Cl(1)—O(5)	1.401 (4)	C(1)—C(2)	1.366 (7)
Cl(2)—O(6)	1.416 (4)	C(2)—C(3)	1.386 (7)
Cl(2)—O(7)	1.404 (4)	C(3)—C(4)	1.379 (7)
Cl(2)—O(8)	1.405 (4)	C(3)—C(8)	1.488 (7)
Cl(2)—O(9)	1.413 (4)	C(4)—C(5)	1.365 (7)
O(1)—C(13)	1.223 (6)	C(6)—C(7)	1.377 (7)
N(1)—C(1)	1.335 (7)	C(7)—C(8)	1.374 (7)
N(1)—C(5)	1.340 (7)	C(8)—C(9)	1.377 (7)
N(1)—C(11)	1.489 (7)	C(9)—C(10)	1.376 (7)
N(2)—C(6)	1.334 (7)	C(12)—C(13)	1.520 (7)
O(2)—Cl(1)—O(3)	105.3 (4)	N(1)—C(1)—C(2)	121.3 (6)
O(2)—Cl(1)—O(4)	109.4 (4)	C(1)—C(2)—C(3)	120.1 (5)
O(2)—Cl(1)—O(5)	109.9 (4)	C(2)—C(3)—C(4)	117.2 (5)
O(3)—Cl(1)—O(4)	110.4 (4)	C(2)—C(3)—C(8)	121.1 (4)
O(3)—Cl(1)—O(5)	110.7 (3)	C(4)—C(3)—C(8)	121.7 (4)
O(4)—Cl(1)—O(5)	111.0 (3)	C(3)—C(4)—C(5)	121.0 (5)
O(6)—Cl(2)—O(7)	110.0 (3)	N(1)—C(5)—C(4)	120.5 (6)
O(6)—Cl(2)—O(8)	108.0 (3)	N(2)—C(6)—C(7)	120.2 (6)
O(6)—Cl(2)—O(9)	110.5 (3)	C(6)—C(7)—C(8)	120.8 (6)
O(7)—Cl(2)—O(8)	109.2 (3)	C(3)—C(8)—C(7)	121.6 (5)
O(7)—Cl(2)—O(9)	110.9 (3)	C(3)—C(8)—C(9)	120.8 (4)
O(8)—Cl(2)—O(9)	108.2 (3)	C(7)—C(8)—C(9)	117.6 (5)
C(1)—N(1)—C(5)	120.1 (5)	C(8)—C(9)—C(10)	119.9 (6)
C(1)—N(1)—C(11)	120.5 (5)	N(2)—C(10)—C(9)	121.1 (5)
C(5)—N(1)—C(11)	119.3 (5)	N(2)—C(12)—C(13)	110.1 (4)
C(6)—N(2)—C(10)	120.3 (5)	O(1)—C(13)—N(3)	125.6 (5)
C(6)—N(2)—C(12)	119.6 (5)	O(1)—C(13)—C(12)	121.5 (5)
C(10)—N(2)—C(12)	120.1 (5)	N(3)—C(13)—C(12)	112.8 (5)

Data collection and cell refinement used *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994*a*). The structures were solved by the direct-methods program *SIR*88 (Burla *et al.*, 1989). Atoms were also located using *DIRDIF* (Parthasarathi, Beurskens & Slot, 1983) and difference Fourier techniques. All non-H atoms were refined anisotropically by full-matrix least squares. The H atoms of the solvate water molecule in (2) were not located. All the remaining H atoms were refined isotropically. The largest extinction corrections were for the 040 reflection in (1) of 0.530 and for $10\bar{4}$ in (2) of 0.952. Best-plane calculations were performed using *BP*70 (Ito, 1982). All other calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1994*b*). Molecular mechanics calculations were performed using the *HyperMM+* program in *HyperChem* (Hypercube Inc., 1995), in which default parameters were used and atomic charges were taken into consideration to account for the electrostatic contribution.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hydrated Structures of *N*-Methylated Cholamide Derivatives

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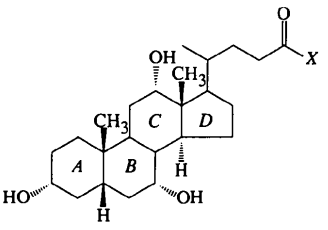
Abstract

The crystal structures of *N*-methylcholamide quarter-hydrate (*N*-methyl-3α,7α,12α-trihydroxy-5β-cholan-24-amide 0.25-hydrate, $C_{25}H_{43}NO_4.0.25H_2O$), recrystallized from acetone by diffusion of water, *N*-methylcholamide sesquihydrate (*N*-methyl-3α,7α,12α-trihydroxy-5β-cholan-24-amide 1.5-hydrate, $C_{25}H_{43}NO_4.1.5H_2O$), recrystallized from a 10:1 ethyl acetate–absolute ethanol solution by slow evaporation, and *N*,*N*-dimethylcholamide hemihydrate (*N*,*N*-dimethyl-3α,7α,12α-trihydroxy-5β-cholan-24-amide 0.5-hydrate, $C_{26}H_{45}NO_4.0.5H_2O$), recrystallized from a 1:1 absolute methanol–ethyl acetate solution by slow evaporation, have been determined. These structures are the first reported crystal structures of both *N*-methylcholamide and *N*,*N*-dimethylcholamide. Each structure contains water molecules that sit on special positions. The *N*-methylcholamide sesquihydrate and *N*,*N*-dimethylcholamide hemihydrate forms are isostructural.

Comment

Steroids often display the ability to crystallize into multiple solvated forms (Byrn, 1982). One such example is the bile acid cholic acid (3α,7α,12α-trihydroxy-5β-cholan-24-oic acid) and its various derivatives, *e.g.* methyl cholate (3α,7α,12α-trihydroxy-5β-cholan-24-oic acid methyl ester), sodium cholate (sodium 3α,7α,12α-trihydroxy-5β-cholan-24-oate) and cholamide [3α,7α,12α-trihydroxy-5β-cholan-24-amide, (I)]. Four different solvates of cholamide are known (Sada, Kondo, Miyata & Miki, 1994; Sada, Kondo, Miyata,

Tamada & Miki, 1993; Wahle & Byrn, 1997). No crystal structures have been reported for the *N*-methyl or *N,N*-dimethyl derivatives of cholamide. We initiate here our examination of cholamide derivatives by reporting the first solvated forms of *N*-methylated cholamide, namely, *N*-methylcholamide quarterhydrate, (I), *N*-methylcholamide sesquihydrate, (II), and *N,N*-dimethylcholamide hemihydrate, (III).



X	Compound
OH	Cholic acid
OMe	Methyl cholate
O^-Na^+	Sodium cholate
NH_2	Cholamide
NHMe	(I) and (II)
NMe_2	(III)

The *ORTEP*II (Johnson, 1976) diagrams for compounds (I)–(III) are presented in Figs. 1–3, respectively. In each structure, the asymmetric unit contains two independent molecules per unit cell. The conformational differences result from different values for torsion angles in each side chain. Compound (I) adopts a layered pattern with a column of water molecules running parallel to the *b* axis. Compound (II) is isostructural with compound (III), adopting a propeller-like packing pattern with water tunnels running parallel to the *c* axis. The presence of the additional amide methyl group in compound (III) does not allow space for an additional water molecule as seen in (II). In compounds (I) and (III), the water molecules sit on special positions, whereas in (II) only two of the four water molecules sit on special positions. The packing diagrams and hydrogen-bonding patterns for compounds (I)–(III) are presented in Fig. 4. Compound (I) has been previously reported (Sada & Miyata, 1996) without mention of its X-ray structural data, which is forthcoming (Sada, 1996).

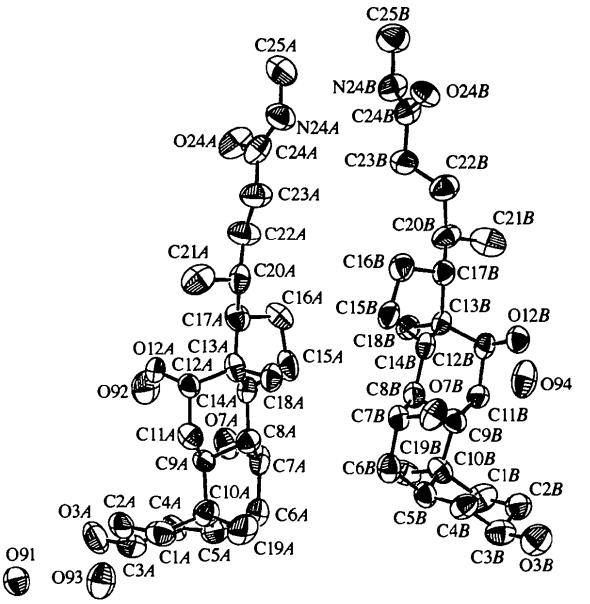


Fig. 2. *ORTEP*II (Johnson, 1976) diagram for (II) showing 50% probability displacement ellipsoids for non-H atoms. The water molecule is also included. Drawn to scale with Figs. 1 and 3.

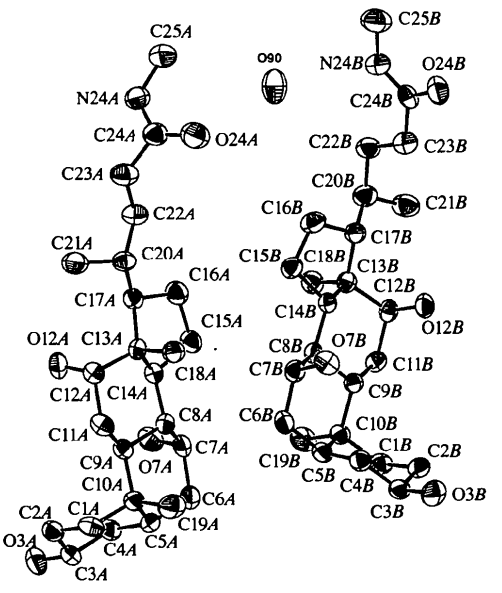


Fig. 1. *ORTEP*II (Johnson, 1976) diagram for (I) showing 50% probability displacement ellipsoids for non-H atoms. The water molecule is also included. Drawn to scale with Figs. 2 and 3.

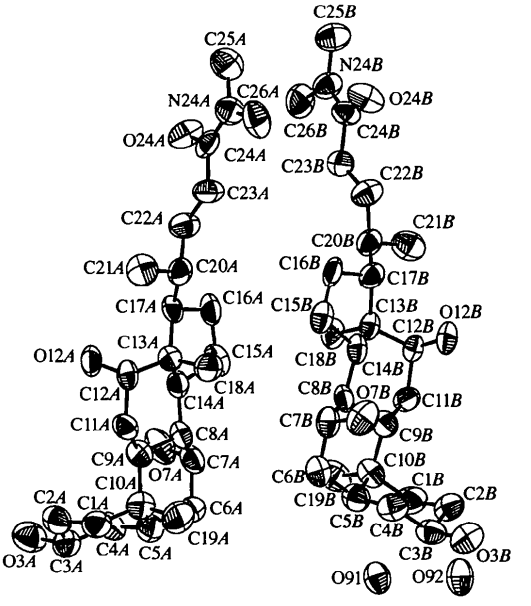


Fig. 3. *ORTEP*II (Johnson, 1976) diagram for (III) showing 50% probability displacement ellipsoids for non-H atoms. The water molecule is also included. Drawn to scale with Figs. 1 and 2.

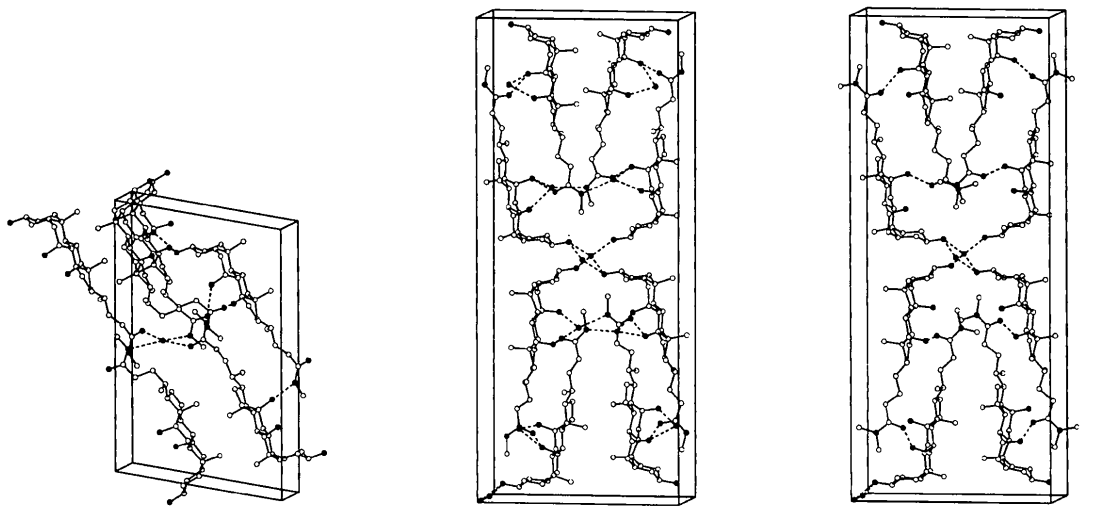


Fig. 4. Packing diagrams for compounds (I)–(III) shown left to right, respectively. Compound (I) is viewed down the *b* axis and compounds (II) and (III) down the *c* axis. C, O and N atoms are represented by open, shaded and filled circles, respectively. Hydrogen bonds are represented by dashed lines.

For compound (I), steroid–steroid hydrogen bonds exist between the hydroxy O12*A* and amide N24*A* atoms, between the hydroxy O3*A* and O12*B* atoms, between the hydroxy O12*A* and amide O24*B* atoms, and finally between the hydroxy O7*A* and amide O24*B* atoms (Table 2). Four steroid–water hydrogen bonds hold the water molecule in a cavity. The O90 water atom hydrogen bonds to two different amide N24*B* and two different amide O24*A* atoms. For compound (II), steroid–steroid hydrogen bonds exist between the hydroxy O7*A* and amide O24*B* atoms, between the hydroxy O12*B* and amide O24*A* atoms, between the hydroxy O7*B* and amide O24*A* atoms, and finally between the amide O24*B* and hydroxy O12*A* atoms (Table 4). Four steroid–water hydrogen bonds hold the O91 and O93 water molecules in a tunnel along the *c* axis. The O91 water atom hydrogen bonds to two different hydroxy O3*A* atoms and to two different hydroxy O3*B* atoms. The O93 water atom also hydrogen bonds to two different hydroxy O3*A* and to two different hydroxy O3*B* atoms. The water O92 and O94 atoms also share similar hydrogen-bonding patterns. The O92 water atom hydrogen bonds to the hydroxy O7*A* and O12*A* atoms and to the amide N24*A* atom. Consequently, the O94 water atom hydrogen bonds to the hydroxy O7*B* and O12*B* atoms and to the amide N24*B* atom. For compound (III), steroid–steroid hydrogen bonds exist between the hydroxy O7*A* and amide O24*B* atoms, between the hydroxy O12*A* and amide O24*B* atoms, between the amide O24*A* and hydroxy O12*B* atoms, and finally between the amide O24*A* and hydroxy O7*B* atoms (Table 6). Four steroid–water hydrogen bonds hold each water molecule in a tunnel along the *c* axis. The O91 water atom hydrogen bonds to two different hydroxy O3*A* atoms and to two different hydroxy O3*B* atoms. The O92 water atom likewise hydrogen bonds to two different hydroxy O3*A* atoms and to two different hydroxy O3*B* atoms.

Experimental

The two *N*-methylated derivatives of cholamide were synthesized from cholic acid (Sigma Chemical Co., St Louis, MO, USA) using a mixed-anhydride technique previously formulated (method *A*; Bellini, Quaglio, Guarneri & Cavazzini, 1983). Elemental and thermogravimetric analyses revealed that the cholamide products included water. The *N*-methylcholamide product included less than 0.5 moles of water, while the *N,N*-dimethylcholamide product included negligible amounts of water. Drying the compounds overnight in a heated vacuum oven and repeating the analyses yielded identical results. Compound (I) was prepared by recrystallization of *N*-methylcholamide from acetone (EM Science, Gibbstown, NJ, USA) by diffusion of water. Compound (II) was prepared by recrystallization of *N*-methylcholamide from a 10:1 ethyl acetate–absolute ethanol solution (ethyl acetate: Mallinckrodt Specialty Chemicals Co., Paris, KY, USA; absolute ethanol: Midwest Grain Products Co., Weston, MO, USA) by slow evaporation. Compound (III) was prepared by recrystallization of *N,N*-dimethylcholamide by slow evaporation from a 1:1 absolute methanol–ethyl acetate solution (absolute methanol: EM Science; ethyl acetate: Mallinckrodt Specialty Chemicals Co.). An identical structure was found in crystals grown from a 1:1 absolute ethanol–ethyl acetate solution.

Compound (I)

Crystal data

$C_{25}H_{43}NO_4.0.25H_2O$
$M_r = 426.13$
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å

Monoclinic
$P2$
$a = 14.012\,(1)$ Å
$b = 8.0111\,(5)$ Å
$c = 21.696\,(1)$ Å
$\beta = 99.123\,(5)°$
$V = 2404.5\,(5)$ Å^3
$Z = 4$
$D_x = 1.18$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 24$–$45°$
$\mu = 0.585$ mm^{-1}
$T = 296$ K
Needle
$0.25 \times 0.18 \times 0.13$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4937 measured reflections
4734 independent reflections
3689 reflections with $I > 2\sigma(I)$

$R_{int} = 0.023$
$\theta_{max} = 68.13°$
$h = 0 \rightarrow 16$
$k = -9 \rightarrow 0$
$l = -26 \rightarrow 25$
3 standard reflections
frequency: 83 min
intensity decay: 2.33%

Refinement

Refinement on F^2
$R(F) = 0.044$
$wR(F^2) = 0.135$
$S = 1.075$
4734 reflections
572 parameters
H atoms: H1N*A*, H1N*B* and H90O refined isotropically; others not refined ($U = 1.3U_{eq}$ of bonding atom)

$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 0.4889P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.041$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: known fragment

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O3*A*	−0.4442 (2)	1.1190 (4)	0.82035 (15)	0.0548 (9)
O7*A*	−0.1993 (2)	0.7780 (4)	0.73861 (14)	0.0509 (9)
O12*A*	−0.1151 (2)	1.2787 (4)	0.66255 (13)	0.0489 (10)
O24*A*	0.3549 (2)	1.0604 (6)	0.51233 (15)	0.0846 (14)
N24*A*	0.2666 (3)	1.1205 (6)	0.4202 (2)	0.0525 (10)
C1*A*	−0.1890 (3)	1.2599 (6)	0.8735 (2)	0.0476 (12)
C2*A*	−0.2911 (3)	1.2706 (5)	0.8379 (2)	0.0432 (10)
C3*A*	−0.3463 (3)	1.1173 (6)	0.8522 (2)	0.0421 (10)
C4*A*	−0.2976 (3)	0.9600 (5)	0.8340 (2)	0.0413 (10)
C5*A*	−0.1913 (3)	0.9471 (5)	0.8672 (2)	0.0418 (10)
C6*A*	−0.1433 (3)	0.7860 (6)	0.8490 (2)	0.0501 (10)
C7*A*	−0.1142 (3)	0.7899 (5)	0.7839 (2)	0.0447 (10)
C8*A*	−0.0559 (3)	0.9488 (5)	0.7748 (2)	0.0379 (10)
C9*A*	−0.1104 (2)	1.1071 (5)	0.7901 (2)	0.0350 (10)
C10*A*	−0.1320 (3)	1.1046 (6)	0.8584 (2)	0.0398 (10)
C11*A*	−0.0598 (3)	1.2674 (5)	0.7745 (2)	0.0417 (10)
C12*A*	−0.0306 (3)	1.2722 (5)	0.7089 (2)	0.0380 (10)
C13*A*	0.0281 (2)	1.1181 (5)	0.6978 (2)	0.0342 (10)
C14*A*	−0.0322 (3)	0.9615 (5)	0.7088 (2)	0.0372 (10)
C15*A*	0.0222 (3)	0.8167 (5)	0.6841 (2)	0.0450 (10)
C16*A*	0.0711 (3)	0.8960 (6)	0.6317 (2)	0.0489 (12)
C17*A*	0.0456 (3)	1.0827 (5)	0.6296 (2)	0.0364 (10)
C18*A*	0.1250 (3)	1.1230 (6)	0.7419 (2)	0.0450 (12)
C19*A*	−0.0372 (3)	1.1013 (8)	0.9062 (2)	0.0603 (14)
C20*A*	0.1172 (3)	1.1977 (6)	0.6023 (2)	0.0423 (10)
C21*A*	0.0744 (4)	1.3709 (6)	0.5873 (2)	0.0581 (16)
C22*A*	0.1501 (3)	1.1186 (7)	0.5453 (2)	0.0518 (12)
C23*A*	0.2180 (3)	1.2316 (7)	0.5135 (2)	0.0577 (15)
C24*A*	0.2861 (3)	1.1304 (7)	0.4818 (2)	0.0504 (12)
C25*A*	0.3258 (4)	1.0292 (7)	0.3824 (2)	0.0600 (14)
O3*B*	0.4451 (2)	0.6530 (5)	1.08700 (13)	0.0559 (8)
O7*B*	0.4347 (2)	0.9475 (4)	0.88660 (14)	0.0492 (9)
O12*B*	0.4793 (2)	0.4239 (4)	0.82094 (13)	0.0490 (9)
O24*B*	0.7959 (2)	0.5724 (4)	0.62908 (15)	0.0573 (10)
N24*B*	0.6862 (3)	0.6253 (6)	0.5448 (2)	0.0561 (12)
C1*B*	0.2497 (3)	0.4961 (6)	0.9618 (2)	0.0428 (12)
C2*B*	0.3448 (3)	0.4899 (5)	1.0077 (2)	0.0421 (10)
C3*B*	0.3561 (2)	0.6508 (5)	1.0440 (2)	0.0406 (12)
C4*B*	0.3544 (3)	0.7986 (5)	1.0004 (2)	0.0400 (10)
C5*B*	0.2639 (3)	0.8073 (5)	0.9505 (2)	0.0399 (10)
C6*B*	0.2683 (3)	0.9555 (5)	0.9069 (2)	0.0454 (10)
C7*B*	0.3347 (3)	0.9342 (5)	0.8580 (2)	0.0399 (10)
C8*B*	0.3145 (3)	0.7688 (5)	0.8228 (2)	0.0342 (10)
C9*B*	0.3175 (2)	0.6211 (5)	0.8688 (2)	0.0329 (10)
C10*B*	0.2425 (2)	0.6412 (5)	0.9145 (2)	0.0365 (10)
C11*B*	0.3109 (3)	0.4531 (5)	0.8344 (2)	0.0398 (10)
C12*B*	0.3820 (3)	0.4337 (5)	0.7881 (2)	0.0373 (10)
C13*B*	0.3710 (2)	0.5755 (5)	0.7403 (2)	0.0346 (10)
C14*B*	0.3843 (3)	0.7397 (5)	0.7767 (2)	0.0326 (10)
C15*B*	0.3907 (3)	0.8701 (5)	0.7262 (2)	0.0434 (10)
C16*B*	0.4436 (3)	0.7795 (6)	0.6794 (2)	0.0499 (12)
C17*B*	0.4504 (3)	0.5944 (5)	0.6983 (2)	0.0386 (10)
C18*B*	0.2706 (3)	0.5618 (6)	0.6991 (2)	0.0446 (12)
C19*B*	0.1381 (2)	0.6386 (7)	0.8789 (2)	0.0530 (12)
C20*B*	0.4500 (3)	0.4749 (6)	0.6424 (2)	0.0474 (12)
C21*B*	0.4552 (4)	0.2915 (6)	0.6597 (2)	0.0575 (15)
C22*B*	0.5286 (3)	0.5227 (6)	0.6033 (2)	0.0483 (12)
C23*B*	0.6317 (3)	0.5194 (7)	0.6388 (2)	0.0530 (12)
C24*B*	0.7108 (3)	0.5742 (5)	0.6033 (2)	0.0455 (10)
C25*B*	0.7585 (4)	0.6943 (9)	0.5098 (3)	0.081 (2)
O90	1/2	0.8410 (7)	1/2	0.0707 (17)

Table 2. *Hydrogen-bonding data (Å) for (I)*

O90···O24*A*	2.733 (5)	O12*A*···O24*B*^{ii}	2.708 (4)
O90···N24*B*	3.152 (5)	O90···O24*A*^{iii}	2.733 (5)
O3*A*···O7*B*^{i}	2.758 (4)	O90···N24*B*^{iii}	3.152 (5)
O7*A*···O24*B*^{i}	2.883 (4)	N24*A*···O12*A*^{iv}	2.851 (5)
O3*A*···O12*B*^{ii}	2.668 (3)		

Symmetry codes: (i) $x-1, y, z$; (ii) $x-1, y+1, z$; (iii) $1-x, y, 1-z$; (iv) $-x, y, 1-z$.

Compound (II)

Crystal data

$C_{25}H_{43}NO_4.1.5H_2O$
$M_r = 448.64$
Orthorhombic
$P2_12_12$
$a = 16.8089\,(9)$ Å
$b = 38.765\,(1)$ Å
$c = 7.887\,(5)$ Å
$V = 5139\,(3)$ Å^3
$Z = 8$
$D_x = 1.16$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 21$–$43°$
$\mu = 0.597$ mm^{-1}
$T = 297$ K
Needle
$0.25 \times 0.15 \times 0.12$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4436 measured reflections
4436 independent reflections
2367 reflections with $I > 2\sigma(I)$

$\theta_{max} = 61.08°$
$h = 0 \rightarrow 8$
$k = -19 \rightarrow 0$
$l = -43 \rightarrow 0$
3 standard reflections
frequency: 83 min
intensity decay: 2.85%

Refinement

Refinement on F^2
$R(F) = 0.065$
$wR(F^2) = 0.237$
$S = 1.200$
4436 reflections
582 parameters
H atoms not refined ($U = 1.3U_{eq}$ of bonding atom)
$w = 1/[\sigma^2(F_o^2) + (0.1005P)^2 + 0.6139P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.030$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick 1993)
Extinction coefficient: 0.70×10^{-3}
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: known fragment

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O3*A*	0.0862 (4)	0.0328 (2)	0.5328 (10)	0.086 (3)
O7*A*	0.2556 (3)	0.1042 (2)	0.1877 (8)	0.067 (2)
O12*A*	0.2790 (3)	0.16065 (14)	0.6649 (7)	0.0547 (17)
O24*A*	0.3744 (4)	0.3341 (2)	0.4266 (9)	0.080 (2)
N24*A*	0.4990 (5)	0.3539 (2)	0.4801 (12)	0.075 (3)
C1*A*	0.2977 (6)	0.0359 (2)	0.6860 (13)	0.074 (4)
C2*A*	0.2076 (6)	0.0422 (2)	0.6898 (11)	0.066 (3)
C3*A*	0.1709 (6)	0.0265 (2)	0.5366 (14)	0.072 (3)
C4*A*	0.2064 (6)	0.0402 (2)	0.3752 (12)	0.061 (3)
C5*A*	0.2979 (6)	0.0374 (2)	0.3707 (12)	0.065 (3)
C6*A*	0.3324 (6)	0.0514 (2)	0.2063 (12)	0.068 (3)
C7*A*	0.3356 (5)	0.0912 (2)	0.1995 (12)	0.061 (3)
C8*A*	0.3729 (5)	0.1059 (2)	0.3611 (11)	0.052 (2)
C9*A*	0.3335 (5)	0.0913 (2)	0.5207 (11)	0.050 (3)
C10*A*	0.3404 (5)	0.0512 (2)	0.5269 (13)	0.061 (3)
C11*A*	0.3656 (5)	0.1099 (2)	0.6816 (10)	0.055 (3)
C12*A*	0.3605 (5)	0.1487 (2)	0.6727 (11)	0.052 (3)
C13*A*	0.4056 (5)	0.1623 (2)	0.5166 (11)	0.052 (3)
C14*A*	0.3697 (5)	0.1452 (2)	0.3574 (10)	0.048 (3)
C15*A*	0.4061 (6)	0.1640 (2)	0.2099 (11)	0.069 (3)
C16*A*	0.4144 (6)	0.2020 (2)	0.2769 (12)	0.069 (3)
C17*A*	0.3936 (5)	0.2009 (2)	0.4706 (12)	0.058 (3)
C18*A*	0.4964 (4)	0.1545 (2)	0.5358 (12)	0.062 (3)
C19*A*	0.4267 (5)	0.0387 (2)	0.5343 (15)	0.081 (4)
C20*A*	0.4358 (5)	0.2302 (2)	0.5641 (12)	0.060 (3)
C21*A*	0.4138 (7)	0.2301 (3)	0.7522 (13)	0.083 (4)
C22*A*	0.4163 (6)	0.2653 (2)	0.4863 (16)	0.076 (3)
C23*A*	0.4686 (5)	0.2944 (2)	0.5477 (16)	0.078 (3)
C24*A*	0.4449 (6)	0.3291 (2)	0.4773 (13)	0.067 (3)
C25*A*	0.4810 (7)	0.3891 (3)	0.4274 (17)	0.098 (5)
O3*B*	0.9083 (4)	0.0300 (2)	0.0304 (10)	0.085 (2)
O7*B*	0.7976 (4)	0.1259 (2)	0.3510 (8)	0.070 (2)
O12*B*	0.8070 (3)	0.18356 (15)	−0.1271 (8)	0.0610 (18)
O24*B*	0.6853 (4)	0.37094 (14)	0.1024 (8)	0.064 (2)
N24*B*	0.5644 (4)	0.3761 (2)	−0.0139 (12)	0.066 (3)
C1*B*	0.7144 (6)	0.0623 (3)	−0.1366 (14)	0.078 (4)
C2*B*	0.8035 (6)	0.0558 (2)	−0.1320 (12)	0.064 (3)
C3*B*	0.8240 (6)	0.0359 (2)	0.0265 (14)	0.071 (3)
C4*B*	0.7999 (6)	0.0560 (2)	0.1794 (11)	0.064 (3)
C5*B*	0.7106 (6)	0.0649 (2)	0.1814 (11)	0.058 (3)
C6*B*	0.6894 (6)	0.0853 (2)	0.3407 (11)	0.063 (3)
C7*B*	0.7113 (5)	0.1234 (2)	0.3365 (12)	0.055 (3)
C8*B*	0.6843 (5)	0.1409 (2)	0.1765 (11)	0.054 (2)
C9*B*	0.7164 (5)	0.1209 (2)	0.0202 (11)	0.054 (2)
C10*B*	0.6817 (5)	0.0836 (2)	0.0188 (11)	0.055 (2)
C11*B*	0.7032 (5)	0.1396 (2)	−0.1537 (10)	0.053 (3)
C12*B*	0.7215 (5)	0.1786 (2)	−0.1481 (11)	0.052 (3)
C13*B*	0.6786 (4)	0.1963 (2)	−0.0027 (10)	0.043 (2)
C14*B*	0.7069 (5)	0.1788 (2)	0.1641 (10)	0.047 (2)
C15*B*	0.6776 (6)	0.2026 (2)	0.3036 (11)	0.060 (3)
C16*B*	0.6767 (6)	0.2390 (2)	0.2249 (12)	0.067 (3)
C17*B*	0.6993 (5)	0.2348 (2)	0.0348 (11)	0.053 (3)
C18*B*	0.5889 (4)	0.1929 (2)	−0.0333 (14)	0.061 (3)
C19*B*	0.5909 (5)	0.0819 (2)	0.0019 (15)	0.077 (3)
C20*B*	0.6621 (5)	0.2624 (2)	−0.0773 (14)	0.067 (3)
C21*B*	0.6845 (8)	0.2583 (3)	−0.2659 (14)	0.089 (4)
C22*B*	0.6802 (5)	0.2998 (2)	−0.0211 (15)	0.074 (3)
C23*B*	0.6124 (6)	0.3192 (2)	0.0432 (18)	0.089 (4)
C24*B*	0.6228 (5)	0.3576 (2)	0.0476 (12)	0.057 (3)
C25*B*	0.5651 (6)	0.4137 (2)	−0.0155 (17)	0.090 (4)
O91	0	0	0.7821 (11)	0.067 (3)
O92	0.1598 (4)	0.1474 (2)	0.4195 (10)	0.084 (3)
O93	0	0	0.2849 (14)	0.091 (4)
O94	0.9135 (4)	0.1530 (2)	0.1074 (10)	0.091 (3)

Table 4. *Hydrogen-bonding data (Å) for (II)*

O3*A*···O91	2.754 (10)	O7*B*···O24*A*^{ii}	2.674 (10)
O3*A*···O93	2.746 (11)	O24*B*···O12*A*^{ii}	2.708 (9)
O12*A*···O92	2.833 (9)	O94···N24*B*^{iii}	2.872 (10)
O7*A*···O92	2.956 (10)	O93···O3*B*^{iv}	2.785 (11)
O7*B*···O94	2.931 (10)	O91···O3*B*^{v}	2.750 (11)
O12*B*···O94	2.834 (9)	O3*B*···O93^{vi}	2.785 (11)
O7*A*···O24*B*^{i}	2.750 (9)	O3*B*···O91^{vii}	2.750 (11)
O24*A*···O12*B*^{i}	2.708 (9)	O93···O3*A*^{viii}	2.746 (11)
N24*A*···O92^{ii}	2.817 (11)	O91···O3*A*^{viii}	2.754 (10)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (ii) $x + \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (iii) $x + \frac{1}{2}, \frac{1}{2} - y, -z$; (iv) $1 - x, -y, z$; (v) $1 - x, -y, z + 1$; (vi) $x + 1, y, z$; (vii) $x + 1, y, z - 1$; (viii) $-x, -y, z$.

Compound (III)

Crystal data

$C_{26}H_{45}NO_4.0.5H_2O$
$M_r = 444.65$
Orthorhombic
$P2_12_12$
$a = 16.565$ (3) Å
$b = 39.504$ (4) Å
$c = 7.824$ (8) Å
$V = 5120$ (4) Å^3
$Z = 8$
$D_x = 1.15$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 20 reflections
$\theta = 19$–$24°$
$\mu = 0.566$ mm^{-1}
$T = 297$ K
Plate
0.25 × 0.15 × 0.06 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5256 measured reflections
5256 independent reflections
1941 reflections with $I > 2\sigma(I)$
$\theta_{max} = 68.13°$
$h = -9 \rightarrow 0$
$k = 0 \rightarrow 19$
$l = -47 \rightarrow 0$
3 standard reflections
frequency: 83 min
intensity decay: 2.11%

Refinement

Refinement on F^2
$R(F) = 0.070$
$wR(F^2) = 0.256$
$S = 1.057$
5256 reflections
588 parameters
H atoms: H92O refined isotropically, others not refined ($U = 1.3U_{eq}$ of bonding atom)
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick 1993)
Extinction coefficient: 0.14×10^{-2}
Scattering factors from *International Tables for Crystallography* (Vol. C)

$w = 1/[\sigma^2(F_o^2) + (0.0975P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.061$

Flack parameter for absolute configuration determination = 0.0 (8)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (III)*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O3A	0.0829 (4)	0.0339 (2)	0.5902 (10)	0.099 (3)
O7A	0.2407 (4)	0.1011 (2)	0.2078 (8)	0.089 (2)
O12A	0.2704 (3)	0.1658 (2)	0.6887 (8)	0.072 (2)
O24A	0.3809 (4)	0.33557 (15)	0.3973 (9)	0.087 (2)
N24A	0.5085 (5)	0.3525 (2)	0.4555 (10)	0.073 (2)
C1A	0.2994 (6)	0.0430 (2)	0.7363 (12)	0.078 (4)
C2A	0.2075 (6)	0.0465 (2)	0.7423 (11)	0.078 (3)
C3A	0.1695 (6)	0.0287 (2)	0.5885 (12)	0.077 (3)
C4A	0.2064 (6)	0.0416 (2)	0.4201 (12)	0.073 (3)
C5A	0.2971 (6)	0.0396 (2)	0.4150 (12)	0.072 (3)
C6A	0.3300 (7)	0.0531 (2)	0.2472 (12)	0.078 (4)
C7A	0.3238 (6)	0.0911 (2)	0.2250 (11)	0.074 (3)
C8A	0.3611 (5)	0.1094 (2)	0.3843 (10)	0.060 (3)
C9A	0.3274 (5)	0.0958 (2)	0.5501 (11)	0.061 (2)
C10A	0.3370 (6)	0.0566 (2)	0.5696 (14)	0.078 (3)
C11A	0.3573 (5)	0.1161 (2)	0.7082 (11)	0.063 (3)
C12A	0.3534 (5)	0.1549 (2)	0.6835 (10)	0.058 (3)
C13A	0.3906 (5)	0.1670 (2)	0.5235 (12)	0.059 (3)
C14A	0.3487 (5)	0.1476 (2)	0.3714 (10)	0.059 (3)
C15A	0.3780 (6)	0.1653 (2)	0.2117 (12)	0.076 (3)
C16A	0.3856 (6)	0.2032 (2)	0.2661 (11)	0.076 (3)
C17A	0.3739 (5)	0.2038 (2)	0.4648 (11)	0.057 (3)
C18A	0.4823 (5)	0.1601 (2)	0.5241 (13)	0.075 (3)
C19A	0.4290 (6)	0.0475 (2)	0.5773 (16)	0.098 (4)
C20A	0.4253 (5)	0.2327 (2)	0.5470 (12)	0.065 (3)
C21A	0.4121 (6)	0.2340 (2)	0.7418 (11)	0.083 (3)
C22A	0.4050 (5)	0.2674 (2)	0.4687 (16)	0.081 (3)
C23A	0.4731 (5)	0.2928 (2)	0.4956 (15)	0.076 (3)
C24A	0.4513 (6)	0.3281 (2)	0.4437 (12)	0.066 (3)
C25A	0.4859 (7)	0.3876 (3)	0.4126 (15)	0.107 (4)
C26A	0.5908 (6)	0.3460 (3)	0.5038 (15)	0.097 (4)
O3B	0.9149 (4)	0.0297 (2)	0.0797 (10)	0.099 (2)
O7B	0.7964 (4)	0.1210 (2)	0.3966 (8)	0.093 (2)
O12B	0.7987 (3)	0.1801 (2)	−0.1023 (8)	0.0723 (18)
O24B	0.6713 (4)	0.36116 (15)	0.0516 (9)	0.086 (2)
N24B	0.5449 (4)	0.3707 (2)	−0.0381 (10)	0.071 (2)
C1B	0.7138 (7)	0.0584 (2)	−0.0912 (14)	0.095 (4)
C2B	0.8055 (6)	0.0531 (2)	−0.0907 (11)	0.072 (3)
C3B	0.8282 (6)	0.0345 (2)	0.0737 (11)	0.071 (3)
C4B	0.8000 (6)	0.0534 (2)	0.2303 (12)	0.071 (3)
C5B	0.7103 (6)	0.0610 (2)	0.2242 (11)	0.073 (3)
C6B	0.6867 (7)	0.0812 (2)	0.3866 (13)	0.089 (4)
C7B	0.7091 (5)	0.1180 (2)	0.3841 (11)	0.068 (3)
C8B	0.6818 (5)	0.1357 (2)	0.2190 (9)	0.054 (2)
C9B	0.7136 (6)	0.1163 (2)	0.0566 (10)	0.062 (3)
C10B	0.6816 (6)	0.0792 (2)	0.0606 (11)	0.068 (3)
C11B	0.6992 (5)	0.1345 (2)	−0.1102 (10)	0.061 (3)
C12B	0.7150 (5)	0.1726 (2)	−0.1126 (10)	0.051 (2)
C13B	0.6712 (5)	0.1897 (2)	0.0357 (10)	0.053 (2)
C14B	0.7053 (5)	0.1728 (2)	0.1985 (10)	0.058 (3)
C15B	0.6803 (6)	0.1967 (2)	0.3446 (11)	0.068 (3)
C16B	0.6751 (5)	0.2312 (2)	0.2667 (11)	0.072 (3)
C17B	0.6898 (5)	0.2281 (2)	0.0688 (12)	0.064 (3)
C18B	0.5795 (4)	0.1842 (2)	0.0241 (13)	0.071 (3)
C19B	0.5887 (5)	0.0776 (2)	0.0461 (15)	0.093 (4)
C20B	0.6430 (5)	0.2531 (2)	−0.0359 (11)	0.065 (3)
C21B	0.6602 (6)	0.2503 (2)	−0.2256 (12)	0.089 (4)
C22B	0.6599 (5)	0.2904 (2)	0.0190 (13)	0.076 (3)
C23B	0.5884 (5)	0.3126 (2)	−0.0035 (14)	0.077 (3)
C24B	0.6048 (5)	0.3498 (2)	0.0028 (11)	0.061 (3)
C25B	0.5568 (6)	0.4072 (2)	−0.0420 (14)	0.089 (4)
C26B	0.4628 (6)	0.3595 (3)	−0.0812 (15)	0.095 (4)
O91	1.0000	0.0000	0.8311 (11)	0.078 (3)
O92	1.0000	0.0000	0.3382 (12)	0.088 (3)

Table 6. *Hydrogen-bonding data (Å) for (III)*

O91···O3B^{i}	2.673 (10)	O91···O3B^{iv}	2.673 (10)
O3B···O92	2.730 (10)	O92···O3A^{v}	2.751 (10)
O7B···O24A^{ii}	2.739 (10)	O91···O3A^{v}	2.689 (11)
O24B···O12A^{ii}	2.821 (9)	O92···O3A^{vi}	2.751 (10)
O12B···O24A^{iii}	2.750 (9)	O91···O3A^{vi}	2.689 (11)
O24B···O7A^{iii}	2.768 (10)	O92···O3B^{vii}	2.730 (10)

Symmetry codes: (i) $2-x, -y, z+1$; (ii) $x+\frac{1}{2}, \frac{1}{2}-y, 1-z$; (iii) $x+\frac{1}{2}, \frac{1}{2}-y, -z$; (iv) $x, y, z+1$; (v) $1-x, -y, z$; (vi) $x+1, y, z$; (vii) $2-x, -y, z$.

The average C—C bond lengths agree with normally accepted values, but the e.s.d.'s for compounds (II) and (III) are large. The e.s.d. ranges are 0.004–0.007, 0.010–0.014 and 0.010–0.013 Å for compounds (I), (II) and (III), respectively.

For all compounds, data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: *PROCESS* in *MolEN* (Fair, 1990); program(s) used to solve structures: *SIR* (Altomare *et al.*, 1994) (direct methods); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CIF VAX* in *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1286). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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