Korean J. Crystallography
Vol. 12, No. 3, pp.150~156, 2001

The Crystal and Molecular Structures of *Neo*-inositol and Two Forms of *Scyllo*-inositol

Younghee Yeon

Department of Chemistry, Korea Air Force Acdemy, Cheongwon, Chungbuk 363-849, Korea

Neo-inositol 및 *Scyllo*-inositol의 結晶 및 分子 構造

延 洋 熙

空軍士官學校 化學科

요 약

Inositol 9개의 입체이성질체중 *Neo*-inositol 및 *Scyllo*-inositol의 결정 구조를 X-선 회절법을 이용하여 규명한 결과, *Neo*-inositol의 단위세포 상수는 $a = 4.799(1)$, $b = 6.520(1)$, $c = 6.505(1)$ Å, $\alpha = 70.61(1)$, $\beta = 69.41(1)$, $\gamma = 73.66(1)^\circ$를 갖는 삼사정계로 공간군은 $P\bar{1}$, $Z = 1$ 이었다. *Scyllo*-inositol은 2개의 형태로 결정화가 되었으며, A형의 단위세포 상수는 $a = 5.089(1)$, $b = 6.645(1)$, $c = 11.948(2)$ Å, $\beta = 116.98(2)^\circ$를 갖는 단사정계로 공간군은 $P2_1/c$, $Z = 2$였고, 반면에 B형은 $a = 6.725(1)$, $b = 6.797(1)$, $c = 8.635(2)$ Å, $\alpha = 95.45(2)$, $\beta = 99.49(2)$, $\gamma = 99.19(2)^\circ$를 갖는 삼사정계로 공간군은 $P\bar{1}$, $Z = 2$였다. B형의 결정구조는 결정격자 내에서 2개의 중심대칭 분자들이 거의 비슷한 배열과 방향을 갖는 유사단사정계이다. 결정 내에 있는 *Neo*-inositol의 Q(puckering parameter) = 0.609(2), *Scyllo*-A는 Q = 0.581(2) Å 그리고 Scyllo-B는 Q = 0.566(2) Å으로 의자형 구조였다. C-C 결합길이는 1.505~1.531 Å, C-O의 결합길이는 1.415~1.440 Å이었으며, C-C-C 결합각은 108.2~112.9°으로 정상 값이었다. 분자들은 O-H---H 수소결합으로 연결되어 3차원 구조를 형성하였다.

Abstract

Neo-inositol is triclinic, $P\bar{1}$, with $a = 4.799(1)$, $b = 6.520(1)$, $c = 6.505(1)$ Å, $\alpha = 70.61(1)$, $\beta = 69.41(1)$, $\gamma = 73.66(1)^\circ$, $Z = 1$, molecular symmetry $\bar{1}$. *Scyllo*-inositol, form A, is monoclinic, $P2_1/c$, with $a = 5.089(1)$, $b = 6.645(1)$, $c = 11{,}948(2)$ Å, $\beta = 116.98(2)^\circ$, $Z = 2$, molecular symmetry $\bar{1}$. Form B is triclinic, $P\bar{1}$, with $a = 6.725(1)$, $b = 6.797(1)$, $c = 8.635(2)$ Å, $\alpha = 95.45(2)$, $\beta = 99.49(2)$, $\gamma = 99.19(2)^\circ$, $Z = 2$, molecular symmetry $\bar{1}$. This crystal structure is pseudo-monoclinic, having two centrosymmetrical molecules with the almost identical conformation and orientation in the crystal lattice. The molecules have the expected chair conformations with puckering parameters of Q = 0.609(2) Å for *neo*, 0.581(2) Å for *Scyllo*-A, and 0.566(2) Å for *Scyllo*-B. The bond lengths and angles are normal, C-C, 1.505 to 1.531 8A, C-O, 1.415 to 1.440 Å, C-C-C, 108.2 to 112.9°. The molecules are linked by systems of finite and infinite chains of hydrogen bonds.

1. Introduction

The inositol compounds, 1,2,3,4,5,6-cyclohexanol, are widely distributed in nature either as the free molecules or as phosphoric esters. The inositol compounds have nine stereoisomers of which are seven forms and one is a D, L pair.

Crystal structure analyses have been reported for the following inositols and their derivatives: anhydrous *myo*-inositol,[1] the dihydrate,[2] the 2-phos-

Table 1. Crystal data and structure determination and refinement data for *neo*- and *scyllo*-inositols; $C_6H_{12}O_6$, mol. wt. 180.2

	Neo	*Scyllo*, form A	*Scyllo*, form B
Crystal Data			
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Z	1	2	2
a (Å)	4.799(1)	5.089(1)	6.725(1)
b (Å)	6.502(1)	6.645(1)	6.797(1)
c (Å)	6.505(1)	11.948(2)	8.635(2)
α (degr)	70.61(1)	90.00	95.45(2)
β (degr)	69.64(1)	116.98(2)	99.49(2)
γ (degr)	73.66(1)	90.00	99.19(2)
V (Å^3)	176.34	360.03	381.32
based on 25 reflections with	22°<θ<30° using Ni-filtered CuKα radiation	15°<θ<24° using Nb-filtered MoKα radiation	20°<θ<29° using Ni-filtered CuKα radiation
μ (cm^{-1})	12.86	1.41	11.91
D_m (g cm^{-3})	1.654	1.651	1.554
D_x (g cm^{-3})	1.697	1.662	1.569
Structure determination and refinement data			
Crystal dimensions (mm)	0.69×0.18×0.0.6	0.55×0.45×0.32	0.65×0.12×0.08
No. reflections measured	897	5,473	1,864
No. unique reflections	712	4,611	1,481
No. observed reflections	662	3,036	1,344
Residual electron difference density (e/Å^3)	0.04	0.08	0.03
Final agreement factors :			
$R(F)$	0.039	0.042	0.045
$R_w(F)$	0.058	0.064	0.068
S (goodness of fit)	2.31	1.91	2.29

Intensit data processed by BUFFALO[a]. Structure determined by SHELX97[b]. Function minimized : $R = w|kF_o - F_c|^2$, $w = (\sigma(F) + 0.02F_o)^{-1}$, $\sigma(F)$ based on counting statistics.

[a]ref. 10. [b]ref. 11.

phate monohydrate,[3] the calcium bromide pentahydrate,[4] the magnesium chloride tetrahydrate,[5] *epi*-inositol,[6] the strontium chloride pentahydrate,[7] *muco*-inositol[8] and *chiro*-inositol.[9] The analyses reported herein add to the crystal structure data on these compounds, leaving the two *meso*, *cis* and *allo*, and the enantiomorphic D(L) or racemic D,L crystal structures undetermined.

2. Experimental

Samples of *scyllo*- and *neo*-inositol were kindly provided by Professor L. Anderson, University of Wisconsin-Madison. Crystals suitable for X-ray diffraction were obtained from water-ethanol solution by vapor diffusion method. The *scyllo*-inositol crystallized simultaneously in two distinctly different morphologies, prisms (A) and needles (B), which have no significant difference in melting point, ~360°C. The X-ray crystallographic measurements were made using a Nonius CAD-4 diffractometer at room temperature. The crystal data and details of the analyses are given in Table 1. The atomic notation and thermal ellipsoids are shown in Fig. 1. Atomic parameters are given in Table 2 and the molecular geometry is given in Table 3.

3. Results and Discussion

The molecules of *neo*- and *scyllo*-inositol have C_2^h (2/*m*) symmetry, which is retained in their crystal structures. That of *scyllo*-inositol form B is unusual

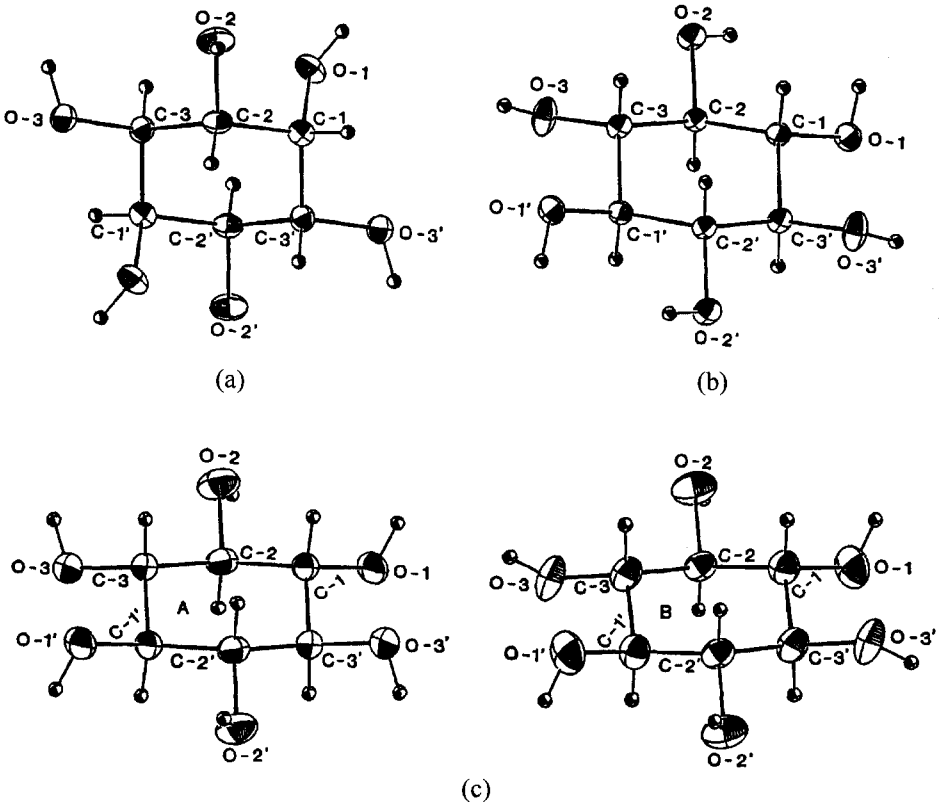

Fig. 1. Atomic notation and thermal ellipsoids (at 50% probability) : (a) *neo*-inositol; (b) *scyllo*-inositol, form A; (c) *scyllo*-inositol, form B.

in having two centrosymmetric molecules in space group $P\bar{1}$ centered on (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$). With a ≈ b and an angle of 90.60(2)° between [110] and [1$\bar{1}$0], the structure is pseudo-monoclinic, C2/c.

As anticipated, the molecules of *neo*- and *scyllo*-inositol have ideal chair-ring conformations. That of

Table 2. Atomic positional parameters and equivalent thermal parameters for the crystal structures of *neo*-inositol and *scyllo*-inositol, forms A amd B[a]

Atom	x/a	y/b	z/c	B_{eq}/B_{iso} (Å^2)
Neo-inositol :				
O-1	7264(2) ×10^{-4}	7869(2) ×10^{-4}	−844(2) ×10^{-4}	182(4) ×10^{-2}
O-2	6574(3)	7076(2)	−4654(2)	191(4)
O-3	7682(3)	2352(2)	−3092(2)	167(3)
C-1	4487(3)	7435(2)	−803(2)	142(4)
C-2	5091(3)	5977(2)	−2391(2)	138(4)
C-3	7068(3)	3748(2)	−1612(2)	140(4)
H-O-1	751(6) ×10^{-3}	913(4) ×10^{-3}	−165(4) ×10^{-3}	41(5) ×10^{-1}
H-O-2	540(5)	741(3)	−543(4)	29(4)
H-O-3	946(6)	248(3)	−400(3)	31(4)
H-C-1	308(4)	883(3)	−125(3)	13(3)
H-C-2	327(4)	572(3)	−238(3)	15(3)
H-C-3	896(4)	398(3)	−165(3)	16(3)

Table 2. Continued

Atom	x/a	y/b	z/c	B_{eq}/B_{iso} (Å^2)
Scyllo-inositol form A :				
O-1	9413(1) $\times10^{-4}$	−2736(1) $\times10^{-4}$	434(3) $\times10^{-4}$	176(1) $\times10^{-2}$
O-2	8878(1)	−546(1)	2501(1)	161(1)
O-3	5586(1)	2931(1)	1800(1)	199(1)
C-1	6837(1)	−1794(1)	350(1)	119(1)
C-2	7524(1)	48(1)	1207(1)	114(1)
C-3	4802(1)	1191(1)	1020(1)	117(1)
H-O-1	993(4) $\times10^{-3}$	−345(3) $\times10^{-3}$	107(2) $\times10^{-3}$	40(3) $\times10^{-1}$
H-O-2	1052(3)	−108(2)	263(1)	24(2)
H-O-3	418(4)	338(3)	187(1)	34(3)
H-C-1	554(3)	−273(2)	57(1)	15(2)
H-C-2	889(2)	90(2)	100(1)	14(2)
H-C-3	353(2)	33(2)	126(1)	14(2)
Scyllo-inositol form B :				
O-1A	6355(2) $\times10^{-4}$	8635(2) $\times10^{-4}$	3954(4) $\times10^{-4}$	271(4) $\times10^{-2}$
O-2A	8410(2)	5336(2)	3521(2)	260(3)
O-3A	7756(2)	2350(2)	5544(2)	284(3)
C-1A	5428(2)	6624(2)	4055(2)	201(4)
C-2A	7088(2)	5448(2)	4653(2)	196(4)
C-3A	6145(2)	3325(2)	4872(2)	204(4)
O-1B	3745(2)	11418(2)	9175(2)	294(4)
O-2B	1852(2)	13950(2)	11074(2)	318(4)
O-3B	−2419(2)	12766(2)	10873(2)	289(4)
C-1B	2190(2)	10645(2)	10000(2)	203(4)
C-2B	755(2)	12162(2)	10125(2)	211(4)
C-3B	−1039(2)	11357(3)	10886(2)	217(4)
H-O-1A	644(4) $\times10^{-3}$	873(4) $\times10^{-3}$	302(3) $\times10^{-3}$	35(5) $\times10^{-1}$
H-O-2A	952(4)	606(4)	392(3)	37(5)
H-(4)O-3A	741(4)	112(4)	524(3)	41(6)
H-O-1B	467(4)	1179(4)	980(4)	45(7)
H-O-2B	202(4)	1484(4)	1047(3)	37(5)
H-O-3B	−203(4)	1362(5)	1173(4)	56(7)
H-C-1A	470(3)	598(3)	302(3)	25(4)
H-C-2A	793(3)	614(3)	567(3)	23(4)
H-C-3A	547(3)	262(3)	385(2)	19(4)
H-C-1B	283(3)	1044(3)	1102(3)	26(4)
H-C-2B	17(3)	1241(3)	906(3)	21(4)
H-C-3B	−45(3)	1119(3)	1202(3)	27(4)

[a]E.s.d. values given in parentheses refer to the least significant digit. $B_{eq} = 4/3(\Sigma_{ij}B_{ij}a_ia_j)$, calculated from the refined, anisotropic thermal parameters.

neo-inositol is the most puckered of those reported, with Q = 0.609 Å. The bond lengths and valence angles are normal, with mean values of C-C = 1.522 Å, C-O = 1.428 Å. The largest departures from these mean values are observed in the structure of *scyllo*-inositol form A. The mean valence angles are C-C-C = 110.8°, C-C-O = 109.2°.

The dimensions of *scyllo*-inositol in the A and B forms differ by less than 0.011 Å and 3° in bond lengths and angles, respectively. The two symmetry-independent molecules in form B differ significantly only in the orientation of the O3-H bond, where the C2-C3-O3-H and C1'-C3-O3-H torsion angles are interchanged and change signs.

Table 3. Molecular dimensions in the crystal structures of *neo*-inositol and *scyllo*-inositol, forms A and B

	Neo-inositol	*Scyllo*-inositol form A	*Scyllo*-inositol, Mol. A.	form B Mol. B.
Bond lengths (Å)				
C-1-C-2	1.530(2)	1.531(1)	1.524(2)	1.529(2)
C-2-C-3	1.531(2)	1.505(1)	1.523(2)	1.519(2)
C-3-C-1'	1.524(2)	1.516(1)	1.520(2)	1.519(2)
C-1-O-1	1.428(2)	1.415(1)	1.426(2)	1.421(2)
C-2-O-2	1.427(2)	1.433(1)	1.431(2)	1.420(2)
C-3-O-3	1.438(2)	1.423(1)	1.430(2)	1.436(2)
C-1-H	0.99(2)	1.03(1)	0.97(2)	0.95(2)
C-2-H	0.93(2)	1.01(1)	0.99(2)	0.98(2)
C-3-H	0.95(2)	1.00(1)	0.97(2)	1.02(2)
O-1-H	0.83(3)	0.83(2)	0.83(3)	0.74(3)
O-2-H	0.82(3)	0.86(2)	0.83(3)	0.84(3)
O-3-H	0.86(2)	0.81(2)	0.83(3)	0.87(3)
Valence angles (*degr*)				
C-3'-C-1-C-2	109.5(1)	111.0(1)	112.4(1)	111.2(1)
O-1-C-1-C-2	110.3(1)	112.6(1)	109.2(1)	108.9(1)
C-3'-C-1-O-1	109.1(1)	103.4(1)	108.7(1)	108.9(1)
C-1-C-2-C-3	110.1(1)	112.9(1)	110.8(1)	111.5(1)
C-1-C-2-O-2	109.6(1)	110.7(1)	109.0(1)	109.4(1)
O-2-C-2-C-3	109.8(1)	105.0(1)	108.9(1)	108.1(1)
C-2-C-3-C-1'	110.2(1)	108.2(1)	110.5(1)	110.9(1)
C-2-C-3-O-3	111.1(1)	110.3(1)	108.2(1)	109.6(1)
O-3-C-3-C-1'	109.3(1)	110.2(1)	110.4(1)	109.0(1)
Torsion angles (*degr*)				
O-1-C-1-C-2-O-2	−59.4(1)	−69.0(2)	−63.7(2)	−64.9(2)
O-1-C-1-C-2-C-3	61.4(1)	173.6(1)	176.6(1)	175.7(1)
C-3'-C-1-C-2-O-2	−179.5(1)	175.8(1)	175.5(1)	175.1(1)
C-3'-C-1-C-2-C-3	−58.7(1)	58.4(2)	55.8(2)	55.6(2)
O-2-C-2-C-3-O-3	−59.0(2)	61.9(2)	64.5(2)	63.9(2)
O-2-C-2-C-3-C-1'	179.8(1)	−177.5(1)	−174.5(1)	−175.7(2)
C-1-C-2-C-3-O-3	−179.6(1)	−177.4(1)	−175.7(1)	−175.8(1)
C-1-C-2-C-3-C-1'	59.1(2)	−56.8(2)	−54.7(2)	−55.4(2)
O-1-C-1-C-3'-O-3'	60.3(1)	62.8(2)	63.6(2)	64.1(2)
O-1-C-1-C-3'-C-2'	−62.0(1)	−176.5(1)	−176.8(1)	−175.3(1)
C-2-C-1-C-3'-O-3'	−179.0(1)	−176.3(1)	−175.3(1)	−176.0(1)
C-2-C-1-C-3'-C-2'	58.8(2)	−55.7(2)	−55.6(2)	−55.3(2)
H-O-1-C-1-C-2	102(1)	83(1)	100(2)	103(2)
H-O-2-C-2-C-1	−112(2)	64(1)	109(2)	109(2)
H-O-2-C-2-C-3	127(2)	−174(1)	−130(2)	−130(2)
H-O-3-C-3-C-2	99(2)	−163(1)	−151(2)	−88(2)
H-O-1-C-1-C-3'	−138(2)	−158(1)	−137(2)	−136(2)
H-O-3-C-3-C-1'	−139(2)	77(1)	88(2)	150(2)
Puckering parameters, Q (Å)				
	0.609	0.581	0.564	0.566

The hydrogen bonding geometry is shown in Table 4 and schematically in Fig. 2. It consists of infinite chains with a side link in all three crystal structures. Those of the *neo*- and *scyllo*-A are remarkably similar. In the *scyllo* crystal structures, there are four examples, shown in Fig. 3, of chelated unsymmetrical three-center hydrogen bonds to vicinal hydroxyl oxygens.

Table 4. Hydrogen bond geometry in *neo*-inositol and forms A and B of *scyllo*-inositol

		O-H (Å)	H---O (Å)	O---O (Å)	O-H---O (degr)
			Neo-inositol		
O-1-H	O-3 (2655)[a]	0.83	2.01	2.808	170
	O-1 (2675)		2.95	3.064	105
O-2-H	O-3 (2644)	0.82	1.98	2.789	169
O-3-H	O-2 (2764)	0.86	1.86	2.694	165
			Scyllo-inositol, form A		
O-1-H	O-3 (2745)	0.83	2.70	3.204	117
	O-2 (2745)		2.07	2.895	173
	O-1 (1555)		3.00	3.342	121
O-2-H	O-2 (2745)	0.86	1.90	2.743	170
	O-2 (2745)		3.00	3.342	121
O-3-H	O-2 (2655)	0.81	2.14	2.933	167
	O-2 (3655)		2.56	2.730	97
			Scyllo-inositol, form B		
O-1A-H	O-1B (2676)	0.83	1.87	2.688	170
O-2A-H	O-3A (2766)	0.83	1.93	2.748	169
	O-2A (2766)		2.74	-	114
O-3A-H	O-1A (1545)	0.84	1.90	2.703	162
O-1B-H	O-3B (1655)	0.75	2.00	2.718	162
	O-1B (2677)		2.73	2.836	109
O-2B-H	O-3B (2587)	0.84	2.09	2.934	175
	O-2B (2587)		3.00	3.310	115
O-3B-H	O-2A (1466)	0.87	1.80	2.665	172

[a]Symmetry relations : for *neo*-inositol, 2 = $\bar{x}$, $\bar{y}$, $\bar{z}$; for *scyllo*-inositol, 1 = x, y, z, 2 = $\bar{x}$, $^1/_2$ +y, $^1/_2$ −z, 3 = $\bar{x}$, $\bar{y}$, $\bar{z}$.

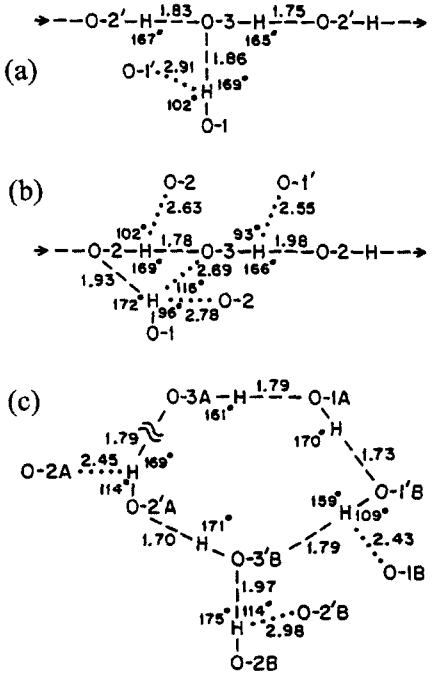

Fig. 2. Hydrogen-bonding schemes, with O-H normalized to 0.97 Å : (a) *neo*-inositol; (b) *scyllo*-inositol, form A; (c) *scyllo*-inositol, form B, molecules A and B (≈ indicate spiral).

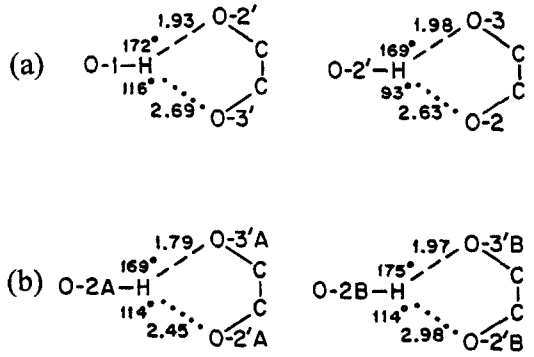

Fig. 3. Three-centered chelated bonding : (a) *scyllo*-inositol, form A; (b) *scyllo*-inositol, form B.

Acknowledgement

This research was supported by KAFA 01-1-3-8 from Korea Air Force Academy.

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