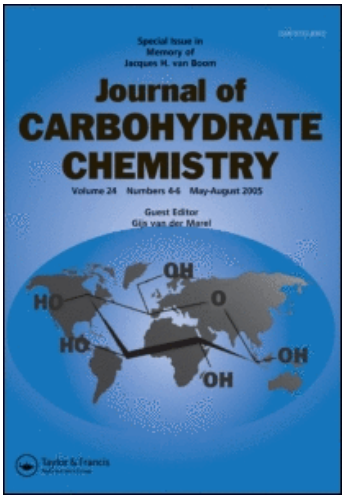

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Communication

SYNTHESIS OF CHIRAL [2.2.1]CRYPTAND INCORPORATING METHYL 4,6-O-[(S)-PHENYLETHYLIDENE]-α-D-MANNOPYRANOSIDE UNIT

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Recently, we described the high-yield synthesis of chiral [2.2.1] cryptands incorporating carbohydrates.[1] Models show that variations of substituents in the carbohydrate fragment, e.g. in 4,6-O-acetals, may lead to asymmetric modifications in close proximity to the molecular cavity of the ligand, and therefore, to changes in enantiomeric differentiation. We wanted to obtain the cryptand 2 with an axial phenyl group, as shown in Fig. 1, which is in contrast to a cryptand (1) obtained earlier[1] with an equatorial phenyl group.

We assumed that the regioselective reaction of methyl α-D-mannopyranoside with α-methoxystyrene should lead predominantly to the formation of the thermodynamically favoured 4,6-O-acetal 3,[2] rather than the kinetically preferred isomer. Indeed, the ratio between kinetic and thermodynamic products was ca. 3:7, and as predicted, the thermodynamic product possessed the axial phenyl group. This controversial point,

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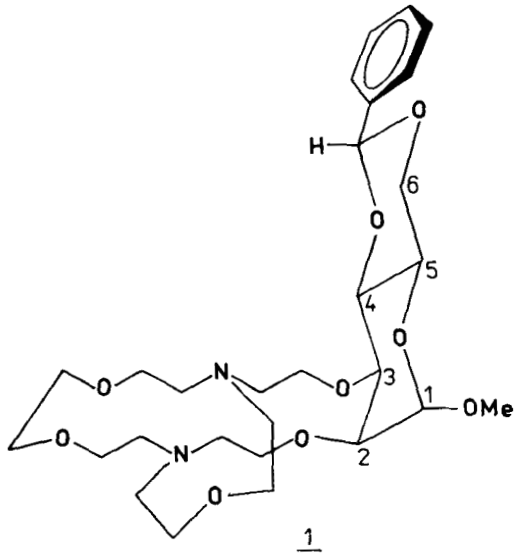

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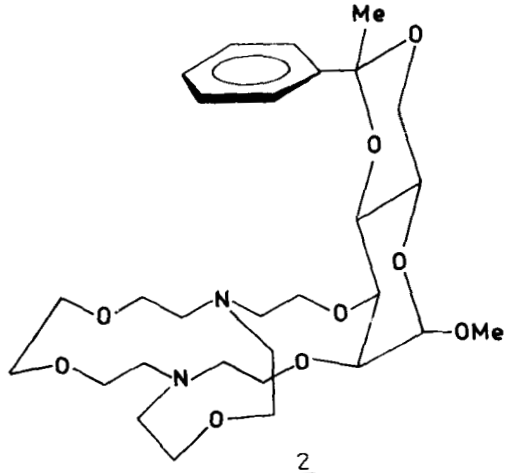

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Figure 1. Comparison of two chiral cryptands 1 and 2. In each case only one conformational diastereoisomer with the five-atom chain anti to the mannoside residue fused to the 18-membered ring is presented.

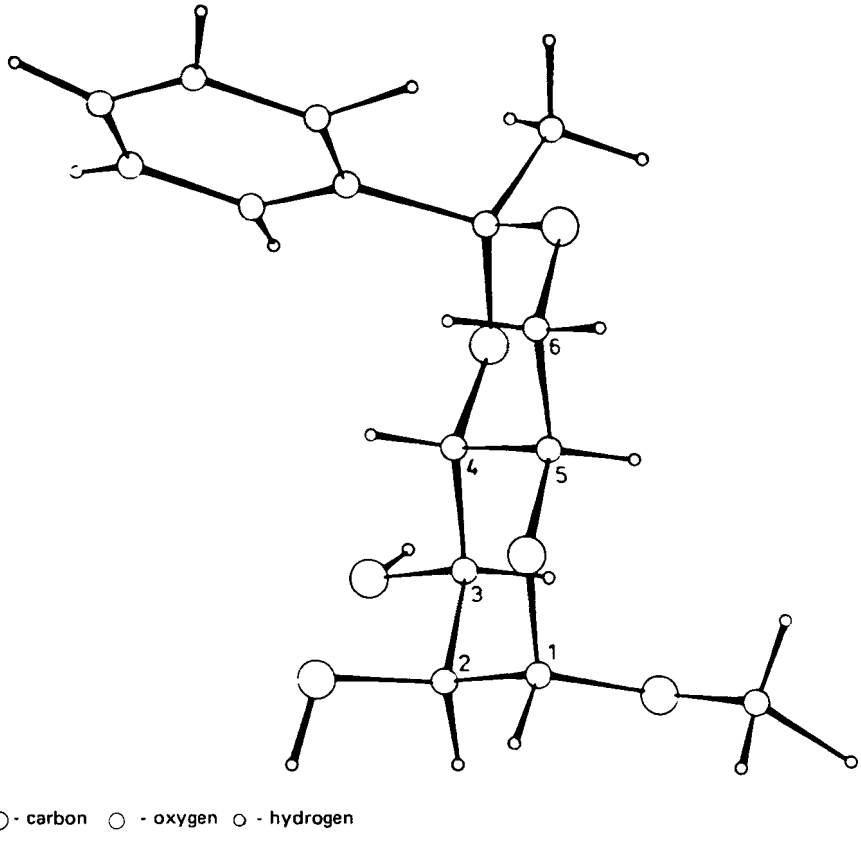

Figure 2. X-ray molecular structure of methyl 4,6-O-[(S)-phenylethylidene]-α-D-mannopyranoside (3).

concerning the absolute configuration of a new chiral center[3] was solved by X-ray analysis[4](**Fig. 2**).

Compound 3[5] was incorporated into N,N'-dimethyldiaza-18-crown-6 (4)[6] by a procedure described earlier.[1] Double quaternization of 4 with bis-(2-iodoethyl) ether under high pressure (8 kbar, acetone, 25°C, 20 h, 100% yield) afforded the bis-quaternary salt which was demethylated with triphenyl-triphenylphosphine in boiling DMF (4 h, 72% yield) to give the chiral cryptand 2[7](Fig. 3).

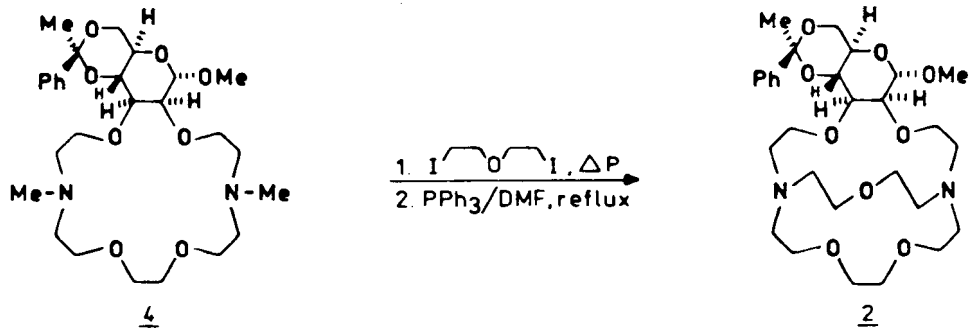

Figure 3. Synthesis of [2.2.1]cryptand incorporating methyl 4,6-O-[(S)]-phenylethylidene]-α-D-mannopyranoside

Analysis of the ^{1}H NMR spectra[7] testifies that the chiral cryptand 2 obtained in this way is a single conformational diastereoisomer. In our opinion, its stereochemistry is as shown in Fig. 2. The second diastereoisomeric possibility, i.e. the one with the five-atom chain syn to the mannoside residue fused to the 18-membered ring, seems to be rather unfavourable from thermodynamic reasons. The stereochemical and complexing properties of the chiral cryptand 2 are under current investigation.

Acknowledgment

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References And Footnotes

1. M. Pietraszkiewicz, P. Salanski, and J. Jurczak, J. Chem. Soc., Chem. Commun., 1184(1983); Tetrahedron, 40,2971 (1984).

2. Analogous regioselective reaction with isopropenyl methyl ether: C. Copeland R. V. Stick, Aust. J. Chem., 31, 1371(1978).

3. Contrary to Lipshutz and Morey, Liptak and Fugedi pointed out that thermodynamic product possessed an axial phenyl group, see: B. H. Lipshutz and M. C. Morey, J. Org. Chem., 46, 2419(1981); A. Liptak and P. Fugedi Angew. Chem. Int. Ed., 22, 255(1983).

4. L. Gluzinski, G. D. Andreetti, and G. Bocelli, Acta Crystalogr. C, to be published.

5. Compound 3 was obtained from methyl α-D-mannopyranoside (10 g in 30 mL DMSO) with α-methoxystyrene (1.1 equivalent) and PPTS (50 mg) after stirring for seven days at ambient temperature (61% yield). ^{1}H NMR, $CDCl_3$, δ(ppm): 7.5(m,5H,Ar), 4.7(s,1H,H-1), 4.2-3.6(m,6H), 3.42 (s,3H,OCH_3), 3.3 and 2.92(2xd,2H,2xOH), 1.6(s,3H,Ar-C-CH_3).

6. Compound 4 was obtained from 3 as follows:[1] 3 was O-alkylated with t-butyl bromoacetate under phase-transfer conditions to give the 2,3-O-bis-ester [92% yield; ^{1}H NMR, $CDCl_3$, δ(ppm): 7.5(m,5H,Ar), 5.0 (s,1H,H-1), 4.8-3.7(m, 10H), 3.4(s,3H,OCH_3), 1.6(s,3H,Ar-C-CH_3), 1.55(s,9H,t-Bu)] which was reduced with $LiAlH_4$ to the diol (91% yield), and the diol was tosylated (TsCl/Py, 0°C) to give the bis-tosylate [85% yield; ^{1}H NMR, $CDCl_3$, δ(ppm): 8.0-7.2(m,13H, Ar), 4.55 (s,1H,H-1), 4.3-3.5(m, 14H), 3.34(s,3H,OCH_3), 2.45(s,6H,2xArCH_3), 1.5(s,3H,Ar-C-CH_3)]. The bis-tosylate was condensed with N,N'-bisethoxycarbonyl-3,6-dioxa-1,8-diaminooctane (NaH, DMSO, room temperature, 48 h) to give the diaza-crown framework [41% yield; ^{1}H NMR, $CDCl_3$, δ(ppm): 7.5(m,5H, Ar), 4.65(s,1H, H-1), 4.4-3.4(m,30H), 3.4(s,3H,OCH_3), 1.52(s,3H, Ar-C-CH_3), 1.25(t,6H,2xCH_2CH_3)]. Reduction of the N,N'-bisethoxycarbonyl diaza-crown with $LiAlH_4$ afforded N,N'-dimethyl diaza-crown 4 in 93% yield

[^{1}H NMR, $CDCl_3$, δ(ppm): 7.5 (m,5H,Ar), 4.62(s,1H,H-1), 4.2-3.45(m,18H), 3.37(s,3H,OCH_3), 3.3-2.5 (m,8H,NCH_2), 2.4(s,3H,NCH_3), 2.25(s,3H,NCH_3), 1.5(s,3H,Ar-C-$\underline{CH}_3$).

7. ^{1}H NMR, $CDCl_3$, δ(ppm): 7.5(m,5H,Ar), 4.6(s,1H,H-1), 4.3-3.3(m,22H), 3.35(s,3H,OCH_3), 2.9-2.6(m,12H,NCH_2), 1.52(s,3H,Ar-C-$\underline{CH}_3$).