	3.039(7)	2.335(8)	126.6(4)[a]
5	methanol	N1–H···O81	x, y, z	2.938(7)	2.08(6)	155.9(5)

[a] Slightly shifted position of hydrogen atom.

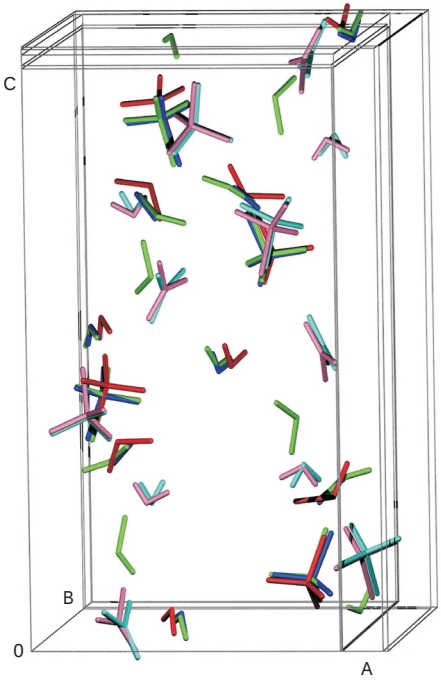


FIG. 4
Comparison of mesylate anion orientations in two structure types (I and II) of dihydroergotoxine mesylates, viewing the $0 \rightarrow y$ direction

ergopeptine moiety *via* contact N2–H···O8 and to the water molecule *via* O9–H···O6, while this molecule of a water in turn links to the ergopeptine moiety *via* N3–H···O9. An additional intermolecular hydrogen bond, O9–H···O4, plays a role of a bridge to another ergopeptine molecule. Another hydrogen bonds are formed by the various solvates presented in the structure (Table IV). For an exemplary case, see the hydrogen-bond network in structure of **3** (Fig. 5).

Hydrogen-bond network in structure of **6** is little bit different. Orientation of mesylate anion and position of water molecule are different, so that there are no hydrogen bonds between water molecule and dihydroergotoxine molecule, link O9–H···O4 and N3–H···O9 in structures of **1–5**. But instead of these hydrogen bonds there is another one between mesylate anion and the dihydroergotoxine molecule N3–H···O7. There is also hydrogen bond connecting two dihydroergotoxine molecules together N1–H···O3, which is not found in structures of **1–5**.

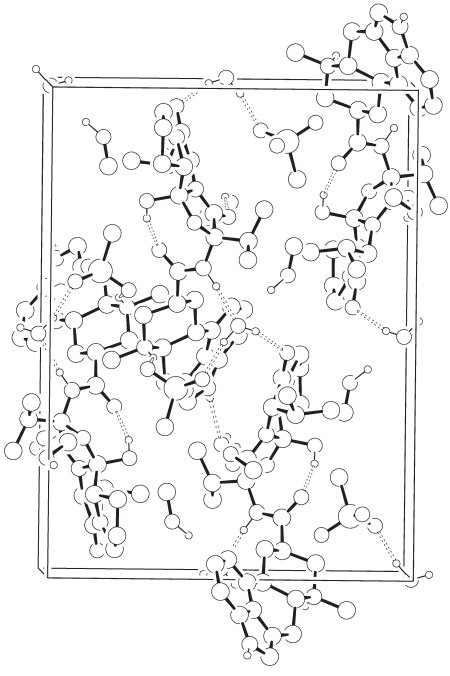


FIG. 5
ORTEP[15] drawing of molecular packing of **3**, dashed bonds indicate hydrogen bonds, viewing the $0 \rightarrow x$ direction

CONCLUSIONS

The similarity of dihydro-α-ergokryptine, dihydro-β-ergokryptine, and dihydroergocornine causes that all these alkaloids share the same conformation of molecules, similar biological activities and also crystallize in the same structure types of their mesylate salts, as well. The hydrogen-bond network and the molecular packing determine the existence of several crystalline forms of their mesylate salts. The results obtained in this work confirm that the diversity of their structures depends particularly on the presence of water and the type of the solvent used for the crystallization. Increasing number of the hydrogen bonds in the structure and increasing boiling point of the solvent used stabilise various solvates in the solid state.

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