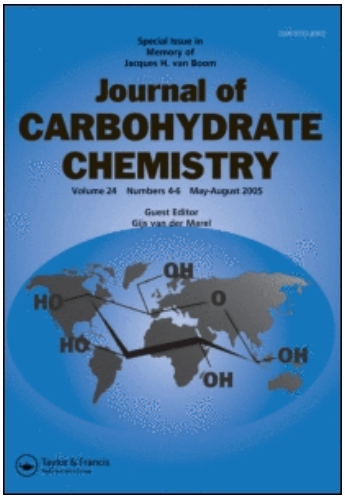


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# NMR AND X-RAY DIFFRACTION STUDY OF SOME INOSITOL DERIVATIVES[1]

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## ABSTRACT

We have determined the preferred conformers in solution by a detailed NMR analysis using COSY and HETCOR experiments of three inositol isomers: *myo* (**1**), *scyllo* (**2**) and *epi* (**3**) plus sixteen derivatives of *myo*-inositol: 1,2,3,4,5,6-hexa-*O*-acetyl-*myo*-inositol (**4**), 1,2-*O*-isopropylidene-*myo*-inositol (**5**), 1,2:4,5-di-*O*-isopropylidene-*myo*-inositol (**6**), 3,4,5,6-tetra-*O*-acetyl-1,2-*O*-isopropylidene-*myo*-inositol (**7**), 3,4,5,6-tetra-*O*-acetyl-*myo*-inositol (**8**), 1,2-*O*-isopropylidene-3,6-di-*O*-tosyl-*myo*-inositol (**9**), 1,2-*O*-isopropylidene-3,4,6-tri-*O*-tosyl-*myo*-inositol (**10**), 1,2:4,5-di-*O*-isopropylidene-3-*O*-tosyl-*myo*-inositol (**11**), 3,6-di-*O*-benzyl-1,2:4,5-di-*O*-isopropylidene-*myo*-inositol (**12**), 3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-*myo*-inositol (**13**), 3,6-di-*O*-benzyl-*myo*-inositol (**14**), 1,2-*O*-cyclohexylidene-*myo*-inositol (**15**), 1,2:4,5-di-*O*-cyclohexylidene-*myo*-inositol (**16**), 1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**17**), 1,3,5-*O*-(orthoformate)-*myo*-inositol (**18**) and 2-benzyl-1,3,5-*O*-(orthoformate)-*myo*-inositol (**19**). The X-ray diffraction structure of compounds **2**, **6-8**, **18** and **19** are reported.

## INTRODUCTION[1]

Cyclitols are building blocks of great potential for the synthesis of new compounds with biological applications. In particular inositol derivatives are widely used as intermediates in synthesis of inositol polyphosphates, important compounds in the transduction of information in living organisms.[2,3] We are particularly interested in using optically active cyclitols as raw material to construct metallic derivatives and boron heterocycles.[4-9] Herein, we report the NMR analysis of three inositol isomers, *myo* (**1**), *scyllo* (**2**) and *epi* (**3**), and some myo-inositol derivatives: three monocyclic esters: 1,2,3,4,5,6-hexa-*O*-acetyl-*myo*-inositol (**4**), 3,4,5,6-tetra-*O*-acetyl-*myo*-inositol (**8**), and 3,6-di-*O*-benzyl-*myo*-inositol (**14**); five bicyclic compounds: 1,2-*O*-isopropylidene-*myo*-inositol (**5**), 3,4,5,6-tetra-*O*-acetyl-1,2-*O*-isopropylidene-*myo*-inositol (**7**), 1,2-*O*-isopropylidene-3,6-di-*O*-tosyl-*myo*-inositol (**9**), 1,2-*O*-isopropylidene-3,4,6-tri-*O*-tosyl-*myo*-inositol (**10**), 3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-*myo*-inositol (**13**); four tricyclic structures: 1,2:4,5-di-*O*-isopropylidene-*myo*-inositol (**6**), 1,2:4,5-di-*O*-isopropylidene-3-*O*-tosyl-*myo*-inositol (**11**), 3,6-di-*O*-benzyl-1,2:4,5-di-*O*-isopropylidene-*myo*-inositol (**12**), 1,2-*O*-cyclohexylidene-*myo*-inositol (**15**); two pentacyclic compounds: 1,2:4,5-di-*O*-cyclohexylidene-*myo*-inositol (**16**), 1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**17**) and two tetracyclic compounds: 1,3,5-*O*-(orthoformate)-*myo*-inositol (**18**), and 2-benzoyl-1,3,5-*O*-(orthoformate)-*myo*-inositol (**19**), Figure 1. Compounds **1-6**, **8** and **12-19** have been previously reported (see references in experimental part).

Assignment of all cyclitol NMR signals is relevant because it allows determination of the static and conformationally dynamic structures of these molecules. Herein, we report the unequivocal assignment of the $^{1}H$ and $^{13}C$ NMR signals of **1-19** (Tables 1 and 3). We have determined the stereochemistry and the preferred conformers of these in solution by detailed NMR analysis using COSY and HETCOR experiments. The coupling constants were obtained from careful experiments of selective irradiation (Tables 2 and 4). For each group of compounds, we have determined their conformation in the solid state, from the X-ray diffraction structures of compounds **2**, **6-8**, **18** and **19**.

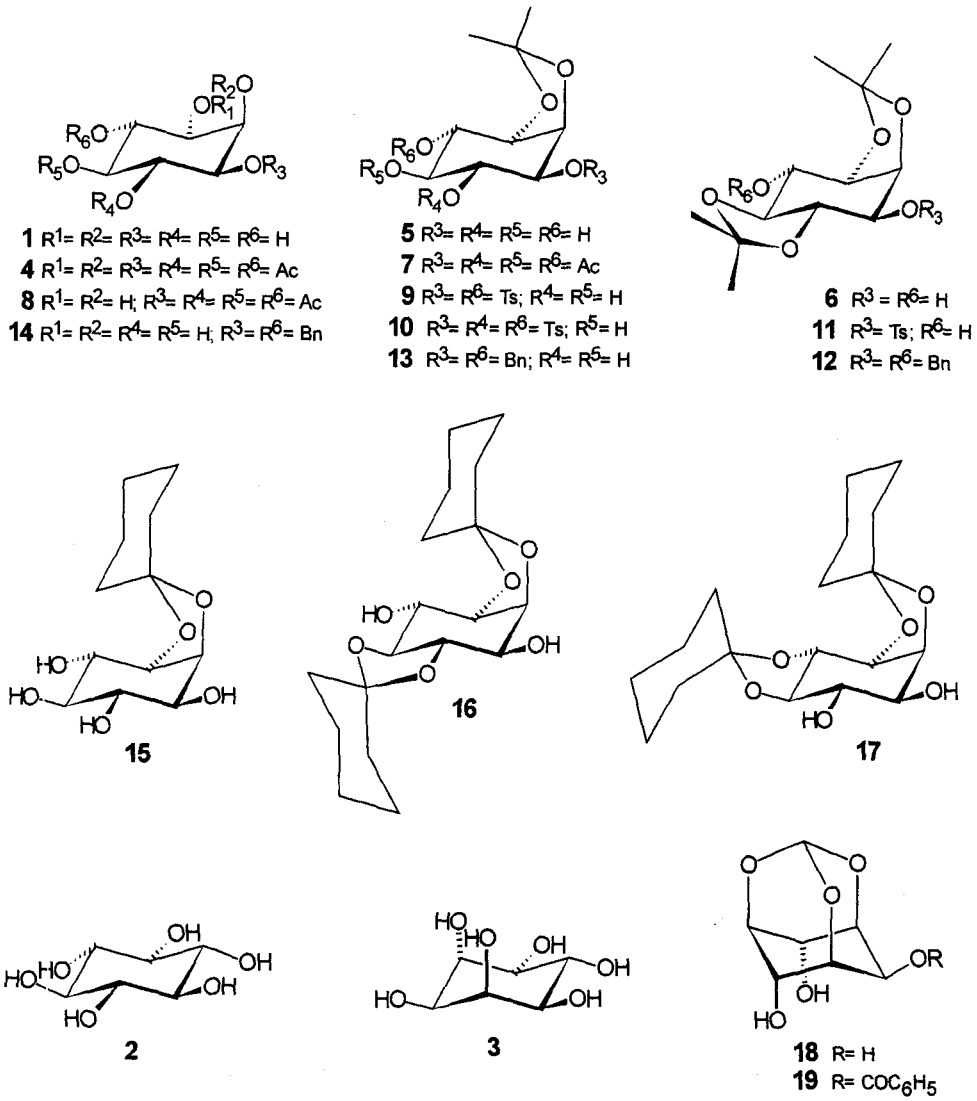


**Figure 1**

All the structures were modeled using a molecular mechanics program (PC Model)[10] which afforded preferred conformations and dihedral angles (Table 4).

### *Myo*-Inositol, 1.

*Myo*-Inositol is one of the most important inositol isomers as it is a natural product involved in cellular activity, principally the transport of ions through cell

**TABLE 1**. Chemical shift (δ, ppm), $^1$H NMR (270 MHz) of compounds **1-19**

| Compd. | H-1 | H-2 | H-3 | H-4 | H-5 | H-6 |
|---|---|---|---|---|---|---|
| **1**[a] | 3.38(dd) | 3.91(t) | 3.38(dd) | 3.47(t) | 3.12(t) | 3.47(t) |
| **1**[b,c] | 3.10(ddd) | 3.68(td) | 3.10(ddd) | 3.32(ddd) | 2.88(ddd) | 3.32(ddd) |
| **2**[a] | | | 4.58(s) | | | |
| **3**[a] | 3.55(t) | 3.88(t) | 3.30(t) | 3.67(dd) | 3.30(t) | 3.88(dd) |
| **4**[c] | 5.09(dd) | 5.60(t) | 5.09(dd) | 5.50(t) | 5.18(t) | 5.50(t) |
| **5**[b] | 3.83(dd) | 4.21(t) | 3.54(dd) | 3.37(t) | 2.98(t) | 3.35(dd) |
| **6**[d] | 4.07(t) | 4.47(t) | 4.05(dd) | 3.85(t) | 3.33(dd) | 3.89(dd) |
| **7**[d] | 4.26(dd) | 4.53(t) | 5.25(dd) | 5.50(dd) | 5.05(t) | 5.29(dd) |
| **8**[d] | 3.75(dd) | 4.26(t) | 4.93(dd) | 5.56(dd) | 5.12(t) | 5.35(dd) |
| **9**[d] | 4.03(dd) | 4.24(t) | 4.65(dd) | 3.96(t) | 3.49(t) | 4.61(dd) |
| **10**[d] | 4.17(t) | 4.34(dd) | 4.70(dd) | 4.81(dd) | 3.75(ddd) | 4.67(dd) |
| **11**[d] | 3.95(t) | 4.42(t) | 4.75(dd) | 3.87(t) | 3.22(dd) | 3.76(dd) |
| **12**[d] | 4.05(t) | 4.29(t) | 3.74(dd) | 4.01(t) | 3.33(dd) | 3.66(dd) |
| **13**[d] | 4.10(dd) | 4.32(t) | 3.55(dd) | 3.97(t) | 3.39(t) | 3.57(dd)) |
| **14**[b] | 3.30(dd) | 3.98(t) | 3.11(dd) | 3.61(t) | 3.15(t) | 3.45(t) |
| **15**[a] | 3.86(t) | 4.29(t) | 3.66(dd) | 3.46(t) | 3.08(t) | 3.39(t) |
| **16**[d] | 4.05(t) | 4.45(t) | 4.02(dd) | 3.83(t) | 3.31(t) | 3.85(dd) |
| **17**[d] | 4.30(dd) | 4.47(dd) | 3.86(t) | 4.02(dd) | 3.38(dd) | 3.89(dd) |
| **18**[a,f] | 4.10(t) | 4.13(ddd) | 4.10(t) | 4.44(ddd) | 4.19(ddd) | 4.44(ddd) |
| **19**[d,e,g] | 4.44(t) | 5.55(dd) | 4.44(t) | 4.57(ddd) | 4.32(tt) | 4.57(ddd) |

a. $D_2O$; b. DMSO-$d_6$; c. $OH_{ax\text{-}2}$ δ= 4.48, $OH_{eq\text{-}5}$ δ=4.58, $OH_{eq\text{-}1}$ and $OH_{eq\text{-}3}$ δ= 4.38, $OH_{eq\text{-}4}$ and $OH_{eq\text{-}6}$ δ= 4.52; d. $CDCl_3$; e. $CD_3OD$.

**TABLE 2**. Experimental coupling constants values,($^3J_{H,H}$ in Hz) for myo-inositol, and calculated values in the two chair conformers: A and B

| | Experimental | | Calculated[10] | |
|---|---|---|---|---|
| | DMSO-$d_6$ | $D_2O$ | A | B |
| H1-H2 | 2.9 | 2.6 | 2.3 | 2.3 |
| H2-H3 | 2.9 | 2.6 | 2.3 | 2.3 |
| H3-H4 | 9.5 | 9.9 | 9.7 | 4.0 |
| H4-H5 | 9.0 | 9.2 | 9.7 | 4.0 |
| H5-H6 | 9.0 | 9.2 | 9.7 | 4.0 |
| H6-H1 | 9.5 | 9.9 | 9.7 | 4.0 |

**TABLE 3.** Chemical shift (δ, ppm) $^{13}C$ NMR (67.8 MHz) of compounds **1-19.**

| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 |
|---|---|---|---|---|---|---|
| **1**[a] | 71.23 | 72.28 | 71.23 | 72.51 | 74.44 | 72.51 |
| **1**[b] | 72.01 | 72.79 | 72.01 | 72.91 | 75.38 | 72.91 |
| **2**[a] | | | 73.13 | | | |
| **3**[a] | 66.37 | 74.05 | 71.31 | 69.59 | 71.31 | 74.05 |
| **4**[c] | 68.50 | 68.22 | 68.50 | 69.49 | 71.01 | 69.49 |
| **5**[b] | 79.46 | 76.89 | 70.24 | 75.27 | 74.23 | 72.19 |
| **6**[c] | 81.93 | 77.71 | 69.72 | 77.96 | 78.22 | 74.71 |
| **7**[c] | 75.70 | 73.21 | 68.71 | 69.44 | 71.09 | 72.13 |
| **8**[c] | 70.27 | 70.09 | 71.19 | 69.63 | 70.70 | 72.54 |
| **9**[c] | 76.23 | 74.03 | 78.23 | 69.91 | 71.09 | 84.25 |
| **10**[c] | 75.37 | 73.02 | 74.39 | 79.39 | 71.90 | 81.51 |
| **11**[c] | 81.83 | 75.85 | 74.06 | 77.13 | 78.02 | 74.39 |
| **12**[c] | 81.08 | 76.70 | 74.37 | 77.14 | 78.86 | 79.88 |
| **13**[c] | 79.22 | 74.03 | 77.00 | 71.55 | 73.01 | 81.97 |
| **14**[b] | 71.44 | 69.74 | 79.78 | 72.26 | 75.04 | 81.81 |
| **15**[a] | 77.67 | 75.17 | 69.12 | 71.75 | 72.20 | 74.59 |
| **16**[c] | 83.47 | 79.33 | 71.81 | 79.53 | 79.98 | 77.00 |
| **17**[c] | 76.25 | 75.85 | 74.37 | 73.06 | 78.07 | 78.10 |
| **18**[a] | 73.77 | 59.50 | 73.77 | 66.71 | 69.21 | 66.71 |
| **19**[c,d] | 71.92 | 63.58 | 71.92 | 67.31 | 68.55 | 67.31 |

a) $D_2O$; b) DMSO-$d_6$; c) $CDCl_3$; d) $CD_3OD$



membranes.[2,3] *Myo*-inositol exists in a chair conformation with five hydroxyl groups in equatorial positions and one in axial position. As some of the signals in the $^{13}C$ NMR spectrum of *myo*-inositol recorded in 1969 have not been correctly assigned,[11a] we decided to reevaluate the $^{13}C$ NMR spectrum of *myo*-inositol as well as that of *epi*-inositol (**3**).

The *myo*-inositol structure **1** has two possible chair conformations, labelled A and B, Figure 2. The preferred conformer A, with five hydroxyl groups in equatorial positions and one in axial position, and the higher energy conformer B have a symmetry plane. The $^1H$ NMR spectrum of *myo*-inositol in DMSO-$d_6$ provides both the chemical shifts and coupling constants of the hydroxyl protons (Table 1, footnote) while the spectrum in $D_2O$ does not. The equatorial H-2 proton has the smallest

**TABLE 4.** Coupling constants values $^3J_{H,H}$ in Hz; torsional angles H-C-C-H calculated from (J values[14b]), {molecular mechanics[10]} or [X-ray diffraction data] for compounds **1-19**.

| Cpd. | H1/H2 | H2/H3 | H3/H4 | H4/H5 | H5/H6 | H1/H6 |
|---|---|---|---|---|---|---|
| **1** | 2.9 - (57) {55} | 2.9 - (57) {55} | 9.5 - (177) {173} | 9.0 - (174) {173} | 9.0 - (174) {173} | 9.5 - (177) {172} |
| **3** | 3.2 - (60) {54} | 2.9 - (59) {53} | 3.2 - (57) {54} | 2.6 - (57) {55} | 9.9 - (177) {173} | 9.9 - (177) {172} |
| **4** | 2.7 - (52) {58} | 2.7 - (43) {54} | 10.2 - (166) {172} | 9.9 - (180) {172} | 9.9 -(177) {175} | 10.2 - (169) {178} |
| **5** | 4.9 - (40) {41} | 4.3 - (53) {50} | 9.3 - (177) {172} | 9.2 - (170) {176} | 9.2 - (178) {173} | 7.7 -(172) {162} |
| **6** | 5.1 - (38) {39} [35] | 4.8 - (50) {50} [49] | 9.8 - (180) {175} [179] | 8.8 -(168) {176} [175] | 10.2 - (179) {175} [178] | 6.1 - (161) {160} [158] |
| **7** | 5.6 - (44) {40} [43] | 3.8 - (56) {49} [50] | 10.0 - (178) {174} [178] | 8.3 - (176) {179} [180] | 9.0 - (170) {176} [176] | 6.5 - (164) {162} [164] |
| **8** | 2.5 - (58) {58} [54] | 2.6 - (43) {57} [60] | 10.1 - (176) {174} [169] | 10.1 - (176) {174} [168] | 9.9 - (177) {176} [165] | 9.9 - (180) {178} [174] |
| **9** | 4.9 - (39) {42} | 4.1 - (54) {50} | 9.6 - (179) {171} | 9.6 - (172) {177} | 9.9 - (177) {176} | 7.3 - (169) {167} |
| **10** | 4.2 - (40) {42} | 4.2 - (54) {47} | 9.4 - (176) {172} | 7.6 - (162) {177} | 8.1 - (178) {177} | 6.0 - (160) {168} |
| **11** | 4.8 - (41) {38} | 4.3 - (53) {50} | 10.5 - (169) {175} | 9.8 - (179) {175} | 11.0 - (180) {175} | 6.4 - (164) {159} |
| **12** | 4.6 - (42) {40} | 4.4 - (52) {51} | 10.2 - (172) {176} | 9.6 - (176) {176} | 10.5 - (179) {177} | 6.6 - (164) {161} |
| **13** | 4.6 - (43) {40} | 4.0 - (55) {51} | 9.2 - (173) {174} | 9.6 - (178) {176} | 9.2 - (173) {172} | 6.9 - (167) {160} |
| **14** | 2.4 - (58) {59} | 2.4 - (66) {57} | 9.8 - (178) {174} | 9.2 - (174) {172} | 9.2 - (173) {175} | 9.6 - (177) {178} |
| **15** | 4.4 - (42) {41} | 4.2 - (54) {50} | 9.7 - (180) {172} | 10.1 - (172) {176} | 9.7 - (176) {173} | 8.0 - (179) {162} |
| **16** | 5.1 - (38) {39} | 4.6 - (51) {50} | 9.4 - (175) {175} | 9.8 - (179) {176} | 10.4 - (180) {175} | 6.2 - (163) {160} |
| **17** | 6.0 - (42) {42} | 4.3 - (53) {47} | 9.2 - (177) {169} | 8.9 - (170) {179} | 10.4 - (180) {177} | 8.4 - (167) {167} |
| **18**[a] | 3.3 - (60) {62} [68] | 3.3 - (59) {63} [67] | 3.7 - (62) {58} [59] | 3.5 - (63) {58} [58] | 3.5 - (63) {57} [61] | 3.7 - (62) {57} [59] |
| **19**[b] | 2.6 - (65) {63} [64] | 2.6 -(70) {64} [67] | 3.9 - (63) {58} [64] | 3.9 - (62) {58} [57] | 3.9 - (61) {57} [58] | 3.9 - (61) {58} [54] |

a. $^4J_{H3,H5} = {}^4J_{H4,H6} = 1.83$; b. $^4J_{H3,5} = {}^4J_{H4,H6} = 1.98$ Hz.

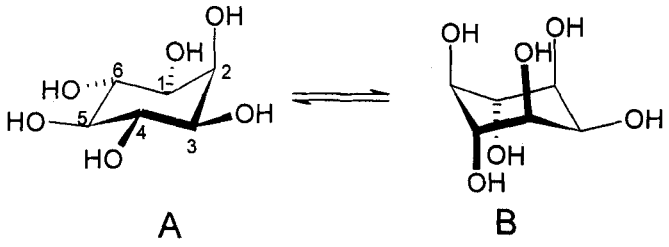


**Figure 2**

chemical shift (3.91) ppm), consistent with the observation that equatorial proton normally appear at higher frequency than the axial ones.[12]

Coupling constants of $^3J$ (≈10 Hz), shown an axial/axial relationship between H3-H4, H4-H5 and H5-H6 (Table 2). Their values were checked by simulation of the spectra using a computational program.[13] The molecular mechanics calculations,[10] showed that chair A is preferred over chair B by 30 KJ/mol, indicating a molar ratio of A:B > 99:1. A conformational analysis of inositols was previously performed using *ab initio* calculations.[14a] The results from the HETCOR $^{13}C/^1H$ experiment showed us that the reported chemical shift assignments for C-4 and C-6 were exchanged with those of C-1 and C-3.[11a] The X-ray diffraction structure has been reported[11b] and the preferred conformer in the solid state is similar to that found in solution (chair A).

***Scyllo*-Inositol 2.** The *scyllo* isomer **2** is a symmetric molecule with six equatorial hydroxy groups. The symmetry of the molecule is reflected in the $^1H$ and $^{13}C$ NMR spectra which presents only one signal at 4.58 and 73.13 ppm, respectively. The X-ray diffraction data show that, as expected, the molecule is in a chair conformation with all six hydroxy groups in equatorial positions. The nonbonding distances between O-H protons and the neighboring oxygen atoms from the X-ray study indicate that there is no hydrogen bonding between them (Figure 3).

***Epi*-Inositol, 3.** The cyclitol *epi*-inositol (**3**) has a symmetry plane through C-2 and C-6.[2,3] The $^1H$ NMR assignments are based on 1D and 2D $^1H$ NMR experiments.

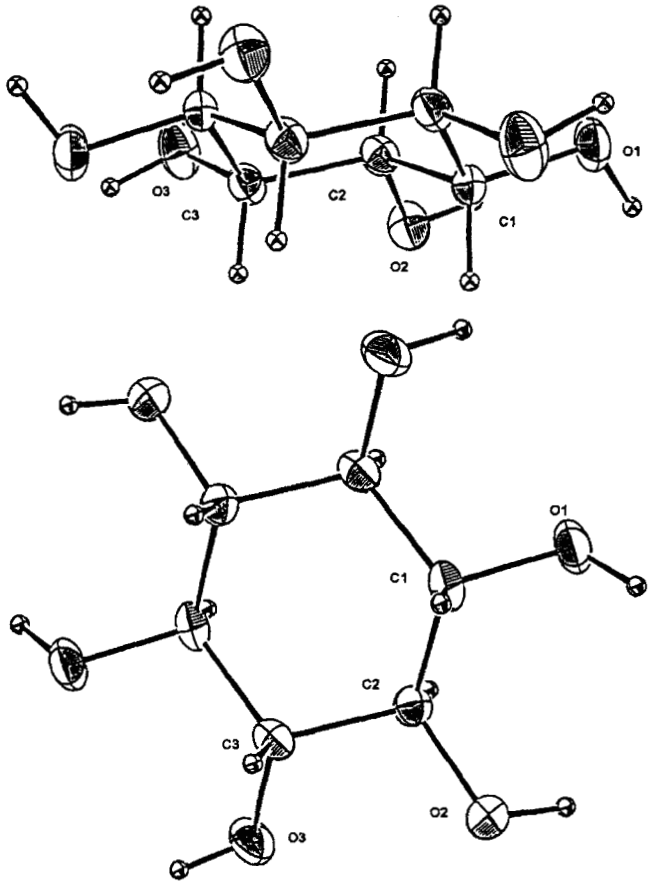


**Figure 3**. Two ORTEP projections of compound **2**



Using the $^{3}J_{H,H}$ values we established that preferred conformer has two axial hydroxyl groups. This is in agreement with results from a X-ray diffraction study.[2a] The H-2 and H-6 protons are equatorial and downfield ($\Delta\delta$= 0.58 ppm) to axial protons H-3 and H-5. In the $^{13}C$ NMR spectrum of **3** when data from compound **2** was used as a reference (73.13 ppm, all equatorial hydroxy groups) it was found that C-1 was shifted to a lower frequency (66.37 ppm) due to the influence of two vicinal axial hydroxy groups,[15a] as was the C-4 signal (69.59 ppm).

***Myo*-Inositol derivatives.** The other *myo*-inositol derivatives prepared **4-19** were compared with **1**, their structures were deduced from the data obtained from

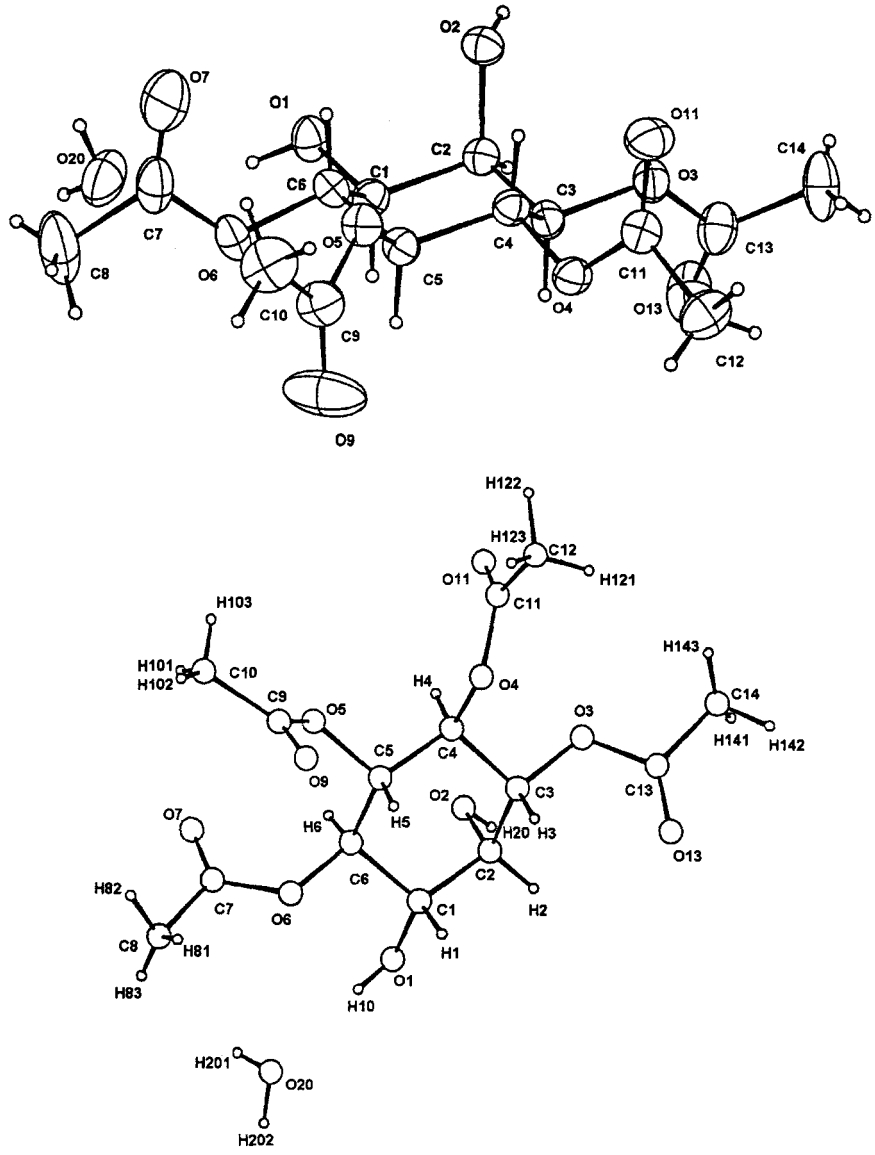


**Figure 4.** Two projections of compound **8.**

COSY $^{1}H/^{1}H$ and HETCOR $^{13}C/^{1}H$ experiments and H-H coupling constants values (Table 4).

**a) Monocyclic derivatives 4, 8 and 14.** We have prepared the acetyl esters **4** and **8** and the dibenzyl ether **14**. These molecules have the same preferred

**Table 5.** X-ray data from compound **2**.

| Bond distances | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.423(3) | O2-C2 | 1.430(3) | O3-C3 | 1.416(4) |
| C2-C3 | 1.506(4) | C2-C1 | 1.504(4) | C3-C1 | 1.505(4) |
| O1-H1 | 0.910(4) | O2-H2 | 0.880(4) | O3-H3 | 0.900(4) |
| C1-H1 | 0.980(3) | C2-H2 | 0.970(3) | C3-H3 | 0.950(3) |
| **Bond angles** | | | | | |
| O1-C1-C2 | 110.9(2) | O2-C2-C1 | 111.2(2) | O3-C3-C2 | 108.6(2) |
| C1-C2-C3 | 111.2(2) | C1-O1-H1 | 111.0(2) | C2-O2-H2 | 111.0(3) |
| C3-O3-H3 | 104.0(3) | O2-C2-H2 | 107.0(2) | C3-C2-H2 | 110.0(2) |
| C1-C2-H2 | 109.0(2) | | | | |
| **Selected Torsional Angles** | | | | | |
| O2-C2-C3-O3 | 60.5 | O2-C2-C1-O1 | 65.9 | C1-C2-C3-O3 | 177.3 |
| C3-C2-C1-O1 | -173.8 | H2-C2-C3-H3 | 176.0 | H2-C2-C1-H1 | 173.0 |



**Table 6.** Fractional atomic coordinates of compound **2.**

| Atom | x | y | z | B(A2) |
|---|---|---|---|---|
| O1 | 0.6025(4) | 0.2259(3) | 0.0432(2) | 2.12(4) |
| O2 | 0.8629(4) | 0.4461(3) | 0.2503(2) | 1.97(4) |
| O3 | 1.1205(4) | 0.7930(3) | 0.1800(2) | 2.24(4) |
| C1 | 0.8521(5) | 0.3222(5) | 0.0352(3) | 1.50(5) |
| C2 | 0.8695(5) | 0.5038(5) | 0.1204(3) | 1.44(5) |
| C3 | 1.1208(5) | 0.6194(4) | 0.1020(3) | 1.44(5) |
| H1 | 0.603(4) | 0.133(6) | 0.107(4) | 5(1) |
| H2 | 0.705(7) | 0.400(6) | 0.269(4) | 5(1) |
| H3 | 1.289(8) | 0.835(7) | 0.181(4) | 7(1) |
| H1A | 0.993(6) | 0.227(5) | 0.060(3) | 2.2(7) |
| H2A | 0.717(6) | 0.590(5) | 0.103(3) | 3.4(8) |
| H3A | 1.270(6) | 0.537(5) | 0.124(3) | 2.5(7) |

conformation as **1**. Compound **4** was obtained by acetylation of **1** in presence of acetic anhydride and pyridine. The molecule has a plane of symmetry, and it has the same coupling pattern as *myo*-inositol. All the methine protons are shifted to higher frequencies due to substitution effects.[15b] In the $^{13}C$ NMR spectrum of **4** all the ring carbon atoms appear at lower frequencies when compared with those of *myo*-inositol **1**. The X-ray diffraction structure of **4**[16a] agrees with the preferred conformer observed in solution.

**Table 7.** X-ray diffraction data from compound **8**.

Bond distances

| | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.416(4) | O2-C2 | 1.420(4) | O3-C3 | 1.442(4) |
| O3-C13 | 1.339(5) | O4-C4 | 1.438(4) | O4-C11 | 1.346(4) |
| O5-C5 | 1.441(4) | O5-C9 | 1.337(4) | O6-C6 | 1.439(4) |
| O6-C7 | 1.357(6) | O7-C11 | 1.183(4) | O13-C13 | 1.188(5) |
| C1-C2 | 1.523(5) | C1-C6 | 1.515(5) | C2-C3 | 1.525(5) |
| C3-C4 | 1.506(5) | C4-C5 | 1.513(5) | C5-C6 | 1.522(5) |
| C7-C8 | 1.477(8) | C9-C10 | 1.476(7) | C11-C12 | 1.488(6) |
| C13-C14 | 1.484(7) | O7-C7 | 1.178(6) | O9-C9 | 1.180(5) |
| C3-H3 | 0.99(4) | C1-H1 | 1.03(4) | C2-H2 | 0.97(4) |
| C6-H6 | 0.96(4) | C4-H4 | 0.96(4) | C5-H5 | 0.98(5) |

Bond angles

| | | | | | |
|---|---|---|---|---|---|
| O1-C1-C2 | 107.8(3) | O1-C1-C6 | 111.3(3) | O2-C2-C1 | 109.5(3) |
| O2-C2-C3 | 110.6(3) | O3-C3-C2 | 110.1(3) | O3-C3-C4 | 106.1(3) |
| O3-C13-C14 | 110.2(4) | O4-C4-C3 | 108.1(3) | O4-C4-C5 | 106.9(3) |
| O4-C11-C12 | 110.1(4) | O5-C5-C4 | 108.8(3) | O5-C5-C6 | 107.2(3) |
| O5-C9-C10 | 111.6(4) | O6-C6-C5 | 107.7(3) | O6-C7-C8 | 110.3(6) |
| O7-C7-C8 | 126.5(6) | O11-C11-C12 | 126.0(4) | O13-C13-C14 | 127.3(5) |
| O3-C13-O13 | 122.4(4) | O4-C11-O11 | 123.9(4) | O5-C9-O9 | 123.4(4) |
| O6-C7-O7 | 123.2(4) | C3-O3-C13 | 116.5(3) | C4-O4-C11 | 117.9(3) |
| C5-O5-C9 | 118.6(3) | C6-O6-C7 | 117.5(3) | C1-C2-C3 | 108.2(3) |
| C1-C6-C5 | 111.3(3) | C2-C1-C6 | 110.4(3) | C2-C3-C4 | 112.2(3) |
| C3-C4-C5 | 109.0(3) | C4-C5-C6 | 111.1(3) | O6-C6-C1 | 107.0(3) |
| O9-C9-C10 | 125.0(5) | | | | |

Selected Torsional Angles

| | | | | | |
|---|---|---|---|---|---|
| C1-C6-C5-C4 | -56.0 | C2-C1-C6-C5 | 56.8 | C3-C2-C1-C6 | -57.7 |
| C5-C4-C3-C2 | -58.3 | C6-C5-C4-C3 | 55.6 | H1-C1-C6-H6 | 174.0 |
| H2-C2-C1-H1 | -54.0 | H4-C4-C3-H3 | 169.0 | H5-C5-C4-H4 | 168.0 |
| H6-C6-C5-H5 | -165.0 | | | | |

**b) Polycyclic derivatives 5-7, 9-13, 15-19.** The bicyclic compounds **5, 7, 9, 10** and **13** were prepared by selectively forming the dioxolane ring in C-1 and C-2. In all these compounds an important deformation of the cyclohexane ring was observed from the coupling constants $^3J_{H1,H2}$ indicating dihedral angles values, (H1-C-C-H2) in the range of 40-44°.

The 1,2-O-isopropylidene-*myo*-inositol **5**[4,5] was obtained as a racemic mixture. The new asymmetric compound has six different methine hydrogen signals in its $^1H$

**TABLE 8.** Fractional atomic coordinates of compound **8**.

| Atom | x/a | y/b | z/c | U(iso) | Occ |
|---|---|---|---|---|---|
| O1 | 0.8677(2) | -0.1186(3) | 0.9109(2) | 0.0424 | 1.0000 |
| O2 | 1.0632(2) | 0.0412(3) | 0.9224(2) | 0.0424 | 1.0000 |
| O3 | 1.0311(2) | 0.3248(3) | 0.8540(2) | 0.0428 | 1.0000 |
| O4 | 0.9580(2) | 0.2548(3) | 0.6835(2) | 0.0401 | 1.0000 |
| O5 | 0.9236(2) | -0.0472(3) | 0.6463(2) | 0.0418 | 1.0000 |
| O6 | 0.7940(2) | -0.1860(3) | 0.7351(2) | 0.0454 | 1.0000 |
| O7 | 0.9218(4) | -0.3562(4) | 0.7308(3) | 0.0837 | 1.0000 |
| O9 | 0.7541(3) | -0.0059(5) | 0.5446(2) | 0.0835 | 1.0000 |
| O11 | 1.1490(2) | 0.2692(3) | 0.7096(2) | 0.0581 | 1.0000 |
| O13 | 0.9013(3) | 0.4500(4) | 0.8896(2) | 0.0668 | 1.0000 |
| O20 | 0.7257(3) | -0.3561(4) | 0.8814(3) | 0.0693 | 1.0000 |
| C1 | 0.8620(3) | -0.0160(4) | 0.8473(2) | 0.0360 | 1.0000 |
| C2 | 0.9503(3) | 0.1027(4) | 0.8876(2) | 0.0360 | 1.0000 |
| C3 | 0.9456(3) | 0.2130(4) | 0.8193(2) | 0.0350 | 1.0000 |
| C4 | 0.9744(3) | 0.1463(4) | 0.7477(2) | 0.0356 | 1.0000 |
| C5 | 0.8884(3) | 0.0262(4) | 0.7086(2) | 0.0356 | 1.0000 |
| C6 | 0.8878(3) | -0.0855(4) | 0.7746(2) | 0.0368 | 1.0000 |
| C7 | 0.8248(5) | -0.3195(5) | 0.7159(3) | 0.0554 | 1.0000 |
| C8 | 0.7194(8) | -0.4069(8) | 0.6742(4) | 0.0833 | 1.0000 |
| C9 | 0.8458(4) | -0.0634(5) | 0.5683(3) | 0.0538 | 1.0000 |
| C10 | 0.8884(6) | -0.1626(8) | 0.5172(3) | 0.0670 | 1.0000 |
| C11 | 1.0533(4) | 0.3111(4) | 0.6733(2) | 0.0423 | 1.0000 |
| C12 | 1.0198(5) | 0.4317(6) | 0.6110(3) | 0.0588 | 1.0000 |
| C13 | 0.9953(4) | 0.4421(5) | 0.8846(3) | 0.0491 | 1.0000 |
| C14 | 1.0894(6) | 0.5518(7) | 0.9117(4) | 0.0635 | 1.0000 |



NMR spectrum which allowed to establish the position of the isopropylidene group. The $^{13}C$ NMR spectrum of **5** shows a shift to higher frequencies for C-1 (7.47) and C-2 (4.10 ppm) compared to *myo*-inositol.

The $^{1}H$ NMR data from compounds **5** and **7** compared to *myo*-inositol shows a deshielding effect on the methine protons at the acetylated positions. The $^{13}C$ NMR spectrum of compound **7** shows all ring carbon atoms shifted with the exception of C-6. From the values of the coupling constants $^{3}J_{H,H}$, the dihedral angles were calculated. The value of the dihedral angle H1-C-C-H2 (47° in solution and 44° in the solid state) indicates that the molecule has the same structure in solution as in the crystal. The X-ray diffraction structure of compound **7** is shown in Figure 5.

**TABLE 9.** X-ray diffraction data from compound 7.

Bond distances

| | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.402(7) | O2-C2 | 1.398(7) | O3-C3 | 1.436(7) |
| O4-C4 | 1.451(7) | O5-C5 | 1.442(7) | O5-C9 | 1.354(8) |
| O6-C6 | 1.444(6) | O6-C7 | 1.348(7) | O7-C7 | 1.181(7) |
| O9-C9 | 1.177(9) | O11-C11 | 1.168(8) | O1-C15 | 1.427(7) |
| O2-C15 | 1.433(7) | O3-C13 | 1.322(7) | O4-C11 | 1.357(8) |
| C1-C2 | 1.513(8) | C1-C6 | 1.537(8) | C2-C3 | 1.503(9) |
| C3-C4 | 1.523(9) | C4-C5 | 1.526(8) | C5-C6 | 1.494(8) |
| C7-C8 | 1.483(8) | C11-C12 | 1.50(1) | C15-C17 | 1.489(9) |
| C9-C10 | 1.48(1) | C13-C14 | 1.47(1) | C15-C16 | 1.522(9) |
| O13-C13 | 1.170(8) | | | | |

Selected Torsional Angles

| | | | | | |
|---|---|---|---|---|---|
| H1-C1-C2-O2 | 172.0 | H1-C1-C6-O6 | -41.4 | H1-C1-C6-H6 | -164.4 |
| H1-C1-O1-C15 | -148.2 | H2-C2-C1-O1 | -85.5 | H2-C2-C3-O3 | 72.1 |
| H2-C2-C1-H1 | 43.4 | H2-C2-C3-H3 | -50.1 | H2-C2-O2-C15 | 78.6 |
| C3-C2-C1-H1 | -79.3 | H4-C4-C3-O3 | 56.7 | H4-C4-C3-H3 | 178.5 |
| H5-C5-C4-O4 | -55.9 | H5-C5-C4-H4 | -180.0 | H6-C6-O6-C7 | -12.8 |
| H6-C6-C5-O5 | 48.7 | H6-C6-C5-H5 | 176.0 | | |

Bond angles

| | | | | | |
|---|---|---|---|---|---|
| O1-C1-C2 | 103.8(5) | O1-C1-C6 | 111.7(5) | O2-C2-C1 | 100.3(5) |
| O2-C2-C3 | 111.3(5) | O3-C3-C2 | 110.1(5) | O3-C3-C4 | 108.7(5) |
| O4-C4-C5 | 106.4(5) | O4-C4-C3 | 109.6(5) | O5-C5-C6 | 107.9(5) |
| O5-C5-C4 | 109.1(5) | O5-C9-O9 | 123.0(7) | O6-C6-C1 | 106.0(4) |
| O6-C6-C5 | 109.5(5) | O6-C7-O7 | 123.5(6) | O6-C7-C8 | 110.8(5) |
| O7-C7-C8 | 125.7(6) | O1-C15-O2 | 106.7(5) | O1-C15-C16 | 108.2(5) |
| O3-C13-O13 | 122.0(6) | O4-C11-O11 | 123.9(9) | O2-C15-C17 | 108.0(5) |
| O1-C15-C17 | 110.3(5) | O2-C15-C16 | 111.4(7) | O5-C9-C10 | 111.4(7) |
| O3-C13-C14 | 112.1(7) | O4-C11-C12 | 110.7(7) | O13-C13-C14 | 125.9(7) |
| O9-C9-C10 | 125.6(8) | O11-C11-C12 | 125.3(8) | C3-O3-C13 | 117.8(5) |
| C1-O1-C15 | 106.4(4) | C2-O2-C15 | 105.0(4) | C6-O6-C7 | 118.8(5) |
| C4-O4-C11 | 118.0(5) | C5-O5-C9 | 119.3(5) | C2-C1-C6 | 112.7(5) |
| C1-C2-C3 | 115.1(5) | C1-C6-C5 | 115.1(5) | C2-C3-C4 | 113.4(5) |
| C3-C4-C5 | 107.8(5) | C16-C15-C17 | 111.8(6) | C4-C5-C6 | 109.6(5) |

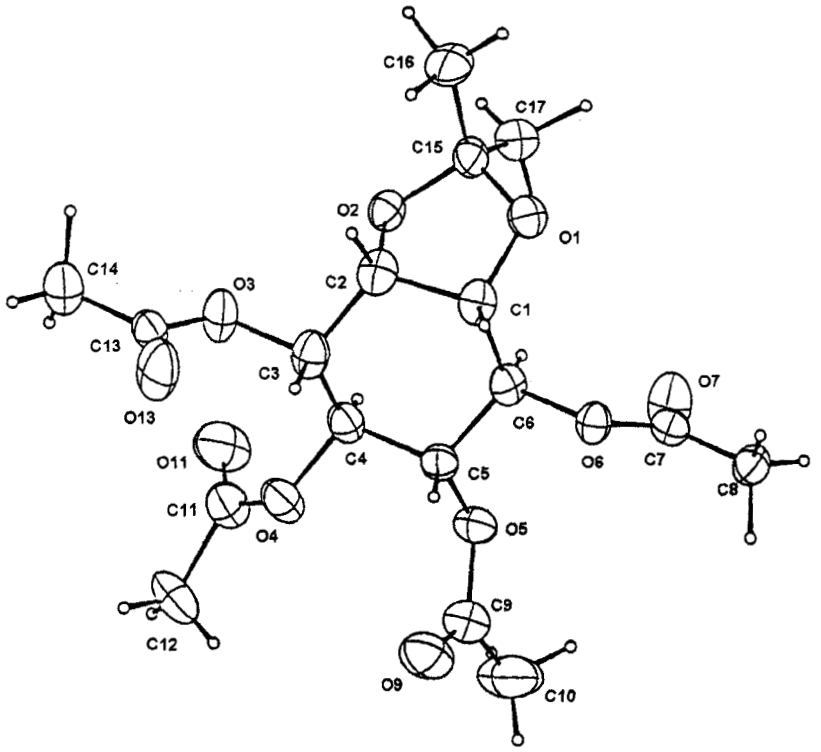


**Figure 5.** ORTEP projection of compound 7.



We have prepared and isolated two different O-tosyl derivatives **9** and **10**, from the regioselective reaction of compound **5** with an excess of tosyl chloride. The reaction of compound **6** with two equivalents of tosyl chloride gave, after selective hydrolysis of the 4,5-*O*-dioxolane group, compound **9**.

Comparison of the $^{1}H$ chemical shifts from **9**, **10** and **5** allowed us to assign the positions of the tosyl groups. The resonances of C-3 and C-6 in compound **9** are shifted to higher frequencies (7.99 and 12.09 ppm respectively) with respect of those of compound **5**. In compound **10**, C-3, C-4 and C-6 are shifted 4.15, 4.12 and 9.32 ppm to higher frequencies respectively. Thus, it was concluded that tosylation of compounds **9** occurs only at C-4.

Compound **13**, with two *O*-benzyl groups (C-3 and C-6), was obtained by selective hydrolysis of one isopropylidene group in compound **12**. Identification of the

**TABLE 10.** Fractional atomic coordinates of compound **7**.

| Atom | x/a | y/b | z/c | U(iso) | Occ |
|---|---|---|---|---|---|
| O1 | -0.0641(3) | 0.0464(2) | 0.5016(4) | 0.0515 | 1.0000 |
| O2 | 0.0060(3) | 0.1453(2) | 0.6355(4) | 0.0485 | 1.0000 |
| O3 | 0.2030(4) | 0.2356(2) | 0.6114(5) | 0.0605 | 1.0000 |
| O4 | 0.3699(4) | 0.1185(3) | 0.6614(5) | 0.0609 | 1.0000 |
| O5 | 0.2954(3) | -0.0372(2) | 0.6684(4) | 0.0548 | 1.0000 |
| O6 | 0.1172(3) | -0.0754(2) | 0.4858(4) | 0.0474 | 1.0000 |
| O7 | 0.0587(5) | -0.1410(3) | 0.6692(5) | 0.0692 | 1.0000 |
| O9 | 0.4579(4) | -0.0366(3) | 0.5536(6) | 0.0876 | 1.0000 |
| O11 | 0.3457(5) | 0.1653(4) | 0.8717(6) | 0.0871 | 1.0000 |
| O13 | 0.2909(5) | 0.2796(3) | 0.4316(6) | 0.0841 | 1.0000 |
| C1 | 0.0520(5) | 0.0564(3) | 0.4778(5) | 0.0473 | 1.0000 |
| C2 | 0.0740(5) | 0.1403(4) | 0.5192(6) | 0.0492 | 1.0000 |
| C3 | 0.1952(5) | 0.1592(4) | 0.5515(6) | 0.0521 | 1.0000 |
| C4 | 0.2506(5) | 0.1003(4) | 0.6472(6) | 0.0491 | 1.0000 |
| C5 | 0.2441(5) | 0.0200(3) | 0.5798(6) | 0.0473 | 1.0000 |
| C6 | 0.1231(5) | -0.0024(3) | 0.5597(5) | 0.0442 | 1.0000 |
| C7 | 0.0820(5) | -0.1401(4) | 0.5521(6) | 0.0493 | 1.0000 |
| C8 | 0.0796(5) | -0.2085(3) | 0.4590(7) | 0.0532 | 1.0000 |
| C9 | 0.4015(6) | -0.0628(4) | 0.6414(9) | 0.0708 | 1.0000 |
| C10 | 0.4366(7) | -0.1242(6) | 0.0738(1) | 0.0999 | 1.0000 |
| C11 | 0.4060(6) | 0.1481(4) | 0.7822(8) | 0.0674 | 1.0000 |
| C12 | 0.5326(6) | 0.1550(5) | 0.7842(9) | 0.0824 | 1.0000 |
| C13 | 0.2553(5) | 0.2908(4) | 0.5411(7) | 0.0531 | 1.0000 |
| C14 | 0.2598(6) | 0.3655(4) | 0.6160(8) | 0.0788 | 1.0000 |
| C15 | -0.0950(5) | 0.1032(3) | 0.6015(6) | 0.0488 | 1.0000 |
| C16 | -0.1843(6) | 0.1566(4) | 0.5396(8) | 0.0695 | 1.0000 |
| C17 | -0.1366(5) | 0.0639(4) | 0.7273(7) | 0.0593 | 1.0000 |



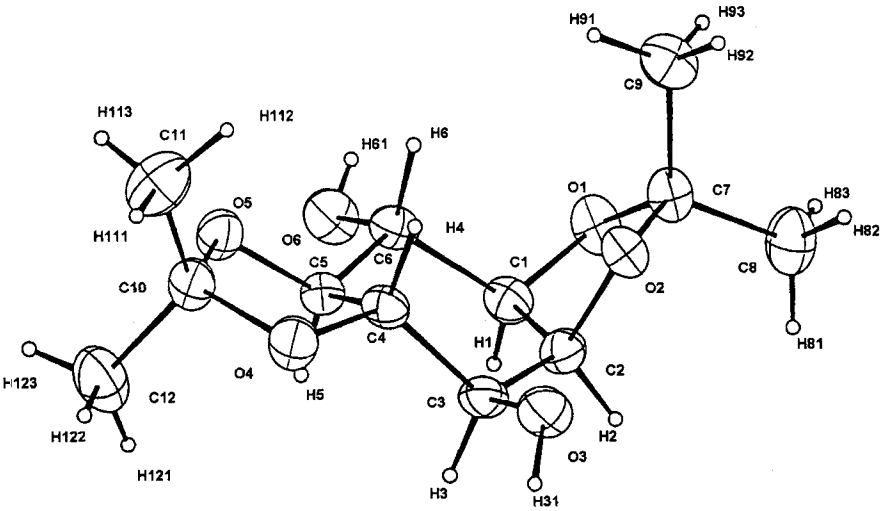


**Figure 6**. ORTEP projections of compound **6**.

**TABLE 11.** X-ray diffraction data from compound **6**.

Bond distances

| | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.430(3) | O1-C7 | 1.439(3) | O2-C2 | 1.424(3) |
| O2-C7 | 1.421(3) | O3-C3 | 1.419(3) | O4-C4 | 1.440(3) |
| O4-C10 | 1.449(3) | O5-C5 | 1.434(3) | O5-C10 | 1.440(3) |
| O6-C6 | 1.422(3) | C1-C2 | 1.531(4) | C2-C3 | 1.528(3) |
| C3-C4 | 1.495(3) | C4-C5 | 1.493(4) | C5-C6 | 1.499(3) |
| C6-C1 | 1.548(3) | C7-C8 | 1.514(4) | C7-C9 | 1.502(4) |
| C10-C11 | 1.490(4) | C10-C12 | 1.506(4) | | |

Bond angles

| | | | | | |
|---|---|---|---|---|---|
| O1-C1-C2 | 101.8(2) | O1-C1-C6 | 110.0(2) | O1-C7-C8 | 108.5(2) |
| O1-C7-C9 | 111.1(2) | O2-C2-C1 | 101.6(2) | O2-C2-C3 | 109.8(3) |
| O2-C7-C8 | 110.9(2) | O2-C7-C9 | 107.9(2) | O3-C3-C2 | 110.3(2) |
| O3-C3-C4 | 112.4(2) | O4-C4-C3 | 114.3(2) | O4-C4-C5 | 101.3(2) |
| O4-C10-C11 | 110.4(2) | O4-C10-C12 | 107.3(2) | O4-C10-O5 | 105.8(2) |
| O5-C5-C4 | 101.6(2) | O5-C5-C6 | 115.0(2) | O5-C10-C11 | 108.1(2) |
| O5-C10-C12 | 110.5(2) | O6-C6-C1 | 110.7(2) | O6-C6-C5 | 108.5(2) |
| O1-C7-O2 | 105.9(2) | C2-O2-C7 | 106.6(2) | C1-O1-C7 | 108.8(2) |
| C4-O4-C10 | 106.6(2) | C5-O5-C10 | 106.1(2) | C1-C2-C3 | 117.9(2) |
| C1-C6-C5 | 106.7(2) | C2-C1-C6 | 115.5(2) | C3-C4-C5 | 110.5(2) |
| C4-C5-C6 | 110.4(2) | C8-C7-C9 | 112.3(3) | C11-C10-C12 | 114.4(3) |
| C2-C3-C4 | 106.9(2) | | | | |

Selected Torsional Angles

| | | | | | |
|---|---|---|---|---|---|
| O1-C1-C2-O2 | -36.3 | O3-C3-C2-O2 | 49.4 | O3-C3-C4-O4 | 66.3 |
| O3-C3-C4-C5 | 179.8 | O3-C3-C2-C1 | 165.0 | O4-C4-C5-O5 | -42.6 |
| O6-C6-C1-O1 | -84.2 | O6-C6-C5-O5 | 65.7 | O6-C6-C5-C4 | 179.8 |
| O6-C6-C1-C2 | 161.2 | H1-C1-C6-H6 | 158.0 | H2-C2-C1-H1 | -35.0 |
| H2-C2-C3-H3 | 49.0 | H3-C3-C4-H4 | 179.0 | H5-C5-C6-H6 | -178.0 |
| H4-C4-C5-H5 | 175.0 | | | | |



*mono*-isopropylidene **13** was based on $^{13}C$ NMR spectrum data, where C3 and C6 are shifted to higher fields when compared to compound **5**.

1,2-*O*-cyclohexylidene-*myo*-inositol **15** was prepared from reaction of *myo*-inositol and cyclohexanone in the presence of acid.[32,33] The $^{13}C$ NMR spectrum of **15** compared with that of compound **5** indicates that both compounds have the same conformation.

The presence of two dioxolane groups produces similar effects in the NMR spectra of compounds **6, 11, 12, 16** and **17**. Compound **6**. was isolated from a mixture

**TABLE 12.** Fractional atomic coordinates of compound **6.**

| Atom | x/a | y/b | z/c | U(iso) | Occ |
|---|---|---|---|---|---|
| O1 | 0.12545(8) | 0.0549(3) | 0.08255(8) | 0.0349 | 1.0000 |
| O2 | 0.08114(8) | 0.4149(3) | 0.10030(7) | 0.0303 | 1.0000 |
| O3 | 0.00744(8) | 0.5360(4) | 0.17162(9) | 0.0371 | 1.0000 |
| O4 | 0.10128(8) | 0.4034(4) | 0.30098(8) | 0.0344 | 1.0000 |
| O5 | 0.18832(7) | 0.1571(3) | 0.31431(8) | 0.0333 | 1.0000 |
| O6 | 0.19862(9) | -0.1840(4) | 0.21544(9) | 0.0367 | 1.0000 |
| C1 | 0.1070(1) | 0.0199(5) | 0.1375(1) | 0.0310 | 1.0000 |
| C2 | 0.0562(1) | 0.2193(5) | 0.1273(1) | 0.0301 | 1.0000 |
| C3 | 0.0427(1) | 0.3129(5) | 0.1864(1) | 0.0298 | 1.0000 |
| C4 | 0.1053(1) | 0.3454(5) | 0.2390(1) | 0.0273 | 1.0000 |
| C5 | 0.1406(1) | 0.1063(5) | 0.2530(1) | 0.0285 | 1.0000 |
| C6 | 0.1653(1) | 0.0440(5) | 0.2001(1) | 0.0280 | 1.0000 |
| C7 | 0.1092(1) | 0.3027(5) | 0.0588(1) | 0.0313 | 1.0000 |
| C8 | 0.0626(2) | 0.2882(7) | -0.0095(1) | 0.0456 | 1.0000 |
| C9 | 0.1673(1) | 0.4484(6) | 0.0633(2) | 0.0427 | 1.0000 |
| C10 | 0.1584(1) | 0.3082(5) | 0.3490(1) | 0.0336 | 1.0000 |
| C11 | 0.2022(2) | 0.5146(7) | 0.3799(2) | 0.0502 | 1.0000 |
| C12 | 0.1386(2) | 0.1529(7) | 0.3951(2) | 0.0490 | 1.0000 |



of products from the reaction of **5** and 2,2-dimethoxypropane in acetone with acidic catalysis at 50 °C. Compound **6** is a racemic mixture. From the dihedral angles between the methine protons (X-ray and NMR data) it is evident that the five membered ring formed with the two equatorial oxygen atoms does not produce an important deformation (Table 4).

Reaction of compound **6** with tosyl chloride afforded, among other products, the *mono*-tosyl derivative **11**. The position of the tosyl group was deduced from comparison of its NMR data with those of compound **6.** The conformation of the cyclohexane in **11** is the same as in compound **6**.

Compound **12** was obtained from the benzylation reaction mixture of compound **6**. The structure was deduced from comparison of its NMR spectra with those of compound **6**.

Two pentacyclic isomers, **16** and **17,** were obtained from reaction of *myo*-inositol with cyclohexanone in the presence of *p*-toluensulfonic acid. Spectroscopic

data of compound **16** is similar to that of **6**. The 1,2- and 5,6-di-*O* substitution of **17** was determined by analysis of its NMR data.

The only compounds in which the conformation B of *myo*-inositol is retained are the 1,3,5-*O*-(orthoformate)-*myo*-inositol **18** and 2-O-benzoyl-1,3,5-*O*-(orthoformate)-*myo*-inositol **19,** Figure 2. Both molecules are rigid with only one oxygen atom (C-2) in equatorial position. The small coupling constants $^{3}J_{H,H}$, 2.6 to 3.6 Hz, and $^{4}J_{H3,H5}$= $^{4}J_{H4,H6}$= 1.83 for **18** $^{4}J_{H3,H5}$= $^{4}J_{H4,H6}$= 1.98 Hz for **19**, let us establish their structures. The effect of an *O*-benzoyl group at C-2, is shown in the $^{13}C$ NMR spectrum by a shift of 4.08 ppm, and in $^{1}H$ NMR spectrum by 1.42 ppm. The X-ray diffraction structure of compounds **18** and **19** show that the four rings each has a chair conformation (Figures 7 and 8).



## CONCLUSIONS

We have prepared several inositol derivatives, and performed a very careful NMR study in order to unequivocally assign their $^{1}H$ and $^{13}C$ chemical shift. We have determined the values of the $^{3}J_{H,H}$ and $^{4}J_{H,H}$ coupling constants and the preferred conformations of these compounds in solution and in the solid state. All the studied compounds **1-19** have the same chair conformation and ring distortion in solution and in solid state. The coupling constants $^{3}J_{H,H}$ allowed reasonable prediction of the dihedral angles and ring structures. The NMR and X-ray diffraction data agree with the molecular mechanics calculations regarding ring conformation. The X-ray diffraction studies of six molecules allowed us to provide additional information on the crystalline structures of these molecules.

## EXPERIMENTAL

Crystals were mounted on glass fibres and data were collected using an Enraf-Nonius CAD4 diffractometer equipped with MoKα radiation (λ= 0.7107 Å). H atoms were found in a Fourier map. Compound **2** was solved using MOLEN,[17a] **6-8**, **18** and **19** using CRYSTALS.[17b] Scattering factors were taken from reference.[17c] Data collection was performed under the conditions given in Table 17.[48]

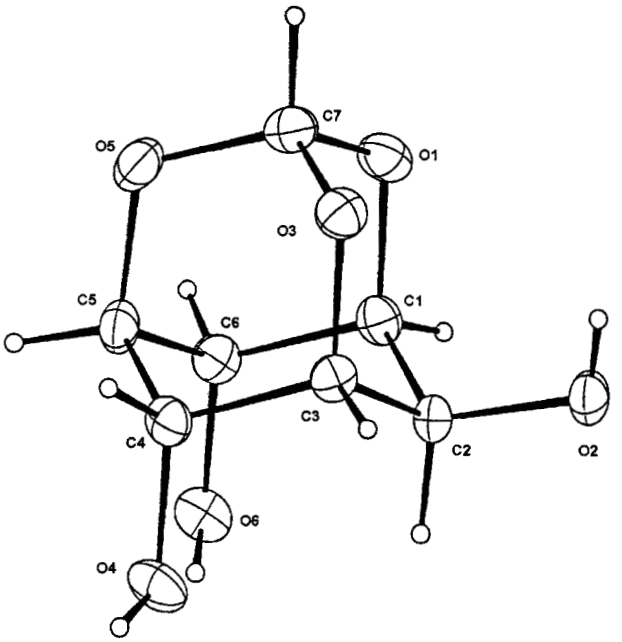


**Figure 7.** ORTEP projection of compound **18**.

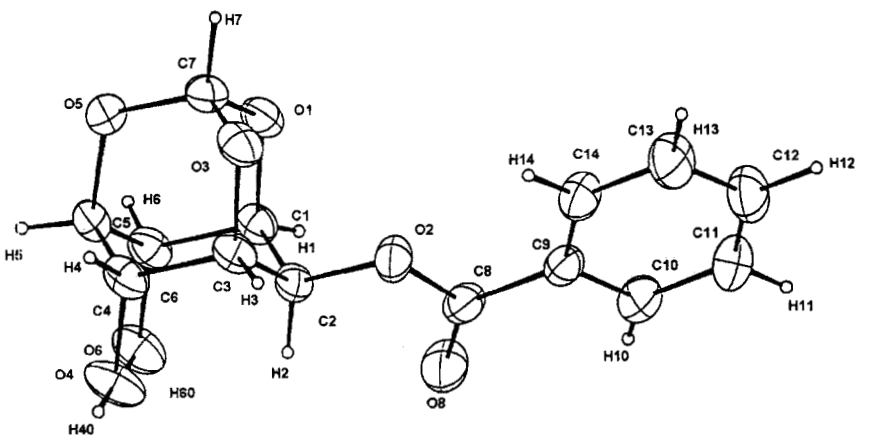


**Figure 8.** ORTEP projection of compound **19**.

**TABLE 13.** X-ray diffraction data from compound **18**.

Bond distances

| | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.438(2) | O1-C7 | 1.397(2) | O2-C2 | 1.426(2) |
| O3-C3 | 1.435(2) | O3-C7 | 1.404(2) | O4-C4 | 1.421(2) |
| O5-C5 | 1.438(2) | O5-C7 | 1.403(2) | O6-C6 | 1.419(2) |
| C1-C2 | 1.518(2) | C1-C6 | 1.518(2) | C2-C3 | 1.517(2) |
| C3-C4 | 1.523(2) | C4-C5 | 1.519(2) | C5-C6 | 1.519(2) |
| C1-H1 | 0.95(2) | C2-H2 | 1.00(2) | C3-H3 | 0.97(2) |
| C4-H4 | 0.96(2) | C5-H5 | 0.97(2) | C6-H6 | 0.94(2) |
| C7-H7 | 1.01(2) | | | | |

Bond angles

| | | | | | |
|---|---|---|---|---|---|
| O1-C1-C2 | 108.9(1) | O1-C1-C6 | 108.0(1) | O2-C2-C1 | 111.7(1) |
| O2-C2-C3 | 113.2(1) | O3-C3-C2 | 109.4(1) | O3-C3-C4 | 108.4(1) |
| O4-C4-C3 | 110.1(1) | O4-C4-C5 | 109.9(1) | O5-C5-C4 | 107.0(1) |
| O5-C5-C6 | 106.9(1) | O6-C6-C1 | 111.8(1) | O6-C6-C5 | 113.9(2) |
| O1-C7-O3 | 111.0(1) | O1-C7-O5 | 111.3(1) | O3-C7-O5 | 110.8(2) |
| C5-O5-C7 | 111.7(1) | C1-O1-C7 | 110.6(1) | C3-O3-C7 | 110.4(1) |
| C2-C3-C4 | 110.2(1) | C1-C2-C3 | 107.2(1) | C1-C6-C5 | 107.1(1) |
| C4-C5-C6 | 112.9(1) | C2-C1-C6 | 111.2(1) | C3-C4-C5 | 107.2(1) |

Selected Torsional Angles

| | | | | | |
|---|---|---|---|---|---|
| O4-C4-C5-O5 | -178.1 | O6-C6-C5-O5 | -176.6 | C7-O1-C1-C2 | -60.2 |
| C7-O3-C3-C2 | 59.7 | C7-O5-C5-C4 | 60.8 | C7-O5-C5-C6 | -60.4 |
| C7-O3-C3-C4 | -60.5 | C7-O1-C1-C6 | 60.7 | H7-C7-O1-C1 | -179.2 |
| H7-C7-O3-C3 | 177.8 | H7-C7-O5-C5 | -178.5 | H5-C5-C4-H4 | -58.4 |
| H6-C6-C5-H5 | 60.8 | H4-C4-C3-H3 | 59.1 | H6-C6-C1-H1 | -59.5 |



**TABLE 14.** Fractional atomic coordinates of compound **18**.

| Atom | x/a | y/b | z/c | U(iso) | Occ |
|---|---|---|---|---|---|
| O1 | 0.7968(1) | -0.2972(2) | 0.3425(1) | 0.0337 | 1.0000 |
| O2 | 0.6075(1) | -0.3348(2) | 0.0779(1) | 0.0314 | 1.0000 |
| O3 | 0.6188(1) | -0.0747(2) | 0.2908(1) | 0.0311 | 1.0000 |
| O4 | 0.7433(1) | 0.2797(2) | 0.1211(1) | 0.0336 | 1.0000 |
| O5 | 0.8272(1) | 0.0371(2) | 0.4267(1) | 0.0345 | 1.0000 |
| O6 | 0.9593(1) | 0.0190(2) | 0.1887(1) | 0.0321 | 1.0000 |
| C1 | 0.8223(2) | -0.2280(3) | 0.2379(2) | 0.0271 | 1.0000 |
| C2 | 0.6932(2) | -0.1609(3) | 0.1311(2) | 0.0249 | 1.0000 |
| C3 | 0.6336(2) | 0.0066(3) | 0.1832(2) | 0.0258 | 1.0000 |
| C4 | 0.7237(2) | 0.1973(3) | 0.2247(2) | 0.0274 | 1.0000 |
| C5 | 0.8545(2) | 0.1248(3) | 0.3271(2) | 0.0288 | 1.0000 |
| C6 | 0.9191(2) | -0.0468(3) | 0.2828(2) | 0.0274 | 1.0000 |
| C7 | 0.7417(2) | -0.1353(3) | 0.3849(2) | 0.0342 | 1.0000 |

**TABLE 15.** X-ray diffraction data from compound **19**.

Bond distances

| | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.444(3) | O1-C7 | 1.398(3) | O2-C2 | 1.440(3) |
| O2-C8 | 1.337(3) | O3-C3 | 1.450(3) | O3-C7 | 1.388(4) |
| O4-C4 | 1.421(4) | O5-C5 | 1.443(3) | O5-C7 | 1.398(4) |
| O6-C6 | 1.412(3) | O8-C8 | 1.207(3) | C1-C2 | 1.507(4) |
| C1-C6 | 1.529(4) | C2-C3 | 1.504(4) | C3-C4 | 1.527(4) |
| C4-C5 | 1.506(4) | C5-C6 | 1.509(4) | C8-C9 | 1.479(4) |
| C9-C10 | 1.378(4) | C9-C14 | 1.382(4) | C10-C11 | 1.374(5) |
| C11-C12 | 1.373(5) | C13-C14 | 1.382(5) | C1-H1 | 0.96(3) |
| C2-H2 | 0.92(3) | C3-H3 | 1.00(3) | C4-H4 | 0.95(3) |
| C5-H5 | 0.97(3) | C6-H6 | 1.02(3) | C7-H7 | 1.01(3) |
| C12-C13 | 1.366(5) | | | | |

Bond angles

| | | | | | |
|---|---|---|---|---|---|
| O1-C1-C2 | 108.4(2) | O1-C1-C6 | 107.0(2) | O2-C2-C1 | 110.3(2) |
| O2-C2-C3 | 107.3(2) | O2-C8-C9 | 112.1(2) | O3-C3-C2 | 109.3(2) |
| O3-C3-C4 | 106.5(2) | O4-C4-C3 | 110.5(3) | O5-C5-C6 | 107.2(2) |
| O4-C4-C5 | 108.2(2) | O5-C5-C4 | 107.5(4) | O8-C8-C9 | 125.0(3) |
| O6-C6-C1 | 111.2(1) | O6-C6-C5 | 114.5(2) | O2-C8-O8 | 122.8(3) |
| O1-C7-O3 | 111.7(3) | O1-C7-O5 | 110.5(3) | C2-O2-C8 | 117.0(2) |
| O3-C7-O5 | 111.8(3) | C1-O1-C7 | 111.1(2) | C1-C2-C3 | 108.6(2) |
| C3-O3-C7 | 110.6(2) | C5-O5-C7 | 110.8(2) | C2-C3-C4 | 110.1(2) |
| C1-C6-C5 | 107.1(2) | C2-C1-C6 | 110.9(2) | C8-C9-C10 | 118.8(3) |
| C5-C4-C3 | 108.1(2) | C4-C5-C6 | 112.8(3) | C9-C14-C13 | 119.5(3) |
| C8-C9-C14 | 121.7(3) | C9-C10-C11 | 120.4(3) | C11-C12-C13 | 120.0(3) |
| C10-C9-C14 | 119.5(3) | C10-C11-C12 | 120.0(3) | C12-C13-C14 | 120.6(3) |

Selected Torsional Angles

| | | | | | |
|---|---|---|---|---|---|
| C1-O1-C7-O3 | -62.0 | C1-O1-C7-O5 | 62.6 | C1-O1-C7-H7 | -177.8 |
| C3-O3-C7-O1 | 62.8 | C3-O3-C7-O5 | -62.8 | C3-O3-C7-O1 | 62.8 |
| C3-O3-C7-O5 | -62.8 | C3-O3-C7-H7 | -177.9 | C7-O1-C1-H1 | -178.6 |
| C7-O1-C1-C2 | 59.0 | C7-O1-C1-C6 | -60.4 | C1-C6-C5-C4 | 59.1 |
| C2-C1-C6-C5 | -59.3 | C3-C2-C1-C6 | 61.0 | C5-C4-C3-C2 | 59.1 |
| C6-C5-C4-C3 | -58.4 | H1-C1-C6-H6 | 54.2 | H2-C2-C1-H1 | 64.0 |
| H2-C2-C3-H3 | -67.0 | H4-C4-C3-H3 | -64.1 | H5-C5-C4-H4 | 57.0 |
| H6-C6-C5-H5 | -58.4 | | | | |

**TABLE 16.** Fractional atomic coordinates of compound **19.**

| Atom | x/a | y/b | z/c | U(iso) | Occ |
|---|---|---|---|---|---|
| O1 | 0.4896(3) | 0.2978(1) | -0.0955(2) | 0.0342 | 1.0000 |
| O2 | 0.4546(3) | 0.1431(1) | -0.0391(2) | 0.0348 | 1.0000 |
| O3 | 0.1430(3) | 0.2583(1) | -0.0583(2) | 0.0359 | 1.0000 |
| O4 | 0.2598(4) | 0.2624(1) | 0.2488(2) | 0.0433 | 1.0000 |
| O5 | 0.2562(4) | 0.3778(1) | -0.0061(2) | 0.0413 | 1.0000 |
| O6 | 0.6642(3) | 0.3111(1) | 0.2038(2) | 0.0394 | 1.0000 |
| O8 | 0.7731(4) | 0.1055(1) | 0.0362(2) | 0.0458 | 1.0000 |
| C1 | 0.5779(4) | 0.2687(2) | 0.0110(2) | 0.0294 | 1.0000 |
| C2 | 0.4439(5) | 0.2018(2) | 0.0454(2) | 0.0288 | 1.0000 |
| C3 | 0.2110(5) | 0.2260(2) | 0.0506(2) | 0.0323 | 1.0000 |
| C4 | 0.1874(5) | 0.2882(2) | 0.1394(2) | 0.0329 | 1.0000 |
| C5 | 0.3283(5) | 0.3535(2) | 0.1062(2) | 0.0344 | 1.0000 |
| C6 | 0.5642(5) | 0.3322(2) | 0.0988(2) | 0.0316 | 1.0000 |
| C7 | 0.2733(5) | 0.3193(2) | -0.0851(3) | 0.0369 | 1.0000 |
| C8 | 0.6314(5) | 0.0995(2) | -0.0363(3) | 0.0339 | 1.0000 |
| C9 | 0.6324(5) | 0.0454(2) | -0.1323(3) | 0.0335 | 1.0000 |
| C10 | 0.8121(6) | 0.0005(2) | -0.1456(3) | 0.0446 | 1.0000 |
| C11 | 0.8221(7) | -0.0485(2) | -0.2360(3) | 0.0503 | 1.0000 |
| C12 | 0.6515(6) | -0.0535(2) | -0.3133(3) | 0.0501 | 1.0000 |
| C13 | 0.4727(6) | -0.0092(2) | -0.3009(3) | 0.0477 | 1.0000 |
| C14 | 0.4605(5) | 0.0402(5) | -0.2101(3) | 0.0406 | 1.0000 |



$^1$H, and $^{13}$C NMR spectra were recorded at 270 and 67.8 MHz respectively, with TMS as an internal reference and $CDCl_3$, $D_2O$ or DMSO-$d_6$ as solvent. Infrared spectra were recorded using a Nicolet MX-1 FT spectrometer. Melting points were obtained a Gallen Kamp instrument and are uncorrected. *Myo-* **1**, *scyllo-* **2**, *epi*-inositol **3** and 1,3,5-*O*-(ortoformate)-*myo*-inositol **18** were from commercial sources.

**1,2,3,4,5,6-*O*-Hexaacetyl-*myo*-inositol, 4.**[16] A solution of **1** (1 g, 5.5 mmol) and acetic anhydride (3.11 mL, 33 mmol) in dry pyridine (3 mL) was stirred 24 h at room temperature. The resulting mixture was treated with 50 mL of HCl (10%), extracted 3 times with $CHCl_3$ and the organic phase was dried with sodium sulfate. Compound **4** was obtained as a white solid (1.20 g, 53 %), mp. 154 °C (mp was not reported in lit.).[16] IR $\nu_{max}$ (KBr): 1752(C=O), 1366(C-H) cm$^{-1}$.

**1,2-*O*-Isopropylidene-*myo*-inositol, 5.**[18-23] A mixture of **1** (15 g, 83.25 mmol), 2,2-dimethoxypropane (25.5 mL, 207.37 mmol) and a catalytic amount of *p*-

**TABLE 17.** Crystal data from compounds **2, 6-8, 18** and **19**[a].

| | **2** | **6** | **7** | **8** | **18** | **19** |
|---|---|---|---|---|---|---|
| Crystal Data | $C_6H_{12}O_6$ | $C_{12}H_{20}O_6$ | $C_{17}H_{24}O_{10}$ | $C_{14}H_{20}O_{10}$ - $H_2O$ | $C_7H_{10}O_6$ | $C_{14}H_{14}O_7$ |
| fw | 180.16 | 260.29 | 388.37 | 366.32 | 190.15 | 294.26 |
| Crystal Dimensions | 0.5 x 0.3 x 0.4 | 0.5 x 0.3 x 0.4 | 0.4 x 0.3 x 0.4 | 0.5 x 0.3 x 0.4 | 0.4 x 0.3 x 0.4 | 0.5 x 0.4 x 0.4 |
| System | Monoclinic P | Monoclinic C | Monoclinic C | Monoclinic P | Monoclinic P | Monoclinic P |
| Space group | $P2_1/n$ | C 2/c | C c | P $2_1/a$ | P $2_1/a$ | P $2_1/n$ |
| a (Å) | 5.076(1) | 22.5495(1) | 9.805(3) | 12.2773(2) | 11.198(1) | 6.1752(3) |
| b (Å) | 6.619(2) | 5.4073(2) | 17.089(6) | 9.2399(1) | 6.377(1) | 17.7266(1) |
| c (Å) | 10.600(3) | 22.1357(1)) | 11.620(5) | 16.8970(3) | 11.699(2) | 11.7237(3) |
| β (°) | 91.85(3) | 110.40(3) | 91.271(3) | 110.595(2) | 115.05(1) | 91.636(4) |
| V, ($Å^3$) | 359.9(5) | 2529.7(2) | 1980(1) | 1794.298(5) | 756.89(1) | 1282.81(1) |
| Z | 2 | 8 | 4 | 4 | 4 | 4 |
| linear abs coeff, $cm^{-1}$ | 1.40 | 1.024 | 1.01 | 1.11 | 1.40 | 1.16 |
| F (000) | 96 | 1120 | 825 | 776 | 400 | 616 |
| ρ(calc), g $cm^{-3}$ | 1.68 | 1.367 | 1.30 | 1.356 | 1.67 | 1.523 |
| θ limits (°) | 1 - 25 | 1 - 25 | 1 - 25 | 1 - 25 | 1.0 - 25 | 1 - 25 |
| scan type | ω/2θ | ω/2θ | ω/2θ | ω/2θ | ω/2θ | ω/2θ |
| scan range (°) | 0.8+0.350 tgθ | 0.8+0.345 tgθ | 0.8+0.345 tgθ | 0.8+0.350 tgθ | 0.8+0.345 tgθ | 0.8+0.350 tgθ |
| octants collected | -8,9;0,9;0,13 | -26,25;0,6;0,26 | 0,14;0,20;-11,11 | -14,13;0,10;0,20 | -13,12;0,7;0,13 | -7,7;0,20;0,13 |
| No. of data collected | 716 | 5106 | 1894 | 3508 | 1530 | 2460 |
| No. of unique data collected | 590 | 2222 | 1745 | 3135 | 1332 | 2253 |
| No. of unique data used with $(Fo)^2 > 3\sigma (Fo)^2$ | 528 | 1392 | 1216 | 1585 | 1032 | 1301 |
| R(int) | 0.046 | 0.01 | 4.14 | 1.26 | 0.093 | 4.1 |
| decay (%) | <1 | <1 | <1 | <1 | <1 | <1 |
| $R = \Sigma(\|\|Fo\|-\|Fo\|\|)/\Sigma\|Fo\|$ | 0.046 | 0.034 | 0.042 | 0.040 | 0.026 | 0.035 |
| Rw | 0.047 w= 1.0 | 0.033 w= 1.0 | 0.039 w= 1.0 | 0.039 w= 1.0 | 0.025 w= 1.0 | 0.033 w= 1.0 |
| No. of variables | 79 | 224 | 244 | 294 | 150 | 234 |
| $\Delta\rho_{min}$ (e/ $Å^3$) | -0.51 | -0.14 | -0.14 | -0.17 | -0.13 | -0.27 |
| $\Delta\rho_{max}$ (e/ $Å^3$) | 0.66 | 0.17 | 0.14 | 0.23 | 0.16 | 0.61 |

a. Structures were obtained using a CAD4-Enraf-nonius instrument at room temperature and radiation MoKα (λ = 0.71069 Å).

toluensulfonic acid in DMSO (48 mL) was heated to 80 °C for 4 h. The solution was then diluted with a mixture of triethylamine (1.5 mL), ethanol (60 mL) and diethyl ether (300 mL) and stirred at room temperature for 8 h. The solids were filtered and dried under vacuum. Compound **5** was obtained as a white solid (7.30 g, 40 %), mp. 183-185 °C (lit. 182-184 °C).[22]

**1,2:4,5-Di-*O*-isopropylidene-*myo*-inositol, 6.**[22,24-25] A mixture of compound **5** (5 g, 22.72 mmol), 2,2-dimethoxypropane (25 mL, 203.26 mmol) and *p*-toluensulfonic acid (0.5 g) in dry acetone (100 mL) was refluxed at 60 °C for 16 h. Then, the resulting mixture was filtered and triethylamine (2.5 mL) was added. A white solid was obtained after evaporation of the solvents under vacuum. The reaction mixture was purified on a chromatographic column of basic alumina (methanol/diethyl ether 19:1). Compound **6** was obtained as a white solid (4.50 g, 20 %), mp. 174 °C (lit. 171-173 °C).[22]



**1,2-*O*-Isopropylidene-3,4,5,6-tetra-*O*-acetyl-*myo*-inositol, 7.** A solution of one equivalent of **5** (5 g, 22.7 mmol) and six equivalents of acetic anhydride (1.74 mL, 136 mmol) in dry pyridine (11 mL) was stirred at room temperature for 48 h. The mixture was treated with 100 mL of HCl (30 %), extracted 3 times with $CHCl_3$ and the organic phase dried with sodium sulfate. A white solid (7) was obtained (5.28 g, 99%), m.p. 114-116 °C. IR $\nu_{max}$ (KBr): 2890(C-H), 1750(C=O), 1367($CH_3$) $cm^{-1}$.

Anal. Calcd for $C_{17}H_{14}O_7$: C, 52.58; H. 6.22. Found: C, 52.50; H, 6.21.

**3,4,5,6-Tetra-*O*-acetyl-*myo*-inositol, 8.**[26-28] Compound **1** (2 g, 5.15 mmol) was refluxed with glacial acetic acid-water (4:1) for 1 h. The reaction mixture was concentrated to dryness and the residue was recrystallized from ethanol. Colorless needles of **8** were obtained (1.43 g, 80 %), mp 126-128°C (lit. 139 °C).[27]

**1,2-*O*-Isopropylidene-3,6-di-*O*-tosyl-*myo*-inositol, 9 and 1,2-*O*-Isopropylidene-3,4,6-tri-*O*-tosyl-*myo*-inositol, 10.** A solution of **5** (0.3 g, 1.36 mmol) and tosyl chloride (1.07 g, 5.45 mmol) in dry pyridine (6 mL) was stirred at 5 °C for 4 h and then stirred at room temperature for 6 days. A solution of HCl (2 %, 2 mL) was added and the mixture extracted with $CHCl_3$. The organic phase was dried with $Na_2SO_4$ and the solvent removed under vacuum. The resulting solid was separated using a silica

chromatography column (butanone/toluene 40:14). Two crystalline products were obtained, compounds **9** (0.053 g, 15 %) and **10** (0.34 g, 50 %).

Compound **9**: Mp 178-180 °C. IR $\nu_{max}$ (KBr): 3502(OH), 1566($SO_2$), 1372($CH_3$) $cm^{-1}$.

Anal. Calcd for $C_{23}H_{28}O_{10}S_2$: C, 52.26; H. 5.33. Found: C, 51.95; H, 5.28.

Compound **10**: Mp 158 °C. IR $\nu_{max}$ (KBr): 3505(OH), 1560($SO_2$), 1369($CH_3$) $cm^{-1}$.

Anal. Calcd for $C_{30}H_{33}O_{11}S_3$: C, 54.13; H. 4.99. Found: C, 53.50; H, 5.21.

**1,2:4,5-Di-*O*-isopropylidene-3-*O*-tosyl-*myo*-inositol, 11.** To a solution of **6** (0.3 g, 1.15 mmol) in dry pyridine (7 mL), tosyl chloride (0.45 g, 2.30 mmol) was added. The mixture was stirred for 6 days at room temperature. Compound **11** was separated by precipitation at 0 °C and obtained as a white solid (0.143 g, 30 %), mp 170-173 °C. IR $\nu_{max}$ (KBr): 1752(C=O), 1366(C-H) $cm^{-1}$.

Anal. Calcd for $C_{19}H_{26}O_8S$: C, 55.03; H. 6.31. Found: C, 54.90; H, 6.10.

**3,6-Di-*O*-benzyl-1,2:4,5-di-*O*-isopropylidene-*myo*-inositol, 12.**[22,24-25] A mixture of compound **6** (2 g, 7.7 mmol), with an excess of benzyl bromide (3.5 mL, 32 mmol) and sodium hydride in N,N-dimethylformamide was stirred for 48 h at 20 °C. The reaction mixture was separated using an alumina chromatography column (diethyl ether-hexane 1:1). Compound **12** was obtained as a white solid (1.80 g, 53 %), mp 153-155 °C. IR $\nu_{max}$ (KBr): 1615(Ar), 1366(C-H) $cm^{-1}$.

Anal. Calcd for $C_{26}H_{32}O_6$: C, 70.89; H. 4.99. Found: C, 70.60; H, 4.70.

**3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-*myo*-inositol, 13.**[24-25, 29-31] A solution of **12** (3 g, 7.5 mmol) and *p*-toluensulphonic acid monohydrate (0.22 g) in acetone (45 mL) water (1.2 mL) was kept at 20 °C for 45 min. The reaction mixture was purified using an alumina chromatography column ($CHCl_3$-ethyl acetate 1:1). Compound **13** was isolated as a white solid (1.08 g, 40 %), mp 160-2°C (lit. 161-3 °C).[29]

**3,6-Di-*O*-benzyl-*myo*-inositol, 14.**[22] A solution of **12** (2 g, 4.54 mmol) in glacial acetic acid-water (4:1) was heated at 100 °C (1 h), cooled, and diluted with water. The product was filtered and recrystallized from ethanol. A white solid was obtained (1.4 g, 70 %), mp 204-206 °C (lit. 205-207 °C).[22]

**1,2-*O*-cyclohexylidene-*myo*-inositol, 15.**[32,33] A reaction of **1** (10 g, 55.31 mmol), cyclohexanone (87.23 mL, 0.85 mol), TsOH (10 % in DMF, 2.55 mL) in DMF (97.8 mL) and toluene (21.3 mL) was heated to reflux under stirring using a Dean-

Stark separator filled with toluene. Four additional portions (2.55 mL) of TsOH (10 % soln) were added at 2 h intervals. After 9 h, water separation (5 mL) has finished. The clear, pale yellow mixture obtained was concentrated and the viscous residue diluted with 11 mL of absolute EtOH. Crystals of **15** were removed by filtration (13 g, 93 %), mp 174-176 °C (lit. mp 174-177 °C).[32]

**1,2:4,5-Di-*O*-cyclohexylidene-*myo*-inositol, 16**[28,34-39] **and 1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol, 17.**[28,34,37,38,40-43] A mixture of *myo*-inositol **1** (20 g, 0.11 mol), cyclohexanone (30 mL, 0.3 mol) and TsOH (0.2 g, 1.1 mmol) in benzene (50 mL) was heated to reflux using a Dean-Stark trap and vigorous stirring for 3.5 h. The hot mixture was filtered, to remove the unreacted inositol and the filtrate was washed with saturated aqueous solution of $NH_4OH$ (4 x 40 mL). After addition of sodium carbonate (0.3 g), the mixture was steam distilled to remove benzene and cyclohexane. The organic layer was diluted with 180 mL of benzene and again distilled in order to remove the moisture. The resulting mixture was separated using an alumina chromatography column packed in hexane. Compound **16** was eluted with $CHCl_3$ and recrystallized in benzene (2.6 g, 30 % yield), mp 168-170 °C (lit. 173-4 °C).[35] Compound **17** was eluted with ethanol and recrystallized from $C_6H_6$:hexane [6:9]. A white solid was obtained (16.52 g, 40 %), mp 136-138 °C (lit. 132-133 °C).[35]

**2-Benzoyl-1,3,5-*O*-(orthoformate)-*myo*-inositol, 19.**[23] To a solution of 1,3,5-*O*-(orthoformate)-*myo*-inositol **18**[44-47] (0.5 g, 2.62 mol) in pyridine (15 mL), benzoyl chloride (0.4 mL, 3.4 mmol) and a catalytic amount of 4-dimethylaminopyridine were added at 0 °C. The mixture was stirred at room temperature overnight. Ethyl acetate was added to the reaction mixture which was then washed with saturated $KHSO_4$, $NaHCO_3$ solution and brine. The solvent was removed and the resulting mixture was purified using a silica gel chromatography column (AcOEt/hexane 1:2). Compound **19** was isolated as a white solid (0.51 g. 70 %), mp 202-204 °C. IR $\nu_{max}$ (KBr): 1761(C=O) $cm^{-1}$.

Anal. Calcd for $C_{14}H_{14}O_7$: C, 57.15; H. 4.79. Found: C, 57.20; H, 4.75.

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