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Carbohydrate Research 328 (2000) 217–227

CARBOHYDRATE RESEARCH

Crystal structures of heptakis(2,6-di-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose, heptakis(2-*O*-methyl-3,6-di-*O*-*tert*-butyldimethylsilyl)-cyclomaltoheptaose and heptakis(2-*O*-methyl)-cyclomaltoheptaose

Joseph H. Reibenspies, Dawn Kirby Maynard, Agnes Derecskei-Kovacs, Gyula Vigh *

Department of Chemistry, Texas A&M University, College Station, TX 77842-3012, USA

Received 2 November 1999; accepted 6 March 2000

Abstract

Crystal structures of heptakis(2,6-di-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose, heptakis(2-*O*-methyl-3,6-di-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose and heptakis(2-*O*-methyl)cyclomaltoheptaose were determined from X-ray diffraction patterns obtained for single crystals of the title compounds grown from ethyl acetate and ethanol, respectively, as solvent. The crystal structures prove conclusively that quantitative migration of the *tert*-butyldimethylsilyl group from the 2-*O*- to the 3-*O*-position [D. Icheln, B. Gehrcke, Y. Piprek, P. Mischnick, W.A. Konig, M.A. Dessoy, A.F. Morel, *Carbohydr. Res.*, 280 (1996) 237–250] was achieved during methylation of heptakis(2,6-di-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose by iodomethane–sodium hydride.

Keywords: Heptakis(2,6-di-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose; Heptakis(2-*O*-methyl-3,6-di-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose; Heptakis(2-*O*-methyl)cyclomaltoheptaose; X-ray crystal structure

1. Introduction

Cyclomaltoheptaose (β-cyclodextrin, βCD) and its derivatives have been used as powerful resolving agents for the capillary electrophoretic (CE) separation of enantiomers [1–4]. While most of these separations were accomplished with non-ionic βCD derivatives, electrophoretic separation of non-charged analytes requires the use of cyclodextrins that carry weak or strong electrolyte functional groups [2]. Most weak and strong electrolyte cyclodextrin derivatives are complex mixtures of many isomers with different degrees and loci of substitution [2]. Recently, well-characterized, single-isomer, pure, sulfated cyclodextrins were synthesized and used for electrophoretic separations [5–8]. (These materials are now commercially available from J&W Scientific, Folsom, CA, USA [9].) A single-isomer cationic βCD derivative was also described [10,11], but it is not yet commercially available.

* Corresponding author. Tel.: +1-409-8452456; fax: +1-409-8454719.

E-mail address: vigh@mail.chem.tamu.edu (G. Vigh).

0008-6215/00/$ - see front matter
PII: S0008-6215(00)00083-5

Our laboratory has been involved in the synthesis of additional 2-*O*- and 3-*O*-substituted, single-isomer, strong electrolyte cyclodextrin derivatives that could broaden the utility of substituted cyclodextrins as resolving agents for CE. Success of these efforts is critically dependent on the availability of a pool of well-characterized, pure cyclodextrin intermediates with readily cleavable protecting groups [12,13]. Heptakis(2,6-di-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose (**1**) is such an intermediate that, according to Ref. [14], can be converted to heptakis(2-*O*-methyl-3,6-di-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose (**2**) by reacting it with iodomethane and sodium hydride. Intermediate **2** can then be converted to heptakis(2-*O*-methyl)cyclomaltoheptaose (**3**) by removing the *tert*-butyldimethylsilyl protecting groups with tetrabutylammonium fluoride. In order to conclusively prove the identity of each intermediate, single crystals of **1**, **2** and **3** were grown and their crystal structures were determined by X-ray diffraction, as described here.

2. Experimental

Synthesis, crystallization and X-ray measurements.—Intermediates **1**, **2** and **3** were synthesized and purified as described in Refs. [12–14]. Crystals of **1** and **2** were obtained by adding 10 mg of pure **1** or **2** (previously reprecipitated from MeOH and EtOH, respectively) into a 4-mL vial, dissolving them in 1.5 mL EtOAc, and filtering the clear solution through a 0.45-μm PTFE membrane filter (Alltech, Deerborn, IL). Single crystals of **3** were obtained by adding 5 g of pure **3** (previously reprecipitated from EtOH) to 35 mL

Table 1
Crystal data, structure determination and refinement data for compounds **1**–**3**

	Compound **1**	Compound **2**	Compound **3**
Crystal data			
Empirical formula	$C_{126}H_{266}O_{35}Si_{14}$	$C_{133}H_{280}O_{35}Si_{14}$	$C_{49}H_{84}O_{35}$
Molecular weight	2734.69	2832.87	1233.19
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Z	4	4	4
Unit cell dimensions at 100(2) K			
a (Å)	18.7857(16)	17.899(4)	12.7608(8)
b (Å)	23.867(2)	19.083(4)	17.3380(11)
c (Å)	38.512(3)	52.416(13)	30.796(2)
V (Å^3)	17,267(3)	17,903(7)	6813.6(8)
D_{calcd} (g cm^{-3})	1.049	1.066	1.404
T (K)	173(2)	173(2)	173(2)
Structure determination and refinement data			
Crystal dimensions (mm^3)	$0.4\times0.2\times0.1$	$0.4\times0.2\times0.2$	$0.25\times0.15\times0.08$
Reflections measured on a Bruker SMART 1000 by ω scans [15]	74,097	43,689	35,573
Independent reflections	22,588	22,934	11,952
Radiation (Mo K$_\alpha$) (Å)	0.71073	0.71073	0.71073
μ(Mo K$_\alpha$) (mm^{-1})	0.164	0.162	0.124
Absorption correction	none	none	none
Extinction correction	none	none	none
2θ Range (°)	3.4–46, 98.9% complete	3.0–46, 99.2% complete	3.4–50, 99.9% complete
Parameters	1573; refinement using SHELXL-97 on F^2	1656; refinement using SHELXL-97 on F^2	865; refinement using SHELXL-97 on F^2
Data to parameter ratio	14.35	13.8	13.8
Final R indices [$I>2\sigma(I)$]	$R(F)=0.0735$, $wR(F^2)=0.1757$	$R(F)=0.0572$, $wR(F^2)=0.1380$	$R(F)=0.0614$, $wR(F^2)=0.1267$
R indices (all data)	$R(F)=0.1216$, $wR(F^2)=0.2008$	$R(F)=0.0709$, $wR(F^2)=0.1477$	$R(F)=0.1162$, $wR(F^2)=0.1433$

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) [a]

	x	y	z	U_{eq}
Compound **1**				
Si-1	6318(4)	355(2)	8377(2)	64(2)
Si-2	5474(2)	2695(1)	7198(1)	91(1)
O-1	5879(2)	2260(2)	8091(1)	49(1)
O-2	6129(2)	2106(2)	8674(1)	40(1)
O-3	6574(3)	1018(2)	8513(1)	68(1)
O-4	6206(3)	2698(2)	7428(1)	60(1)
O-5	7753(3)	1369(2)	8098(1)	70(2)
C-1	5953(4)	1851(3)	8349(2)	47(1)
C-2	6528(4)	1438(3)	8253(2)	56(1)
C-3	7223(4)	1758(3)	8215(2)	50(1)
C-4	7132(4)	2208(3)	7941(2)	45(1)
C-5	6514(4)	2594(3)	8031(2)	48(1)
C-6	6320(4)	3008(3)	7740(2)	56(2)
C-7	6463(12)	163(9)	7915(5)	93(4)
C-8	5320(12)	223(10)	8408(5)	80(4)
C-9	6876(10)	−89(8)	8666(5)	84(3)
C-10	6627(10)	−719(7)	8612(5)	89(4)
C-11	7710(10)	5(8)	8552(5)	90(4)
C-12	6665(12)	100(11)	9029(6)	84(4)
C-13	4673(6)	2605(8)	7478(3)	176(7)
C-14	5466(9)	3326(6)	6946(4)	169(6)
C-15	5568(7)	2091(7)	6907(3)	135(3)
C-16	6226(7)	2156(7)	6690(3)	150(4)
C-17	4875(7)	2058(7)	6665(3)	150(4)
C-18	5628(8)	1545(6)	7130(4)	162(5)
Si-3	5394(1)	1234(1)	10,094(1)	57(1)
Si-4	4180(1)	3932(1)	8613(1)	60(1)
O-6	4905(2)	2806(2)	9274(1)	41(1)
O-7	5802(2)	2906(2)	9675(1)	38(1)
O-8	5660(2)	1806(2)	9880(1)	46(1)
O-9	4924(3)	3607(2)	8718(1)	52(1)
O-10	5969(2)	1309(2)	9211(1)	54(1)
C-19	5184(4)	2601(3)	9587(2)	39(1)
C-20	5368(4)	1994(3)	9564(2)	41(1)
C-21	5866(4)	1899(3)	9260(2)	40(1)
C-22	5591(3)	2156(3)	8932(2)	38(1)
C-23	5390(4)	2778(3)	8982(2)	40(1)
C-24	5003(4)	3011(3)	8675(2)	49(1)
C-25	4395(5)	1180(5)	10,062(3)	111(4)
C-26	5827(6)	600(3)	9916(2)	93(3)
C-27	5658(4)	1345(3)	10,557(2)	58(2)
C-28	5336(5)	1887(3)	10,699(2)	71(2)
C-29	6476(4)	1366(4)	10,593(2)	67(2)
C-30	5380(5)	854(4)	10,780(2)	73(2)
C-31	3506(6)	3808(6)	8943(4)	161(7)
C-32	3901(6)	3700(5)	8175(3)	143(6)
C-33	4418(6)	4676(4)	8600(3)	100(3)
C-34	3782(6)	5061(4)	8567(3)	107(3)
C-35	4844(7)	4803(5)	8264(4)	147(4)
C-36	4872(7)	4818(5)	8900(4)	143(4)
Si-5	7645(1)	3232(1)	10,847(1)	49(1)
Si-6	3739(1)	3871(1)	10,319(1)	72(1)
O-11	5627(2)	4198(2)	10,192(1)	41(1)
O-12	6800(2)	4420(2)	10,056(1)	40(1)
O-13	7271(2)	3686(2)	10,571(1)	42(1)
O-14	4332(2)	3593(2)	10,053(1)	56(1)
O-15	6709(2)	2696(2)	10,235(1)	46(1)
C-37	6333(3)	4226(3)	10,318(2)	39(1)
C-38	6574(4)	3641(3)	10,426(2)	41(1)
C-39	6534(3)	3251(3)	10,128(2)	37(1)
C-40	5779(3)	3249(3)	9981(2)	35(1)
C-41	5523(3)	3844(3)	9895(2)	40(1)
C-42	4744(4)	3889(3)	9804(2)	49(1)
C-43	8258(4)	2759(3)	10,598(2)	57(2)
C-44	6953(5)	2809(4)	11,072(2)	71(2)
C-45	8152(5)	3671(4)	11,166(2)	66(2)
C-46	8805(4)	3932(4)	10,991(2)	68(2)
C-47	7667(5)	4136(4)	11,326(2)	78(2)
C-48	8399(5)	3287(4)	11,468(2)	82(3)
C-49	3042(6)	4218(8)	10,051(4)	187(8)
C-50	4131(6)	4382(4)	10,599(3)	103(4)
C-51	3390(6)	3257(5)	10,561(3)	99(3)
C-52	3981(6)	2993(5)	10,767(3)	125(4)
C-53	2829(5)	3433(5)	10,837(3)	107(3)
C-54	2981(7)	2882(6)	10,319(3)	145(4)
Si-7	8917(2)	6102(2)	10,635(1)	105(1)
Si-8	5367(1)	6200(1)	9744(1)	70(1)
O-16	7135(2)	5825(2)	9711(1)	46(1)
O-17	8314(2)	5597(2)	9596(1)	41(1)
O-18	8677(2)	5750(2)	10,275(1)	54(1)
O-19	5683(3)	5562(2)	9781(2)	67(1)
O-20	7772(3)	4872(2)	10,542(1)	56(1)
C-55	7845(4)	5895(3)	9819(2)	43(1)
C-56	7945(4)	5669(3)	10,181(2)	45(1)
C-57	7731(3)	5067(3)	10,197(2)	40(1)
C-58	6965(3)	5013(3)	10,064(2)	39(1)
C-59	6893(4)	5249(3)	9706(2)	45(1)
C-60	6149(4)	5264(3)	9554(2)	56(2)
C-61	8688(6)	5706(4)	11,032(2)	84(3)
C-62	8326(5)	6832(4)	10,623(3)	101(4)
C-63	9801(7)	6382(5)	10,592(3)	121(3)
C-64	10,263(7)	5804(5)	10,572(3)	117(3)
C-65	9969(7)	6740(5)	10,915(3)	138(4)
C-66	9863(7)	6768(4)	10,269(2)	109(3)
C-67	5840(5)	6693(4)	10,039(2)	88(3)
C-68	5491(7)	6463(4)	9291(2)	112(4)
C-69	4431(5)	6155(4)	9859(3)	112(3)
C-70	4033(5)	6716(4)	9816(3)	120(3)
C-71	4355(5)	5943(5)	10,238(3)	124(4)
C-72	4052(6)	5712(5)	9614(4)	134(4)
Si-9	11,425(1)	5848(1)	9225(1)	59(1)
Si-10	7717(2)	7455(1)	9061(1)	123(1)
O-21	8958(3)	6221(2)	8784(1)	47(1)
O-22	9491(2)	5369(2)	8652(1)	41(1)
O-23	10,631(2)	5623(2)	9084(1)	47(1)
O-24	7863(3)	6831(2)	9182(1)	62(1)
O-25	9771(3)	5607(2)	9706(1)	52(1)
C-73	9606(4)	5921(3)	8766(2)	45(1)
C-74	9957(4)	5901(3)	9116(2)	45(1)
C-75	9477(4)	5598(3)	9364(2)	43(1)
C-76	8755(4)	5910(3)	9373(2)	41(1)
C-77	8448(4)	5963(3)	9012(2)	43(1)
C-78	7773(4)	6317(3)	8994(2)	55(2)

Table 2 (Continued)

	x	y	z	U_{eq}
C-79	11,404(5)	6054(4)	9673(2)	92(3)
C-80	11,996(5)	5232(3)	9164(3)	100(4)
C-81	11,762(6)	6433(5)	8949(3)	103(3)
C-82	12,509(5)	6598(4)	9074(3)	105(3)
C-83	11,264(7)	6954(5)	8997(3)	130(4)
C-84	11,762(7)	6287(6)	8574(3)	126(4)
C-85	6912(9)	7544(9)	8773(5)	283(14)
C-86	7383(6)	7849(5)	9468(3)	142(5)
C-87	8470(6)	7688(6)	8925(3)	129(3)
C-88	8590(7)	7521(6)	8534(3)	143(4)
C-89	9128(6)	7641(5)	9152(3)	131(4)
C-90	8344(11)	8406(7)	8902(5)	231(9)
Si-11	11,555(1)	3927(1)	7891(1)	49(1)
Si-12	7077(1)	5683(1)	7840(1)	84(1)
O-26	9160(2)	4884(2)	7760(1)	40(1)
O-27	9244(2)	3951(2)	7926(1)	39(1)
O-28	10,689(2)	4010(2)	7958(1)	43(1)
O-29	7824(3)	5333(2)	7895(1)	63(1)
O-30	10,795(2)	4897(2)	8461(1)	46(1)
C-91	9592(4)	4406(3)	7761(2)	40(1)
C-92	10,293(4)	4515(3)	7951(2)	39(1)
C-93	10,137(3)	4740(3)	8310(2)	37(1)
C-94	9643(4)	5229(3)	8299(2)	38(1)
C-95	8960(4)	5066(3)	8102(2)	42(1)
C-96	8452(4)	5551(3)	8054(2)	53(2)
C-97	11,820(5)	3425(6)	8239(3)	130(5)
C-98	12,032(5)	4599(4)	7926(3)	93(3)
C-99	11,689(6)	3636(5)	7447(3)	102(3)
C-100	12,469(5)	3583(4)	7349(3)	99(3)
C-101	11,329(7)	4025(6)	7182(3)	126(4)
C-102	11,337(7)	3064(5)	7416(3)	136(4)
C-103	7295(7)	6400(6)	7691(5)	196(9)
C-104	6585(6)	5742(6)	8248(3)	125(4)
C-105	6563(7)	5250(6)	7521(3)	118(3)
C-106	6950(8)	5235(6)	7174(3)	147(4)
C-107	6480(6)	4671(5)	7662(3)	105(3)
C-108	5837(7)	5522(6)	7456(3)	145(4)
Si-13	9628(2)	1447(1)	7756(1)	78(1)
Si-14	8638(1)	3606(1)	6692(1)	58(1)
O-31	8084(2)	3005(2)	7425(1)	46(1)
O-32	7770(2)	2527(2)	7934(1)	45(1)
O-33	9073(3)	1944(2)	7898(1)	54(1)
O-34	8660(2)	3955(2)	7057(1)	49(1)
O-35	9935(3)	2904(2)	8007(1)	57(1)
C-109	8180(4)	2518(3)	7624(2)	48(1)
C-110	8962(4)	2463(3)	7724(2)	48(1)
C-111	9193(4)	2959(3)	7926(2)	44(1)
C-112	9067(4)	3473(3)	7717(2)	41(1)
C-113	8282(4)	3514(3)	7590(2)	44(1)
C-114	8152(4)	3979(3)	7336(2)	48(2)
C-115	10,239(9)	1744(5)	7433(4)	197(9)
C-116	9107(8)	897(5)	7562(5)	189(8)
C-117	10,100(11)	1185(8)	8115(4)	181(5)
C-118	10,609(9)	696(6)	8015(4)	181(5)
C-119	9472(10)	847(7)	8371(4)	180(5)
C-120	10,317(10)	1575(8)	8387(4)	201(6)
C-121	9265(5)	2997(4)	6726(2)	76(3)

Table 2 (Continued)

C-122	7735(5)	3359(4)	6598(2)	70(2)
C-123	8969(5)	4107(4)	6355(2)	72(2)
C-124	9732(5)	4277(4)	6437(2)	83(3)
C-125	8495(5)	4620(4)	6349(2)	77(2)
C-126	8952(6)	3819(4)	5999(2)	95(3)
Si-15	6796(4)	335(2)	8541(2)	63(2)
C-127	6912(15)	83(16)	9007(8)	85(4)
C-128	7626(14)	124(10)	8334(7)	94(5)
C-129	6096(13)	−5(12)	8288(6)	86(4)
C-130	6116(13)	−695(9)	8369(6)	93(5)
C-131	6082(15)	128(12)	7886(7)	96(5)
C-132	5365(17)	201(13)	8531(6)	78(5)
O-36	7539(19)	4240(16)	8880(8)	223(16)
C-133	7270(30)	4680(20)	8839(13)	223(16)
Compound **2**				
Si-1	5889(1)	1696(1)	1195(1)	57(1)
Si-2	8923(1)	2850(1)	2293(1)	69(1)
O-1	8855(2)	2092(2)	1508(1)	39(1)
O-2	7631(2)	1065(2)	1091(1)	50(1)
O-3	6588(2)	1761(2)	1400(1)	45(1)
O-4	7079(2)	3025(2)	1634(1)	36(1)
O-5	8593(2)	2672(2)	2009(1)	53(1)
O-6	9733(2)	3413(2)	982(1)	41(1)
O-7	8373(2)	3311(2)	729(1)	45(1)
C-1	8651(2)	1715(2)	1283(1)	38(1)
C-2	7859(3)	1445(2)	1308(1)	40(1)
C-3	7316(2)	2040(2)	1357(1)	36(1)
C-4	7577(2)	2444(2)	1591(1)	37(1)
C-5	8380(2)	2694(2)	1555(1)	38(1)
C-6	8712(3)	3064(3)	1780(1)	48(1)
C-7	7960(4)	396(3)	1065(1)	78(2)
C-8	6179(4)	1685(4)	855(1)	90(2)
C-9	5268(4)	2477(3)	1238(1)	78(2)
C-10	5400(3)	861(3)	1282(1)	71(2)
C-11	5926(4)	251(4)	1252(2)	121(3)
C-12	4736(5)	740(5)	1101(2)	141(4)
C-13	5124(5)	886(4)	1555(2)	108(3)
C-14	9070(5)	3802(3)	2326(1)	104(3)
C-15	8183(4)	2543(4)	2516(1)	101(3)
C-16	9808(3)	2375(3)	2350(1)	78(2)
C-17	10,414(4)	2626(5)	2168(1)	107(3)
C-18	10,056(5)	2483(5)	2631(1)	122(3)
C-19	9676(5)	1592(4)	2304(2)	118(3)
C-20	9672(3)	3527(2)	710(1)	40(1)
C-21	9029(2)	3084(2)	608(1)	39(1)
C-22	9223(3)	2314(3)	658(1)	43(1)
C-23	9399(2)	2169(2)	936(1)	39(1)
C-24	9915(3)	2712(2)	1055(1)	40(1)
C-26	7709(3)	3023(4)	626(1)	84(2)
Si-3	9991(1)	1461(1)	321(1)	50(1)
Si-4	11,306(1)	1680(1)	1389(1)	52(1)
Si-5	8978(1)	5200(1)	−48(1)	79(1)
O-8	9853(2)	2157(2)	504(1)	45(1)
O-9	8684(2)	2132(2)	1064(1)	38(1)
O-10	10,912(2)	1877(2)	1114(1)	58(1)
O-11	10,919(2)	5616(2)	750(1)	41(1)
O-12	9735(2)	6382(2)	252(1)	48(1)
O-13	9505(2)	4926(2)	188(1)	46(1)

Table 2 (Continued)

	x	y	z	U_{eq}
O-14	9500(2)	4238(2)	680(1)	38(1)
C-25	10,740(3)	2550(3)	1008(1)	47(1)
C-27	10,443(5)	766(4)	514(2)	114(3)
C-28	9088(3)	1123(3)	202(1)	72(2)
C-29	10,589(3)	1793(3)	56(1)	70(2)
C-30	11,323(4)	2071(5)	172(2)	115(3)
C-31	10,790(5)	1204(5)	−130(2)	128(4)
C-32	10,204(5)	2380(4)	−84(1)	106(3)
C-33	10,609(4)	1179(3)	1578(1)	73(2)
C-34	11,589(4)	2487(3)	1563(1)	80(2)
C-35	12,122(3)	1117(3)	1308(1)	62(2)
C-36	12,670(4)	1547(5)	1142(2)	118(3)
C-37	12,541(5)	891(6)	1548(2)	144(4)
C-38	11,898(4)	485(4)	1153(2)	109(3)
C-39	10,506(3)	6156(2)	628(1)	42(1)
C-40	10,186(3)	5882(2)	381(1)	40(1)
C-41	9689(3)	5245(2)	426(1)	38(1)
C-42	10,079(2)	4702(2)	592(1)	36(1)
C-43	10,486(3)	5013(2)	822(1)	39(1)
C-44	11,031(3)	4520(3)	949(1)	48(1)
C-45	10,134(3)	6995(3)	175(1)	66(2)
C-46	8197(3)	5748(4)	62(1)	75(2)
C-47	9560(4)	5670(5)	−303(1)	103(3)
C-48	8689(6)	4422(6)	−217(2)	144(5)
C-49	8219(5)	4589(4)	−457(1)	116(3)
C-50	9368(6)	3995(4)	−307(2)	147(4)
C-51	8132(6)	4010(5)	19(2)	164(5)
Si-6	12,263(2)	4247(1)	608(1)	52(1)
Si-7	11,630(1)	8195(1)	822(1)	42(1)
Si-8	10,284(1)	5577(1)	1676(1)	71(1)
O-15	11,476(2)	4132(2)	772(1)	56(1)
O-16	9374(2)	7184(2)	1377(1)	42(1)
O-17	10,132(2)	8741(2)	1063(1)	44(1)
O-18	10,969(2)	7600(2)	842(1)	48(1)
O-19	9895(2)	6392(2)	779(1)	38(1)
O-20	10,025(2)	5760(2)	1385(1)	52(1)
O-21	6993(2)	7940(2)	1504(1)	39(1)
C-52	12,663(7)	5112(5)	677(2)	72(3)
C-53	12,049(8)	4226(8)	265(2)	97(4)
C-54	12,929(4)	3534(4)	696(1)	40(2)
C-55	13,691(5)	3666(6)	578(2)	47(3)
C-56	12,644(9)	2820(7)	605(3)	60(6)
C-57	13,030(5)	3481(5)	984(2)	57(3)
C-58	9356(2)	7884(3)	1296(1)	40(1)
C-59	10,091(3)	8053(2)	1161(1)	40(1)
C-60	10,215(2)	7565(2)	933(1)	39(1)
C-61	10,065(2)	6794(2)	1001(1)	37(1)
C-62	9373(3)	6695(2)	1169(1)	41(1)
C-63	9325(3)	5970(3)	1284(1)	48(1)
C-64	10,027(3)	9275(3)	1247(1)	64(2)
C-65	11,350(3)	8946(3)	619(1)	66(2)
C-66	11,919(3)	8503(3)	1142(1)	60(2)
C-67	12,436(3)	7705(3)	678(1)	55(1)
C-68	12,632(4)	7058(3)	842(2)	86(2)
C-69	13,132(3)	8185(3)	665(1)	68(2)
C-70	12,267(4)	7467(4)	406(1)	87(2)
C-71	10,396(7)	4589(4)	1700(2)	147(4)

Table 2 (Continued)

C-72	9574(4)	5895(5)	1909(1)	108(3)
C-73	11,212(4)	6011(4)	1721(1)	77(2)
C-74	11,122(4)	6795(4)	1708(1)	90(2)
C-75	11,746(4)	5768(4)	1508(1)	95(2)
C-76	11,540(5)	5799(5)	1982(2)	125(3)
C-77	6497(2)	7788(2)	1301(1)	35(1)
C-78	6703(2)	8247(2)	1076(1)	34(1)
C-79	7520(2)	8170(2)	1002(1)	37(1)
C-80	8040(2)	8209(2)	1233(1)	35(1)
C-81	7762(2)	7751(3)	1453(1)	38(1)
Si-9	8139(1)	8686(1)	549(1)	39(1)
Si-10	7927(2)	8876(2)	2035(1)	72(1)
Si-11	6084(1)	5997(1)	623(1)	43(1)
O-22	6267(2)	8124(2)	855(1)	38(1)
O-23	7707(2)	8707(2)	826(1)	37(1)
O-24	8758(2)	8017(2)	1127(1)	40(1)
O-25	8254(2)	8558(2)	1771(1)	63(1)
O-26	5396(2)	5940(2)	1669(1)	40(1)
O-27	5444(2)	4840(2)	1100(1)	47(1)
O-28	5689(2)	6186(2)	899(1)	40(1)
C-82	8136(3)	7843(3)	1709(1)	53(1)
C-83	5521(3)	8360(3)	874(1)	61(2)
C-84	8976(3)	9249(3)	577(1)	52(1)
C-85	8418(3)	7783(3)	457(1)	54(1)
C-86	7483(3)	9068(3)	305(1)	51(1)
C-87	6837(3)	8557(3)	247(1)	69(2)
C-88	7155(3)	9765(3)	396(1)	66(2)
C-89	7927(4)	9183(3)	50(1)	71(2)
C-90	8094(8)	8301(6)	2312(2)	115(5)
C-91	6903(5)	9048(8)	2002(3)	133(6)
C-92	8448(6)	9705(5)	2069(2)	280(20)
C-93	8380(10)	10,150(7)	1829(3)	134(4)
C-94	8142(9)	10,116(7)	2302(3)	134(4)
C-95	9270(6)	9515(8)	2110(3)	134(4)
C-96	5441(3)	5311(2)	1529(1)	39(1)
C-97	5354(2)	5456(2)	1250(1)	38(1)
C-98	5907(2)	5998(2)	1151(1)	35(1)
C-99	5892(2)	6649(2)	1320(1)	34(1)
C-100	5949(3)	6463(2)	1605(1)	36(1)
C-101	5781(3)	7066(3)	1782(1)	41(1)
C-102	4811(3)	4403(3)	1096(1)	61(2)
C-103	6863(3)	6606(3)	563(1)	70(2)
C-104	6461(4)	5091(3)	606(1)	64(2)
C-105	5296(3)	6134(3)	390(1)	55(1)
C-106	5575(5)	6069(4)	114(1)	93(2)
C-107	4689(3)	5591(4)	438(1)	77(2)
C-108	4953(4)	6868(3)	429(1)	76(2)
Si-12	4286(1)	7456(1)	1794(1)	57(1)
Si-13	4311(1)	3638(1)	1974(1)	68(1)
Si-14	7227(1)	5396(2)	2404(1)	53(1)
O-29	6510(2)	7071(2)	1235(1)	34(1)
O-30	5159(2)	7476(2)	1701(1)	46(1)
O-31	7279(2)	3861(2)	1958(1)	43(1)
O-32	5691(2)	2667(2)	1900(1)	47(1)
O-33	5014(2)	3999(2)	1824(1)	48(1)
O-34	6135(2)	4964(2)	1562(1)	40(1)
O-35	7088(2)	5362(2)	2113(1)	83(1)
C-109	3743(4)	6867(4)	1582(2)	100(2)
C-110	4221(4)	7167(4)	2131(1)	94(2)

Table 2 (Continued)

	x	y	z	U_{eq}
C-111	3946(3)	8367(3)	1749(1)	69(2)
C-112	4050(4)	8605(4)	1475(1)	105(3)
C-113	3119(4)	8430(4)	1820(1)	90(2)
C-114	4417(5)	8864(4)	1925(2)	122(3)
C-115	6943(3)	3212(2)	1891(1)	41(1)
C-116	6108(3)	3295(2)	1940(1)	41(1)
C-117	5779(2)	3847(2)	1765(1)	36(1)
C-118	6222(2)	4534(2)	1785(1)	37(1)
C-119	7061(2)	4439(2)	1799(1)	40(1)
C-121	5901(3)	2105(3)	2064(1)	66(2)
C-122	4555(4)	3390(4)	2310(1)	101(3)
C-123	3921(4)	2864(4)	1791(2)	99(2)
C-124	3588(4)	4335(4)	1983(1)	88(2)
C-125	3392(4)	4562(5)	1712(2)	126(4)
C-126	2864(4)	4029(5)	2100(2)	124(3)
C-127	3905(6)	4974(4)	2128(2)	135(4)
C-120	7450(3)	5081(3)	1902(1)	53(1)
C-128	8163(6)	5726(8)	2477(3)	102(5)
C-129	7103(6)	4491(4)	2532(2)	74(3)
C-130	6489(5)	5980(5)	2541(2)	72(4)
C-131	5721(5)	5760(7)	2445(2)	83(3)
C-132	6642(7)	6736(5)	2448(2)	96(4)
C-133	6484(6)	5947(6)	2837(2)	84(3)
Si-15	12,385(2)	4255(2)	795(1)	50(1)
Si-16	7700(3)	9120(3)	1939(1)	81(2)
Si-17	7376(3)	5781(4)	2384(1)	68(2)
O-36	6774(2)	3865(2)	1138(1)	83(1)
O-37	8782(11)	4299(6)	1326(3)	171(9)
C-152	8361(8)	4378(9)	1192(3)	62(4)
C-153	8054(7)	4631(6)	986(3)	74(4)
C-134	12,706(8)	5148(5)	810(3)	56(4)
C-135	12,683(9)	3856(8)	1106(2)	84(5)
C-136	12,753(7)	3701(6)	531(2)	63(4)
C-137	13,588(8)	3826(11)	496(4)	98(7)
C-138	12,324(11)	3890(11)	282(3)	113(7)
C-139	12,616(17)	2915(8)	576(5)	104(15)
C-140	7071(8)	8656(8)	2154(3)	94(5)
C-141	7051(10)	9646(10)	1728(3)	126(7)
C-142	8373(6)	9734(5)	2079(2)	54(4)
C-143	8815(13)	9361(12)	2286(4)	189(12)
C-144	8840(8)	10,095(7)	1869(2)	69(4)
C-145	7803(9)	10,306(8)	2203(3)	106(6)
C-146	7557(10)	6632(8)	2233(3)	84(6)
C-147	8256(9)	5482(12)	2536(4)	82(7)
C-148	6567(8)	5857(11)	2599(3)	116(13)
C-149	5897(9)	6132(10)	2452(3)	71(5)
C-150	6787(12)	6370(12)	2814(4)	107(8)
C-151	6355(15)	5149(12)	2721(5)	159(12)
Compound **3**				
O-1	2505(3)	3950(2)	1073(1)	36(1)
O-2	865(3)	3759(2)	1397(1)	31(1)
O-3	355(3)	5320(2)	1247(1)	33(1)
O-4	385(3)	5217(2)	346(1)	35(1)
O-5	3863(4)	3665(3)	321(2)	77(1)
C-1	1674(4)	4296(3)	1304(2)	30(1)
C-2	1208(4)	4948(3)	1030(2)	29(1)

Table 2 (Continued)

C-3	809(4)	4600(3)	611(1)	30(1)
C-4	1724(4)	4211(3)	383(1)	30(1)
C-5	2187(4)	3582(3)	673(2)	35(1)
C-6	705(5)	5874(3)	1552(2)	50(2)
C-7	3107(5)	3170(4)	495(2)	58(2)
O-6	1109(3)	2364(2)	2295(1)	30(1)
O-7	−351(3)	1693(2)	2036(1)	28(1)
O-8	−1683(3)	2765(2)	2374(1)	33(1)
O-9	−908(3)	4102(2)	1923(1)	37(1)
O-10	2856(3)	3348(2)	2178(1)	37(1)
C-8	45(4)	2203(3)	2362(2)	26(1)
C-9	−576(4)	2951(3)	2334(2)	27(1)
C-10	−387(4)	3365(3)	1910(2)	30(1)
C-11	765(4)	3475(3)	1835(2)	30(1)
C-12	1362(4)	2711(3)	1882(2)	27(1)
C-13	−2205(4)	3154(3)	2713(2)	41(1)
C-14	2530(4)	2778(3)	1873(2)	30(1)
O-11	−304(3)	−416(2)	2100(1)	31(1)
O-12	−1308(3)	−515(2)	1472(1)	28(1)
O-13	−3086(3)	−200(2)	1900(1)	36(1)
O-14	−2492(3)	1328(2)	2201(1)	37(1)
O-15	1250(3)	414(2)	2611(1)	37(1)
C-15	−1306(4)	−585(3)	1928(1)	29(1)
C-16	−2111(4)	−15(3)	2100(2)	29(1)
C-17	−1773(4)	810(3)	2005(2)	28(1)
C-18	−661(4)	937(2)	2168(1)	26(1)
C-19	82(4)	341(3)	1983(2)	32(1)
C-20	−3995(4)	−89(3)	2158(2)	44(2)
C-21	1187(4)	398(3)	2148(2)	31(1)
O-16	−582(3)	−2045(2)	701(1)	29(1)
O-17	−991(3)	−1246(2)	112(1)	28(1)
O-18	−3072(3)	−1523(2)	209(1)	31(1)
O-19	−3254(3)	−861(2)	1088(1)	32(1)
O-20	4(3)	−2239(2)	1620(1)	38(1)
C-22	−1321(4)	−1873(3)	373(1)	27(1)
C-23	−2383(4)	−1671(3)	570(2)	29(1)
C-24	−2259(4)	−1005(3)	880(1)	29(1)
C-25	−1440(4)	−1196(3)	1216(2)	28(1)
C-26	−417(4)	−1415(3)	1006(1)	28(1)
C-27	−4154(4)	−1580(3)	312(2)	34(1)
C-28	409(4)	−1697(3)	1320(2)	31(1)
O-21	1038(2)	−1252(2)	−738(1)	30(1)
O-22	353(3)	−133(2)	−1047(1)	28(1)
O-23	−1275(3)	−931(2)	−1425(1)	33(1)
O-24	−2177(3)	−1556(2)	−656(1)	32(1)
O-25	2277(3)	−974(2)	51(1)	38(1)
C-29	444(4)	−942(3)	−1085(2)	28(1)
C-30	−656(4)	−1274(3)	−1092(1)	29(1)
C-31	−1194(4)	−1150(3)	−656(1)	28(1)
C-32	−491(4)	−1444(3)	−294(1)	27(1)
C-33	597(4)	−1082(3)	−318(1)	27(1)
C-34	−1206(5)	−1325(3)	−1833(2)	60(2)
C-35	1333(4)	−1418(3)	12(2)	35(1)
O-26	2334(3)	1296(2)	−1387(1)	30(1)
O-27	1245(3)	2262(2)	−1127(1)	30(1)
O-28	−47(3)	2168(2)	−1842(1)	32(1)
O-29	−653(3)	629(2)	−1747(1)	33(1)
O-30	3152(3)	−184(2)	−1348(1)	37(1)
C-36	1639(4)	1902(3)	−1505(2)	28(1)

Table 2 (Continued)

	x	y	z	U_{eq}
C-37	700(4)	1577(3)	−1752(2)	28(1)
C-38	157(4)	959(3)	−1486(1)	27(1)
C-39	935(4)	353(3)	−1340(1)	28(1)
C-40	1847(4)	728(3)	−1103(2)	29(1)
C-41	176(4)	2594(3)	−2233(2)	37(1)
C-42	2720(4)	185(3)	−974(2)	31(1)
O-31	2519(3)	3912(2)	−591(1)	34(1)
O-32	1330(3)	3867(2)	−14(1)	33(1)
O-33	−172(3)	4524(2)	−483(1)	38(1)
O-34	−268(3)	3428(2)	−1217(1)	38(1)
O-35	4199(3)	2801(2)	−514(1)	44(1)
C-43	1628(4)	4247(3)	−407(1)	32(1)
C-44	689(4)	4221(3)	−714(2)	32(1)
C-45	513(4)	3414(3)	−879(2)	32(1)
C-46	1521(4)	3056(3)	−1044(2)	32(1)
C-47	2387(4)	3116(3)	−709(2)	30(1)
C-48	−934(5)	4930(3)	−738(2)	47(2)
C-49	3467(4)	2823(3)	−855(2)	37(1)
O-36	−1381(3)	4487(2)	−1787(1)	46(1)
O-37	3291(3)	−1769(2)	−1421(1)	43(1)
O-38	3798(3)	−1311(2)	−516(1)	40(1)
O-39	−6938(3)	−1800(2)	800(1)	53(1)
O-40	−6428(3)	−1123(2)	1606(1)	48(1)
O-41	−4584(3)	−1941(2)	1497(1)	48(1)
O-42	3755(4)	1443(2)	−113(1)	74(1)
O-43	3336(3)	924(2)	2677(1)	43(1)
O-44	3081(3)	2467(2)	2972(1)	46(1)
O-45	1978(4)	682(3)	43(2)	85(2)
C-50	1104(7)	1010(7)	305(3)	128(4)
C-51	1206(9)	929(7)	759(3)	164(6)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

EtOH and refluxing the slurry for 1 h. After cooling and filtration through a Buchner funnel, the filtrate was allowed to warm back to about 28 °C and filtered through a 0.45-μm PTFE membrane filter. All three of the filtered solutions were concentrated by slow evaporation of the respective solvent until crystals of sufficient size were formed. The crystals selected for X-ray diffractometry were taken from their mother liquor at room temperature and quickly transferred to a LN_2 cold stream.

Structure determination and refinement.— The crystal data, and structure determination and refinement data for compounds **1**–**3** are listed in Table 1. The structures were solved and refined with the SHELXTL program suite [16] in the space group $P2_12_12_1$. All nonhydrogen atoms were located in the difference Fourier maps, and the structures were refined to convergence. Silyl disorder was found for the structures of both **1** and **2**. The disorder was modeled, and the structures were refined to convergence. Hydrogen positions were located on idealized positions with their thermal parameters fixed to those of the attached atom, except for hydrogen atoms connected to oxygens in the secondary hydroxyl groups in structure **3**, which were located in the difference residual electron density map and included as riding models with fixed isotropic parameters. No unusual residual electron densities were seen for any of the structures. Atomic coordinates and equivalent isotropic displacement parameters for compounds **1**–**3** are listed in Table 2.

3. Discussion

The structures of **1**, **2** and **3** are shown in Figs. 1–3, respectively. The parameters that describe the conformation of the inner ring systems are shown in Figs. 4–6 for structures **1**, **2**, and **3**, respectively. In all three structures, the D-glucopyranose units are in the $^4C_1$ chair-conformation. The connectivity differences are seen in the position of the silyl groups located at C-2 position of the D-glucopyranose units for **1** and the C-3 position of the D-glucopyranose units for **2**.

For all three structures, the seven glycosidic oxygen atoms form a heptagon. For **1**, the heptagon is circular in shape, for **2** it is more ellipsoidal, while for **3** the heptagon is again more circular. The glycosidic oxygens are nearly planar for structure **1** within a respective deviation of 0.13 Å, non-coplanar for structure **2** (respective deviation of 0.58 Å) and again nearly planar for structure **3** (within a deviation of 0.13 Å). The radius of the heptagon for **1** is in the range 4.82–5.14 Å, the radius of the heptagon of **2** is in the range 3.93–5.82 Å, while the radius of the heptagon for **3** is found in the range 4.73–5.21 Å.

The side lengths of the heptagon for **1** are distributed in the range 4.30–4.41 Å, those for **2** in the range 4.08–4.73 Å, while for **3**, they range from 4.31 to 4.41 Å. The average glycosidic oxygen atom torsion angle is 106(7)° for **1**, 92(13)° for **2**, and 106(5)° for **3**. The spread

of the glycosidic oxygen atom torsion angles is 96.7–114.7° for **1**, 71.5–109.6° for **2**, and 94.9–114.7° for **3**.

The heptagon of **1** is circular, as indicated by the low spread in the heptagon radii. The planes of the D-glucopyranose residues tend to face toward the center of the ring systems. This is clearly seen in the small spread in the torsion angles (18.1°), which renders the shape of the entire ring system conical. On the other hand, the heptagon of **2** is ellipsoidal as indicated by the high spread of the heptagonal radii. The planes of four of the D-glucopyranose units tend to face the center of the heptagon, while the planes of the other three units are in a plane that contains the centroid. The spread of the torsion angles is 38.1°. The heptagon of **3** is again more circular, as indicated by the low spread in the heptagon radii. The planes of the D-glucopyranose residues tend to face toward the center of the ring systems. In six of the seven secondary hydroxyl groups, the hydrogens are intramolecularly hydrogen-bonded to the methoxy oxygens on the nearby D-glucopyranose residues. In the seventh secondary hydroxyl group, the hydrogen is intermolecularly bonded to an adjacent molecule of **3**.

All three structures contain included solvents. For structure **1**, an included methanol molecule is found in the ring cavity. It is believed to originate from the methanol precipitation step that preceded the final crystal growth step from ethyl acetate. Structure **2** contains an included water molecule and an ethanol molecule in the ring cavity. Again, those are believed to originate from the ethanol precipitation step that preceded the final crystal-growth step from ethyl acetate.

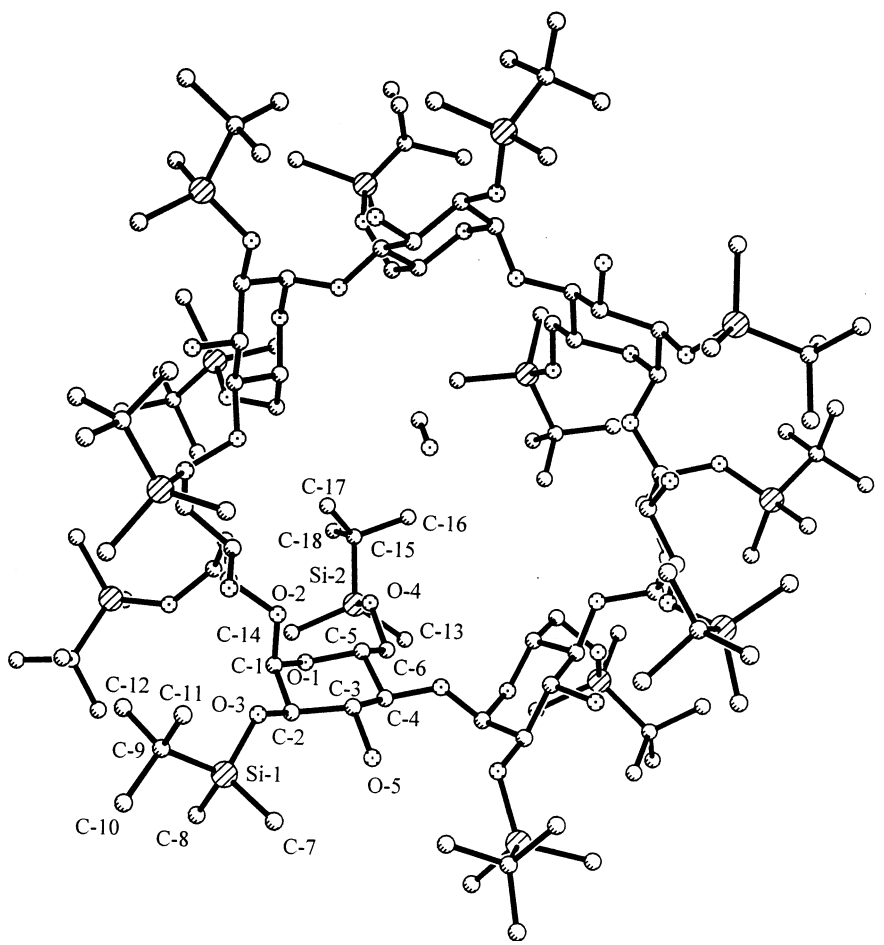


Fig. 1. Ball-and-stick representation of the crystal structure of compound **1**. For clarity, only one D-glucopyranose unit is labeled, and hydrogen atoms are omitted.

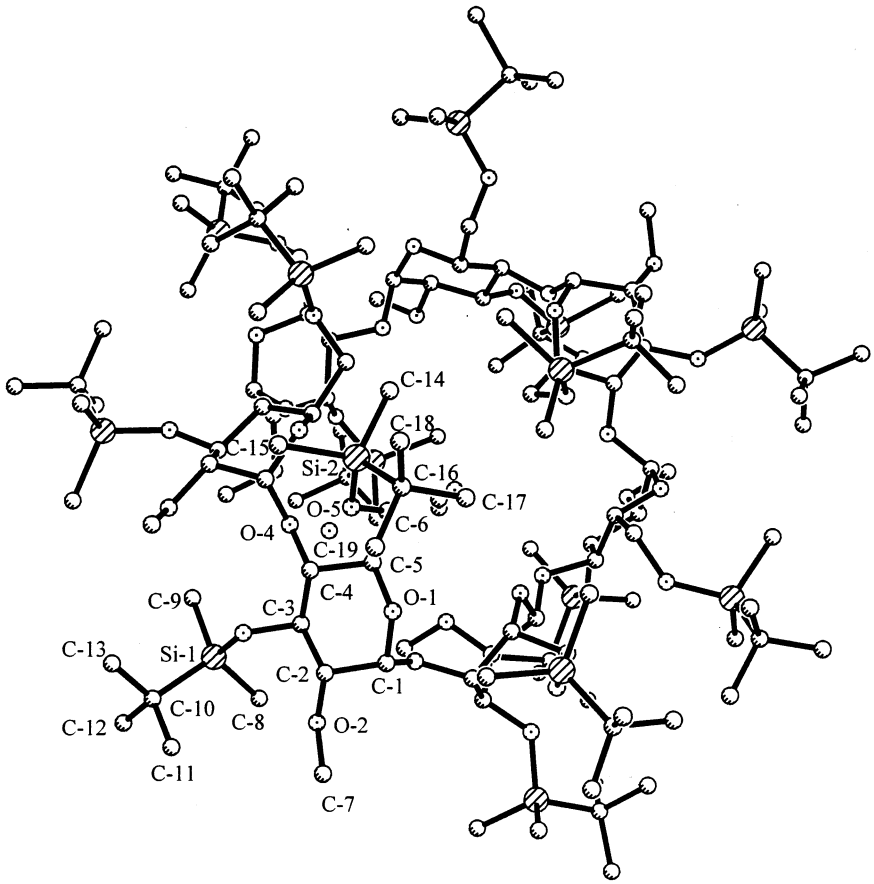


Fig. 2. Ball-and-stick representation of the crystal structure of compound **2**. For clarity, only one D-glucopyranose unit residue is labeled, and hydrogen atoms are omitted.

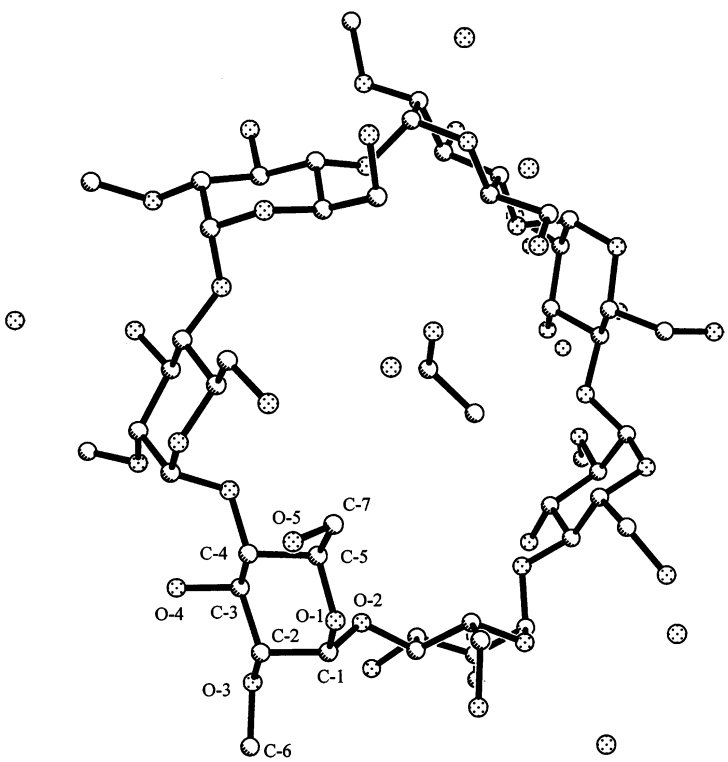
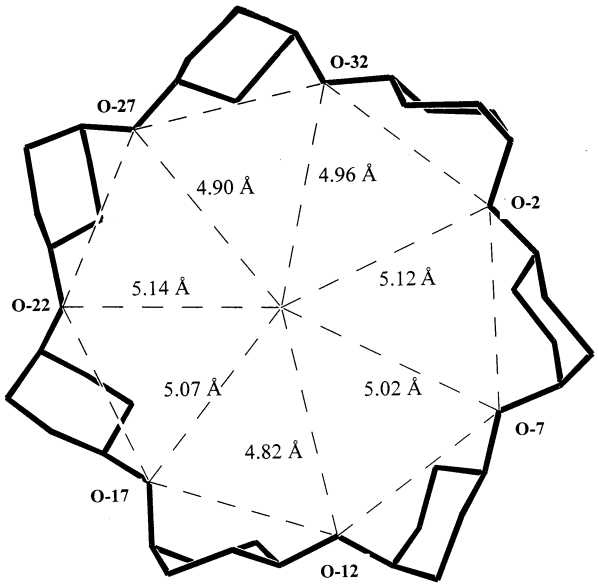


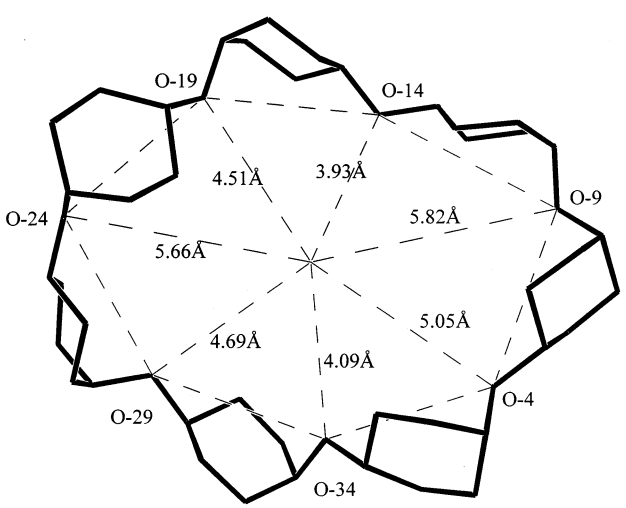
Fig. 3. Ball-and-stick representation of the crystal structure of compound **3**. For clarity, only one D-glucopyranose unit residue is labeled, and hydrogen atoms are omitted.



O-2 ... O-32	4.31 Å	O-2... O-7	4.35 Å
O-7 ... O-12	4.33 Å	O-12... O-17	4.37 Å
O-17 ... O-22	4.30 Å	O-22... O-27	4.41 Å
O-27...O-32	4.38 Å		

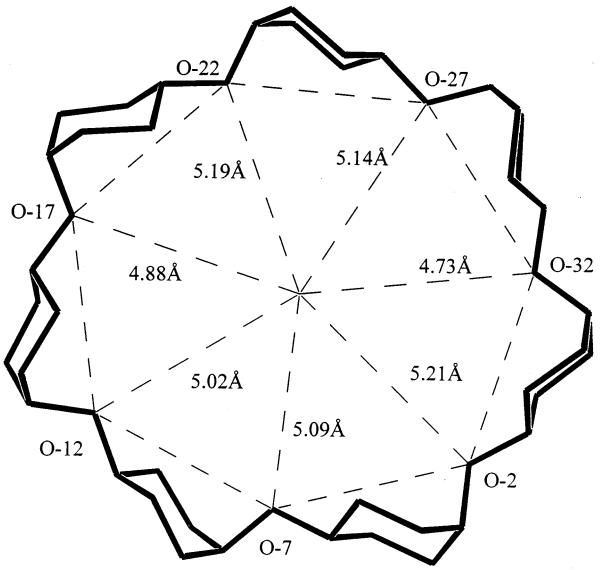
Fig. 4. Stick diagram of the ring system for compound **1**.

One ethanol molecule and one water molecule were found included in the ring cavity of **3**. Oxygen distances for the encapsulated solvents indicate that they are hydrogen-bound to the oxygen atoms of the ring systems.



O-4...O-34	4.08 Å	O-4... O-9	4.48 Å
O-9...O-14	4.73 Å	O-4...O-19	4.20 Å
O-19...O-24	4.13 Å	O-24...O-29	4.45 Å
O-29...O-34	4.42 Å		

Fig. 5. Stick diagram of the ring system for compound **2**.



O-2...O-32	4.39 Å	O-2...O-7	4.37 Å
O-7...O-12	4.37 Å	O-12...O-17	4.40 Å
O-17...O-22	4.41 Å	O-22...O-27	4.31 Å
O-27...O-32	4.42 Å		

Fig. 6. Stick diagram of the ring system for compound **3**.

4. Supplementary material

Full crystallographic details, excluding structure features, have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 136340 for structure **1**, 136341 for structure **2** and 138297 for structure **3**. These data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (tel.: +44-1223-336408; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This project was supported in part by the Texas Coordinating Board of Higher Education (Project No. 010366-052-1999), the R.W. Johnson Pharmaceutical Research Institute (Springhouse, PA) and J&W Scientific, (Folsom, CA). Dr Charles Campana, Bruker Analytical X-ray Instruments (Madison, WI) is acknowledged for collection of the data set for compound **1**. The X-ray instrumentation used to collect the data sets for compounds **2** and **3** was purchased using funds from grant CHE-9807975 by the National Science Foundation.

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