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The preparation, resolution, and phosphorylation of some benzyl ethers of *myo*-inositol: intermediates for the synthesis of *myo*-inositol phosphates of the phosphatidylinositol cycle*

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ABSTRACT

The syntheses of the following chiral compounds are described: 1D-2,3,6-tri-, 1D-2,4,5-tri-, 1D-2,5,6-tri-, 1D-1,2,3,4-tetra-, 1D-1,2,3,6-tetra-, 1D-1,2,4,5-tetra-, and 1D-2,3,5,6-tetra-*O*-benzyl-*myo*-inositol; and 1D-2,5,6-tri-*O*-benzyl-1-*O*-*p*-methoxybenzyl- and 1D-2,3,5,6-tetra-*O*-benzyl-1-*O*-*p*-methoxybenzyl-*myo*-inositol. The absolute configurations were established by reference to 1D-5,6-di-*O*-methyl-*myo*-inositol prepared from known 1D-1,2,4-tri-*O*-benzyl-5,6-*O*-isopropylidene-*myo*-inositol. The preparation of the *meso*-derivative 2,4,5,6-tetra-*O*-benzyl-*myo*-inositol is also described. Several of the benzyl ethers were converted into protected phosphate esters by phosphitylation with bis(benzyloxy)diisopropylaminophosphine or bis(2-cyanoethoxy)diisopropylaminophosphine and subsequent oxidation with *m*-chloroperoxybenzoic acid. On treatment with sodium iodide in acetone, the syrupy octabenzyl esters of 2,5-di-*O*-benzyl-*myo*-inositol 1,3,4,6-tetrakisphosphate and 1D-2,6-di-*O*-benzyl-*myo*-inositol 1,3,4,5-tetrakisphosphate were converted into the crystalline tetrasodium salts of the corresponding tetrakis(benzyl phosphates). These salts are useful compounds for hydrogenolysis to give *myo*-inositol tetrakisphosphates of the phosphatidylinositol cycle since phosphate migration would not be expected to occur. 1D-3,6-di-*O*-octyl-*myo*-inositol and its racemate were prepared and each showed liquid crystalline behaviour on heating.

INTRODUCTION

The intense biological interest (for reviews, see refs. 1 and 5) in the *myo*-inositol phosphates and phosphatidylinositol phosphates of the phosphatidylinositol cycle has stimulated efforts for the chemical synthesis (for reviews, see ref. 5) of these compounds, especially the chiral compounds, by improved methods.

We now describe the resolution of several *myo*-inositol derivatives by crystallisation of their (+)- and/or (−)-ω-camphanates to give chiral benzyl ethers of *myo*-

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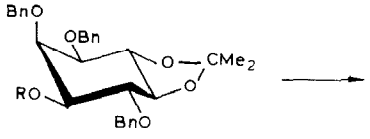
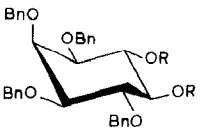
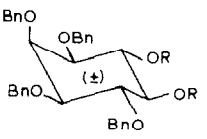
inositol and also the preparation of the *meso*-compound 2,4,5,6-tetra-*O*-benzyl-*myo*-inositol.

Some of these benzyl ethers have been phosphorylated to give protected derivatives of *myo*-inositol phosphates of the phosphatidylinositol cycle.



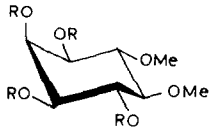


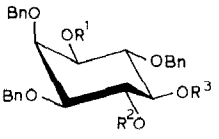


* 1 R = (−) — camph
2 R = H
3 R = Bn

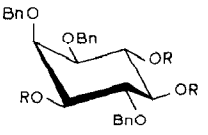
4 R = H
5 R = Me
6 R = (−) — camph

7 R = H
8 R = (−) — camph
9 R = P(OBn)$_2$ (=O)
10 R = P(OCH$_2$CH$_2$CN)$_2$ (=O)
11 R = P(ONa)$_2$ (=O)





(RO)$_2$P — N(CHMe$_2$)$_2$
20 R = CH$_2$CH$_2$CN
21 R = Bn

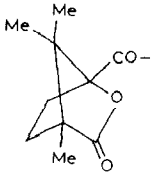


12 R = H
13 R = Ac

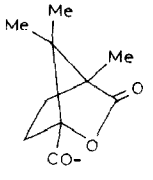
14 R^1 = Bn, R^2 = R^3 = (−) — camph
15 R^1 = Bn, R^2 = R^3 = H
16 R^1 = R^2 = R^3 = H
17 R^1 = (+) — camph, R^2, R^3 = CMe$_2$
18 R^1 = H, R^2, R^3 = CMe$_2$
19 R^1 = (−) — camph, R^2, R^3 = CMe$_2$

22 R = H
23 R = P(OBn)$_2$
24 R = P(OBn)$_2$ (=O)

(−)−camph =



(+)−camph =



* In the formulae, racemic inositol derivatives are indicated with (±) in the ring; chiral inositol derivatives, represented in their correct absolute configurations, are shown with thickened lines in the ring, and *meso*-compounds are shown with neither of these modifications.

RESULTS AND DISCUSSION

In order to establish the absolute configurations of the resolved inositol derivatives described, a chiral reference compound was required and was obtained from the known[6], crystalline (−)-ω-camphanate (**1**) of 1D-1,2,4-tri-*O*-benzyl-5,6-*O*-isopropylidene-*myo*-inositol (**2**). Saponification of **1** gave the alcohol[6] **2** which was converted into the benzyl ether **3**. Acid hydrolysis of **3** gave 1D-1,2,3,4-tetra-*O*-benzyl-*myo*-inositol (**4**) that was converted into the dimethyl ether **5** which, on hydrogenolysis, gave 1D-5,6-di-*O*-methyl-*myo*-inositol (**12**), the chiral reference compound.

Compound **1** has the wrong absolute configuration for the preparation of 1D-2,3,6-tri-*O*-benzyl-*myo*-inositol (**16**) required as an intermediate for the synthesis of the second messenger, 1D-*myo*-inositol 1,4,5-triphosphate. However, (+)-ω-camphanic acid is now available commercially and has been used to prepare the enantiomer of **1**, *i.e.* the (+)-ω-camphanate (**17**) of 1D-2,3,6-tri-*O*-benzyl-4,5-*O*-isopropylidene-*myo*-inositol (**18**) (from the material remaining in the mother liquors after the crystallisation of **1**) and subsequently **16**.

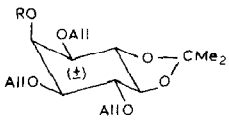
1D-1,2,3,6-Tetra-*O*-benzyl-*myo*-inositol (**15**), the enantiomer of **4**, was required as an intermediate for the synthesis of 1D-*myo*-inositol 4,5-bisphosphate, a component of the phosphatidylinositol cycle in *Dictyostelium discoideum*[7]; before (+)-ω-camphanic acid became available to allow its ready preparation from **17**, using the method described for the preparation of **4** from **1**, the resolution of the racemic 1,2,3,4-tetra-*O*-benzyl-*myo*-inositol[8] (**7**) was investigated. Crystallisation of the mixture of diastereoisomeric bis-(−)-ω-camphanates **8** gave 50% of a pure diastereoisomer, which was shown to be **14** by saponification and comparison of the product **15** with the enantiomer **4**.

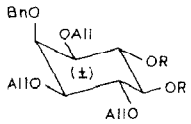
Racemic 1,2,3,4-tetra-*O*-benzyl-*myo*-inositol (**7**) was also used as a model compound for preliminary phosphorylation studies, using the phosphitylating reagents[1] **20** and **21** followed by oxidation with *m*-chloroperoxybenzoic acid, and the preparations of the crystalline, racemic, protected bisphosphates **9** and **10** are described. Alkaline hydrolysis of **10** gave the crystalline tetrasodium salt **11**.

Phosphorylation of the triol[6] **22** (obtained from **1**), using **21** followed by oxidation, gave the crystalline hexabenzyl ester **24**, which is the enantiomer of the intermediate required for the synthesis of 1D-*myo*-inositol 1,4,5-trisphosphate.

The dimethyl ether **12** was also used as a chiral reference compound in the preparation of 1D-2,5,6-tri-*O*-benzyl-*myo*-inositol (**40**), required as an intermediate for the synthesis of 1D-*myo*-inositol 1,3,4-trisphosphate, another component of the phosphatidylinositol cycle.

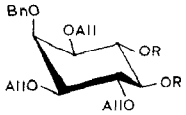
Racemic 1,3,4-tri-*O*-allyl-5,6-*O*-isopropylidene-*myo*-inositol[5] (**25**) was converted into the benzyl ether **26**, acid hydrolysis of which gave the crystalline diol **27** that gave a crystalline diacetate **28**. The racemic diol **27** was converted into the mixture of diastereoisomeric bis-(−)-ω-camphanates **29**, which was resolved by t.l.c., and crystallisation gave 84% of the diastereoisomer **36** with low R_F. The absolute configuration of **36** was established by its conversion, *via* **37**, **39**, and **42**, into 1D-4,5-di-*O*-methyl-*myo*-inositol (**43**) and its acetate **48**, which were compared with the enantiomers **12** and **13** described above.

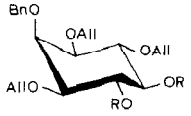




25 R = H
26 R = Bn

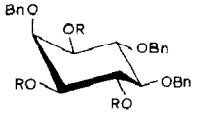
27 R = H
28 R = Ac
29 R = (−) − camph
30 R = (+) − camph

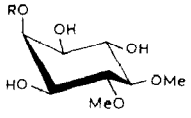




31 R = (−) − camph
32 R = H
33 R = Ac
34 R = Bn
35 R = (+) − camph

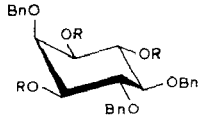
36 R = (−) − camph
37 R = H
38 R = Ac
39 R = Me

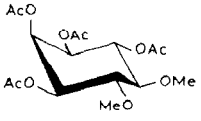




40 R = H
41 R = $P(OCH_2CH_2CN)_2$ (O)

42 R = Bn
43 R = H





44 R = H
45 R = $P(OBn)_2$ (O)
46 R = $P(OBn)(ONa)$ (O)
47 R = $P(OBn)(OH)$ (O)

48

The diastereoisomer **31** (higher R_F value) was isolated by column chromatography after the crystallisation of **36**. Likewise, the bis-(+)-ω-camphanate **35**, the enantiomer of **36**, should now be available by preferential crystallisation from the mixed (+)-ω-camphanates **30**.

Saponification of **31** gave the diol **32** which on benzylation gave **34**. Deallylation of **34** using[9] Pd/C gave the required 1D-2,5,6-tri-*O*-benzyl-*myo*-inositol (**40**). In the same way, the diastereoisomer **36** was converted into 1D-2,4,5-tri-*O*-benzyl-*myo*-inositol (**44**), the enantiomer of **40**.

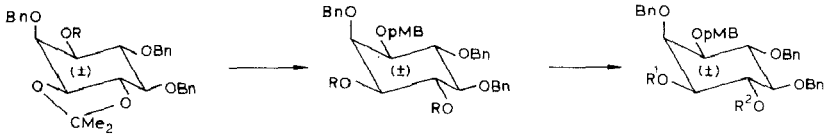
Before (+)-ω-camphanic acid became available, a further route to **40** was investigated in order to avoid the column chromatography of the bis-(−)-ω-camphanate **31**. It has been found previously that crystallisation of the bis-(−)-ω-camphanates of racemic 1,2,5,6-tetra-*O*-benzyl-*myo*-inositol gave[10] the pure bis-(−)-ω-camphanate **58** and that crystallisation of the bis-(−)-ω-camphanates of racemic 2,6-di-*O*-benzyl-1,5-di-*O*-*p*-methoxybenzyl-*myo*-inositol gave[1] the pure bis-(−)-ω-camphanate **59**, each in high yield. Therefore, the crystallisation of the mixed bis-(−)-ω-camphanates **53** of racemic 2,5,6-tri-*O*-benzyl-1-*O*-*p*-methoxybenzyl-*myo*-inositol (**51**) was investigated. Racemic 2,4,5-tri-*O*-benzyl-*myo*-inositol[1,8] was converted, *via* the *O*-isopropylidene derivative **49**, into the *p*-methoxybenzyl ether **50** which, on acid hydrolysis, gave **51**. Crystallisation of the diastereoisomeric bis-(−)-ω-camphanates (**53**) of **51** gave 88% of the bis-(−)-ω-camphanate **60**, thus emulating the behaviour of **58** and **59**. Saponification of **60** gave 1D-2,5,6-tri-*O*-benzyl-1-*O*-*p*-methoxybenzyl-*myo*-inositol (**61**) from which the *O*-*p*-methoxybenzyl group was removed, using dichlorodicyanobenzoquinone[11], to give the required 1D-2,5,6-tri-*O*-benzyl-*myo*-inositol (**40**), identical with the material described above, which therefore established the absolute configuration of **60**.

Phosphorylation of **40**, using the reagent **20** followed by oxidation, gave the protected hexa(2-cyanoethyl) ester **41** as a syrup. Phosphorylation of **44**, using the reagent **21** followed by oxidation, gave the syrupy hexabenzyl ester **45**, which was treated[12] with sodium iodide in acetone to give the trisodium salt **46** that was contaminated with sodium iodide. Therefore, this mixture was acidified to give the pure syrupy acid **47** which was then reconverted into the crystalline sodium salt.

Benzylation of the racemic dibutylstannylene derivative (**54**) of **51**, using the one-pot procedure[5], gave 80% of racemic 2,3,5,6-tetra-*O*-benzyl-1-*O*-*p*-methoxybenzyl-*myo*-inositol (**55**), which was separated readily from the small proportion of the regioisomer **57** by column chromatography. Removal[11] of the *O*-*p*-methoxybenzyl group from **55** gave racemic 1,2,4,5-tetra-*O*-benzyl-*myo*-inositol (**71**), identical with the material characterised as described below, thus establishing the structure of **55**.

This tin-mediated benzylation of the chiral derivative **62** gave **63** as the major product (together with a small quantity of **64**) and removal of the *O*-*p*-methoxybenzyl group then gave 1D-2,3,5,6-tetra-*O*-benzyl-*myo*-inositol (**82**), required as a chiral reference compound in the resolutions described below.

1D-*myo*-Inositol 1,4-bisphosphate is a component of the phosphatidylinositol cycle and 1D-2,3,5,6-tetra-*O*-benzyl-*myo*-inositol (**82**) was required as an intermediate

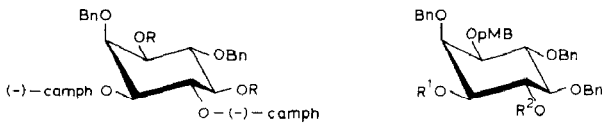


49 R = H
50 R = pMB

51 R = H
52 R = Ac
53 R = (-) – camph

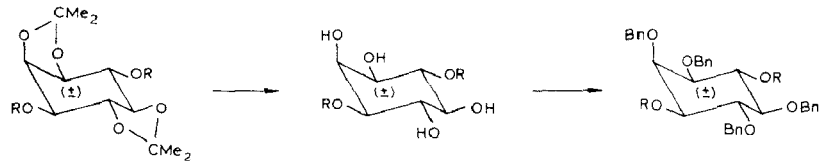
54 $R^1, R^2 = SnBu_2$
71 ← 55 R^1 = Bn, R^2 = H
56 R^1 = Bn, R^2 = Ac
57 R^1 = H, R^2 = Bn

pMB = *p*-methoxybenzyl



58 R = Bn
59 R = pmB

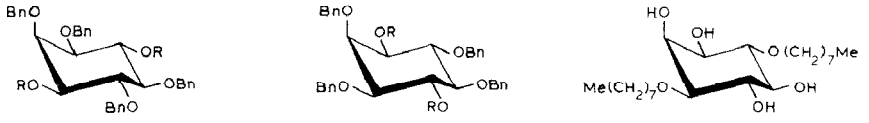
60 $R^1 = R^2$ = (-) – camph
40 ← 61 $R^1 = R^2$ = H
62 $R^1, R^2 = SnBu_2$
82 ← 63 R^1 = Bn, R^2 = H
64 R^1 = H, R^2 = Bn



65 R = H
66 R = $(CH_2)_7Me$

67 R = All
68 R = $(CH_2)_7Me$

69 R = All
70 R = CH = CH – Me
71 R = H
72 R = Ac
73 R = (-) – camph
74 R = (+) – camph
75 R = $P(OCH_2CH_2CN)_2$ (=O)



76 R = (-) – camph
77 R = H
78 R = Ac
79 R = $(CH_2)_7Me$

80 R = (-) – camph
81 R = (+) – camph
82 R = H
83 R = Ac
84 R = $P(OBn)_2$
85 R = $P(OBn)_2$ (=O)

86

for its synthesis. For this purpose, racemic 1,4-di-*O*-allyl-*myo*-inositol[13] (**67**) was converted into the tetrabenzyl ether **69** and the allyl groups were isomerised with potassium *tert*-butoxide in methyl sulphoxide[14] to give the crystalline di(*cis*-prop-1-enyl) ether **70**. Acid hydrolysis of **70** gave racemic 1,2,4,5-tetra-*O*-benzyl-*myo*-inositol (**71**) which was identical with the product obtained above from racemic 1,2,4,5-tetra-*O*-benzyl-3-*O*-*p*-methoxybenzyl-*myo*-inositol (**55**).

The bis-(−)-ω-camphanates **73** were prepared from **71** and crystallisation gave 66% of the bis-(−)-ω-camphanate (**76**) of 1D-1,2,4,5-tetra-*O*-benzyl-*myo*-inositol (**77**). The absolute configuration of **76** was established by saponification and comparison of the product **77** and its diacetate **78** with the enantiomers **82** and **83** prepared from 1D-2,3,5,6-tetra-*O*-benzyl-1-*O*-*p*-methoxybenzyl-*myo*-inositol (**63**) as described above. A small quantity of the pure diastereoisomer **80** was also obtained by crystallisation from the mother liquors after the removal of **76**. Saponification of the contents of the mother liquors, after the crystallisation of **76**, gave the crude racemic diol **71** (enriched with the enantiomer **82**) and this was converted into the (+)-ω-camphanates **74**. Crystallisation of this mixture of diastereoisomers gave the (+)-ω-camphanate **81**, which is the enantiomer of **76**, and saponification then gave 1D-2,3,5,6-tetra-*O*-benzyl-*myo*-inositol (**82**), the enantiomer of **77**.

Phosphitylation of **82** with the reagent **21**, and subsequent oxidation of the bisphosphite **84**, gave the crystalline protected bisphosphate **85** which is a suitable intermediate for the synthesis of 1D-*myo*-inositol 1,4-bisphosphate. Phosphitylation of the racemic diol **71** with the reagent **20** and subsequent oxidation gave the crystalline, protected, racemic bisphosphate **75**.

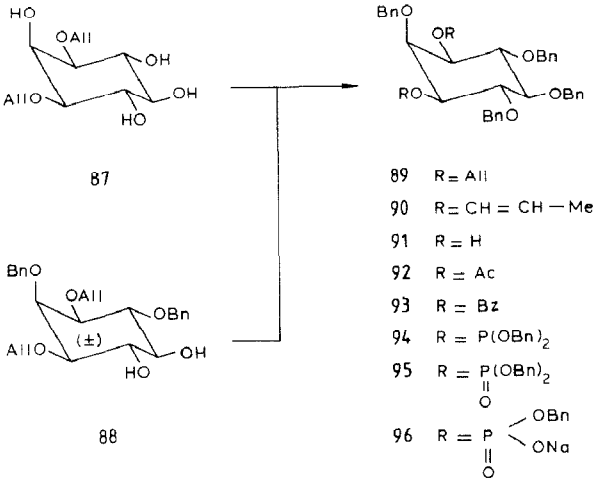
For collaborative studies on liquid crystals, with Professor Klaus Praefcke, racemic (**68**) and chiral (**86**) 1,4-di-*O*-octyl-*myo*-inositol were prepared. Alkylation of racemic 1,2:4,5-di-*O*-isopropylidene-*myo*-inositol[15] (**65**) with octyl bromide gave the crystalline dioctyl ether **66** and acid hydrolysis of the *O*-isopropylidene groups then gave the racemate **68**. Alkylation of the chiral diol **77** with octyl bromide gave the crystalline dioctyl ether **79**, hydrogenolysis of which gave 1D-3,6-di-*O*-octyl-*myo*-inositol (**86**). Both **68**[16] and **86** showed liquid crystalline behaviour on heating.

myo-Inositol 1,3-bisphosphate is a component of the phosphatidylinositol cycle and 2,4,5,6-tetra-*O*-benzyl-*myo*-inositol (**91**) was chosen as an intermediate for its synthesis. Benzylation of 1,3-di-*O*-allyl-*myo*-inositol[5] (**87**) or racemic 1,3-di-*O*-allyl-2,6-di-*O*-benzyl-*myo*-inositol[1] (**88**) gave **89**, and isomerisation[14] of the allyl groups with potassium *tert*-butoxide in methyl sulphoxide gave crystalline 2,4,5,6-tetra-*O*-benzyl-1,3-di-*O*-(*cis*-prop-1-enyl)-*myo*-inositol (**90**). Acid hydrolysis of **90** gave the syrupy diol **91** which afforded a crystalline dibenzoate **93**. Phosphitylation of the diol **91** with the reagent **21** and subsequent oxidation of the bisphosphite **94** gave the syrupy, protected bisphosphate **95**, treatment of which with sodium iodide in acetone[12] gave the crystalline disodium salt **96**.

The crystalline octa(2-cyanoethyl) ester **97** of 2,5-di-*O*-benzyl-*myo*-inositol 1,3,4,6-tetrakisphosphate has been described[1] and we now report the preparation of the corresponding octabenzyl ester **98**, which was obtained as a syrup. Treatment of **98** with sodium iodide in acetone[12] gave the crystalline tetrasodium salt **99** in high yield.

The syrupy octabenzyl ester **100** of 1D-2,6-di-*O*-benzyl-*myo*-inositol 1,3,4,5-tetrakisphosphate has also been described[1]. Treatment of **100** with sodium iodide in acetone at reflux[12] gave the crystalline tetrasodium salt **101** in high yield.

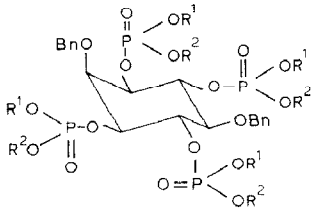
Compounds **99** and **101** and the corresponding free acids are useful compounds for debenzylation by hydrogenolysis, to give the corresponding *myo*-inositol tetrakisphosphates which are both components of the phosphatidylinositol cycle. With compound **99** and **101**, there is no danger of cyclic phosphates being formed (and hence phosphate migration)[17], which could occur on direct hydrogenolysis of **98** and **100** if the benzyl ethers on the ring hydroxyl groups were removed before the benzyl esters on the phosphate groups.



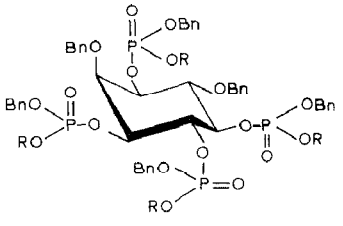
87

88

89 R = All
90 R = CH = CH — Me
91 R = H
92 R = Ac
93 R = Bz
94 R = $P(OBn)_2$
95 R = $P(OBn)_2$ (=O)
96 R = P(=O)(OBn)(ONa)



97 $R^1 = R^2 = CH_2CH_2CN$
98 $R^1 = R^2 = Bn$
99 $R^1 = Bn$, $R^2 = Na$



100 R = Bn
101 R = Na

EXPERIMENTAL

General. — The general methods were as described[5]. ^{31}P-N.m.r. spectra (external phosphoric acid) were recorded for solutions in $CDCl_3$ (unless otherwise stated) using a Jeol FX90Q Fourier-transform spectrometer. Column chromatography was performed on silica gel.

1D-1,2,3,4-Tetra-O-benzyl-5,6-O-isopropylidene-myo-inositol (**3**). — 1D-1,2,4-Tri-*O*-benzyl-5,6-*O*-isopropylidene-*myo*-inositol[6] (**2**) was treated with benzyl bromide and sodium hydride in *N,N*-dimethylformamide and the product isolated in the usual way to give **3**, m.p. 83–84° (from light petroleum), $[\alpha]_D^{27}$ +31° (*c* 1, $CHCl_3$) (Found: C, 76.14; H, 7.13. $C_{37}H_{40}O_6$ calc.: C, 76.52; H, 6.94%).

1D-1,2,3,4-Tetra-O-benzyl-myo-inositol (**4**). — Compound **3** was treated with 1:9 M HCl–MeOH at reflux for 30 min. An excess of sodium hydrogencarbonate was added and the solvents were evaporated. The residue was extracted with CH_2Cl_2 to give **4**, m.p. 105–106° (from light petroleum), $[\alpha]_D^{27}$ −15° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 2.61 (s, 2 H, 2 OH), 3.12–3.52 (m, 3 H), 3.83–4.16 (m, 3 H), 4.55, 4.63, 4.82 (3 s, 6 H, 3 CH_2Ph), 4.87 (ABq, 2 H, CH_2Ph), 7.67 (s, 20 H, aromatic) (Found: C, 75.45; H, 6.81. $C_{34}H_{36}O_6$ calc.: C, 75.53; H, 6.71%).

1D-5,6-Di-O-methyl-myo-inositol (**12**). — The diol **4** was treated with an excess of MeI and sodium hydride in *N,N*-dimethylformamide and the product was isolated in the usual way to give the dimethyl ether **5**, m.p. 62–63° (from light petroleum). Treatment of **5** with hydrogen over Pd/C in EtOH gave **12**, m.p. 196–198° (from 10:3 EtOAc–EtOH), $[\alpha]_D^{26}$ −7° (*c* 1, MeOH) (Found: C, 46.53; H, 7.84. $C_8H_{16}O_6$ calc.: C, 46.15; H, 7.75%).

The tetra-acetate (**13**) of **12** had m.p. 123–125°; $[\alpha]_D^{25}$ −3° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 1.98, 2.06, 2.08, 2.16 (4 s, 12 H, 4 Ac), 3.22 (t, 1 H, *J* 9.5 Hz, H-5), 3.56 (s, 6 H, 2 OMe), 3.60 (t, 1 H, *J* 9.5 Hz, H-4), 4.83–5.03 (m, 2 H, H-1,3), 5.35 (t, 1 H, *J* 9.5 Hz, H-6), 5.50 (t, 1 H, *J* 2.5 Hz, H-2) (Found: C, 51.22; H, 6.36. $C_{16}H_{24}O_{10}$ calc.: C, 51.06; H, 6.43%).

1D-1,2,3,6-Tetra-O-benzyl-4,5-di-O-[(−)-ω-camphanoyl]-myo-inositol (**14**). — Racemic 1,2,3,4-tetra-*O*-benzyl-*myo*-inositol[8] (**7**) was converted into the mixture of diastereoisomeric bis-(−)-ω-camphanates **8**, and the products were isolated in the usual way. T.l.c. (2:1 ether–light petroleum) showed two products, R_F 0.5 and 0.53. ^{1}H-N.m.r. data: δ 0.76 (6 H), 0.81 (6 H), 0.91 (3 H), 0.95 (6 H), 0.97 (3 H), 1.04 (12 H), (6 s, 12 CMe of the camphanate portions). Crystallisation of the mixture from MeOH gave **14** (R_F 0.5, 50% yield of this diastereoisomer), m.p. 176–178°, $[\alpha]_D^{25}$ +11° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 0.76 (6 H), 0.91 (3 H), 0.94 (3 H), 1.03 (6 H), (4 s, 6 CMe of the camphanate portion) (Found: C, 71.64; H, 6.81. $C_{54}H_{60}O_{12}$ calc.: C, 71.98; H, 6.71%).

A second crop of crystals from MeOH was a mixture of diastereoisomers (n.m.r.), but the contents of the mother liquors then gave ^{1}H-n.m.r. data [δ 0.80 (6 H), 0.95 (3 H), 0.97 (3 H), 1.04 (6 H), (4 s, 6 CMe of the camphanate portion)] for the other diastereoisomer **6**, together with only small peaks due to **14**.

1D-1,2,3,6-Tetra-O-benzyl-myo-inositol (**15**). — Saponification of **14** with NaOH in MeOH gave **15**, m.p. 103–104°, $[\alpha]_D^{25}$ +12° (*c* 1, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of its enantiomer **4**.

(+)-ω-Camphanate (**17**) *of 1D-2,3,6-tri-O-benzyl-4,5-O-isopropylidene-myo-inositol* (**18**). — Racemic 2,3,6-tri-*O*-benzyl-4,5-*O*-isopropylidene-*myo*-inositol was converted[6] into the mixture of diastereoisomeric (−)-ω-camphanates. ^{1}H-N.m.r. data: δ 0.80 (3 H), 0.84 (3 H), 0.86 (3 H), 0.94 (3 H), 1.05 (6 H), (5 s, 6 CMe of the camphanate

portions), 1.46 (s, 12 H, 4 CMe of the isopropylidene portions). Crystallisation[6] of the mixture gave the pure diastereoisomer **1** in high yield. ^{1}H-N.m.r. data: δ 0.79, 0.94, 1.05 (3 s, 3 CMe of the camphanate portion), 1.46 (s, 6 H, Ip), 3.45 (t, 1 H, J 9.5 Hz, H-5), 3.72 (dd, 1 H, J 2.4 and 10.4 Hz, H-1), 4.02–4.30 (m, 3 H, H-2,4,6), 4.50–5.09 (m, 7 H, H-3 and 3 CH_2Ph), 7.28, 7.34 (2 s, 15 H, aromatic). The contents of the mother liquor were highly enriched with the non-crystalline[6] diastereoisomer **19**. ^{1}H-N.m.r. data: δ 0.84, 0.86, 1.05 (3 s, 9 H, 3 CMe of the camphanate portion), together with small peaks in the CMe region due to **1**. This product was saponified with NaOH in MeOH, and crude **18** (containing some of the enantiomer **2**) was treated with (+)-ω-camphanoyl chloride in pyridine in the usual way, to give the crude camphanate **17** (contaminated with some of the diastereoisomer derived from **2**). Crystallisation from ether gave **17** (80% from the total crude **18**), m.p. 170–171°, $[\alpha]_D^{27}$ −53° (*c* 1, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of **1**; lit.[6] for **1**, m.p. 168–170°, $[\alpha]_D^{26}$ +53.1° (*c* 1, $CHCl_3$) (Found: C, 71.47; H, 7.22. $C_{40}H_{46}O_9$ calc.: C, 71.62; H, 6.91%).

*1D-2,3,6-Tri-*O*-benzyl-*myo*-inositol* (**16**). — The camphanate **17** was saponified with NaOH in MeOH and the syrupy product **18** was deacetonated, as described[6] for the enantiomer, to give **16**, m.p. 121–123°, $[\alpha]_D^{25}$ +10° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 2.34 (d, 1 H, J 6.1 Hz, OH), 2.67 (m, 2 H, 2 OH), 3.27 (dd, 1 H, J 2.4 and 9.8 Hz, H-3), 3.43–4.07 (m, 5 ring protons), 4.62, 4.82 (2 ABq, 4 H, 2 CH_2Ph), 4.85 (s, 2 H, CH_2Ph), 7.33 (s, 15 H, aromatic); lit.[18] m.p. 117–119°, $[\alpha]_D^{16}$ +15.5° ($CHCl_3$); lit.[19] m.p. 115–115.5°, $[\alpha]_D^{20}$ +8.9° (chloroform); lit.[6] m.p. 118–120°, $[\alpha]_D^{25}$ −9.0° ($CHCl_3$) for the enantiomer (Found: C, 71.85; H, 6.75. $C_{27}H_{30}O_6$ calc.: C, 71.98; H, 6.71%).

*(±)-1,2,3,4-Tetra-*O*-benzyl-*myo*-inositol 5,6-bis(dibenzyl phosphate)* (**9**). — The racemic diol[8] **7** was treated[1] with bis(benzyloxy)diisopropylaminophosphine (**21**). The bisphosphite formed was oxidised with *m*-chloroperoxybenzoic acid and isolated as described[1]. Column chromatography (1:1 ether–light petroleum, followed by ether) of the product gave **9** (82%), m.p. 102–104° (from 10:1 light petroleum–EtOAc). ^{31}P-N.m.r. data: δ −2.02, −1.61 (Found: C, 70.22; H, 5.71; P, 5.77. $C_{62}H_{62}O_{12}P_2$ calc.: C, 70.18; H, 5.89; P, 5.84%).

*(±)-1,2,3,4-Tetra-*O*-benzyl-*myo*-inositol 5,6-bis[di(2-cyanoethyl) phosphate]*[20] (**10**). — The racemic diol[8] **7** was treated[1] with bis(2-cyanoethoxy)diisopropylaminophosphine (**20**). The bisphosphite formed was oxidised with *m*-chloroperoxybenzoic acid and the product was isolated as described[1]. Column chromatography (EtOAc followed by 10:1 EtOAc–MeOH) of the product gave **10** (80%), m.p. 103–105° (from EtOAc–light petroleum). ^{31}P-N.m.r. data: δ −3.43, −3.23 (Found: C, 60.93; H, 5.70; N, 5.99; P, 7.07. $C_{46}H_{50}N_4O_{12}P_2$ calc.: C, 60.52; H, 5.52, N, 6.14; P, 6.79%).

*(±)-1,2,3,4-Tetra-*O*-benzyl-*myo*-inositol 5,6-bis(disodium phosphate)* (**11**). — M Sodium hydroxide (0.25 mL, 0.25 mmol) was added to a solution of **10** (100 mg, 0.11 mmol) in MeOH (5 mL) and the solution was kept at 50° for 1 h. The crystalline product (80 mg, 85%) which separated was collected and recrystallised from EtOH–water (4:1) to give **11**, m.p. 250–255° (dec.). ^{31}P-N.m.r. data (D_2O): δ +3.36 (Found: C, 47.48; H, 4.83; P, 7.0. $C_{34}H_{34}Na_4O_{12}P_2 \cdot 4H_2O$ calc.: C, 47.45; H, 4.92; P, 7.20%).

*1D-1,2,4-Tri-*O*-benzyl-*myo*-inositol 3,5,6-tris(dibenzyl phosphate)* (**24**). — 1D-

1,2,4-Tri-*O*-benzyl-*myo*-inositol[6] (**22**) was treated[1] with bis(benzyloxy)diisopropylaminophosphine (**21**). T.l.c. (15:1 $CHCl_3$–MeOH) showed conversion of **22** (R_F 0.75) into the trisphosphite **23** (R_F 0.95) which was oxidised with *m*-chloroperoxybenzoic acid[1] to give **24** (R_F 0). The product was isolated as described[1] and column chromatography (ether followed by EtOAc) gave **24** (88%), m.p. 113–115° (from 20:1 light petroleum–EtOAc), $[\alpha]_D^{25}$ +3.5° (*c* 1, $CHCl_3$). ^{31}P-N.m.r. data: δ −1.95, −1.68, −1.55 (Found: C, 67.65; H, 5.53; P, 7.60. $C_{69}H_{69}O_{15}P_3$ calc.: C, 67.31; H, 5.65; P, 7.55%) (*cf.* δ −1.36, −1.27, −1.15 for the enantiomer[19]; no data given in refs. 21 and 22).

(±)-*1,3,4-Tri*-O-*allyl*-*2*-O-*benzyl*-myo-*inositol* (**27**). — Racemic 1,3,4-tri-*O*-allyl-5,6-*O*-isopropylidene-*myo*-inositol[5] (**25**) was treated with an excess of benzyl bromide and sodium hydride in *N,N*-dimethylformamide and the product was isolated in the usual way to give impure benzyl ether **26** as a syrup. The crude product was treated with 1:9 M HCl–acetone under reflux for 15 min when t.l.c. (1:2 ether–light petroleum) showed complete conversion of **26** (R_F 0.8) into a product (R_F 0). An excess of sodium hydrogencarbonate was added, the solvents were evaporated, the residue was extracted with CH_2Cl_2, and the extract was concentrated. Column chromatography (1:2 ether–light petroleum followed by ether) of the residue gave **27** (95% from **25**), m.p. 53–55° (from light petroleum) (Found: C, 68.08; H, 7.89. $C_{22}H_{30}O_6$ calc.: C, 67.67; H, 7.75%).

The diacetate (**28**) of **27** had m.p. 122–123° (from light petroleum). ^{1}H-N.m.r. data: δ 2.02 (s, 6 H, 2 Ac), 3.19, 3.22, 3.25, 3.27, 3.30, 3.33, 3.36, 3.39 (8 s, 2 H, H-1,3), 3.79–4.27 (m, 8 H, 3 OCH_2–CH = and H-2,6), 4.85 (s, 2 H, CH_2Ph), 4.96–5.59 (m, 8 H, 3 CH_2 = and H-5,6), 5.61–6.06 (m, 3 H, 3 –CH =), 7.25–7.40 (m, 5 H, aromatic) (Found: C, 65.83; H, 7.18. $C_{26}H_{34}O_8$ calc.: C, 65.80; H, 7.22%).

Bis-(−)-ω-camphanates (**31** *and* **36**) *of* **27**. — A mixture of **27** (2 g, 5.1 mmol) and (−)-ω-camphanoyl chloride (3.25 g, 15 mmol) in dry pyridine (25 mL) was kept at 20° for 10 h. T.l.c. (2:1 ether–light petroleum) then showed the conversion of **27** (R_F 0.1) into the bis-camphanates **29** (R_F 0.4 and 0.45). Water (1 mL) was added, the solution was kept for 30 min at 20°, then diluted with more water (50 mL). The products were extracted with EtOAc, and the extract was washed with M HCl and saturated aq. sodium hydrogencarbonate, and dried ($MgSO_4$). Evaporation of the solvent gave the mixture of diastereoisomers **29** (3.45 g, 90%). ^{1}H-N.m.r. data: δ 0.95 (12 H), 1.01 (3 H), 1.04 (9 H), 1.08 (12 H), (4 s, 12 CMe of the camphanate portion), 4.86 (*s* 2 CH_2Ph).

Crystallisation of **29** from (1:1 EtOAc–light petroleum) gave **36** (1.46 g, 84% of this diastereoisomer), R_F 0.4, m.p. 209–211°, $[\alpha]_D^{25}$ +7° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 0.95 (6 H), 1.01 (3 H), 1.04 (3 H), 1.08 (6 H), (4 s, 6 CMe of the camphanate portion) (Found: C, 67.14; H, 7.37. $C_{42}H_{54}O_{12}$ calc.: C, 67.18; H, 7.25%).

The diastereoisomer **31** (1.07 g, 62% of this diastereoisomer), R_F 0.45, obtained by column chromatography (2:1 ether–light petroleum) of the material in the mother liquors, had m.p. 136–138° (from ether), $[\alpha]_D^{25}$ −21° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 0.95 (6 H), 1.05 (6 H), 1.08 (6 H), (3 s, 6 CMe of the camphanate portion), 1.19 [t, 6 H, *J* 7 Hz, (*Me*CH_2)$_2$O] [Found: C, 67.22; H, 7.79. $C_{42}H_{54}O_{12}\cdot(C_2H_5)_2O$ calc.: C, 66.97; H, 7.82%].

Saponification of **36** with NaOH in MeOH gave the diol **37** as a syrup, $[\alpha]_D^{25}$ +23° (*c* 1, $CHCl_3$), which gave a crystalline diacetate (**38**), m.p. 138–139°, $[\alpha]_D^{25}$ +24° (*c* 1,

$CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of the racemate **28** (Found: C, 65.82; H, 7.30. $C_{26}H_{34}O_8$ calc.: C, 65.80; H, 7.22%).

The diol **37** (regenerated from **38**) was treated with methyl iodide and sodium hydride in *N,N*-dimethylformamide, and the product was isolated in the usual way to give **39**. The allyl groups were removed[5] from **39** by the action[9] of Pd/C in acidic aq. EtOH to give the triol **42** and this was treated with hydrogen over Pd/C in EtOH to remove the benzyl group. Crystallisation of the product from 2:1 EtOAc–EtOH gave 1D-4,5-di-*O*-methyl-*myo*-inositol (**43**), m.p. 199–201°, $[\alpha]_D^{25}$ +8° (*c* 1, MeOH), which gave a tetraacetate **48**, m.p. 124–125°, with a ^{1}H-n.m.r. spectrum identical with that of the enantiomer **13**, thus establishing the absolute configuration of the diastereoisomer with R_F 0.4 as **36** and that with R_F 0.45 as **31**.

1D-5,6-Di-O-acetyl-1,3,4-tri-O-allyl-2-O-benzyl-myo-*inositol* (**33**). — Saponification of **31** gave the diol **32** as a syrup which gave the crystalline diacetate **33**, m.p. 133–135° (from light petroleum), $[\alpha]_D^{25}$ −24° (*c* 1, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of the racemate **28** (Found: C, 65.94; H, 7.36. $C_{26}H_{34}O_8$ calc.: C, 65.80; H, 7.22%).

1D-2,5,6-Tri-O-benzyl-myo-*inositol* (**40**). — (*a*) The diol **32** (200 mg, regenerated from **33**) was treated with benzyl bromide and sodium hydride in *N,N*-dimethylformamide and the product was isolated in the usual way. Column chromatography (1:3 ether–light petroleum) of the product gave the tribenzyl ether **34** (270 mg, 88%) as a syrup that was deallylated[5] with Pd/C in acidified aqueous ethanol under reflux. The reaction was monitored by t.l.c. (EtOAc). Major (R_F 0.7) and minor products (R_F 0.5 and 0.1) were formed. Triethylamine was added to neutralise the acid, and the mixture was filtered and concentrated. Column chromatography (EtOAc) of the residue gave **40** (109 mg, 52%), R_F 0.7, m.p. 103–105° (from 10:1 light petroleum–EtOAc), $[\alpha]_D^{25}$ −27° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 2.37 (d, 1 H, *J* 4.9 Hz, OH), 2.46 (d, 1 H, *J* 6.7 Hz, OH), 2.60 (d, 1 H, *J* 2.4 Hz, OH), 3.21–3.98 (m, 6 ring protons), 4.80 (s, 2 H, C*H*$_2$Ph), 4.83 (ABq, 2 H, C*H*$_2$Ph), 4.86 (s, 2 H, C*H*$_2$Ph), 7.32 (s, 15 H, aromatic); no data given in refs. 23 and 24 (Found: C, 71.60; H, 6.80. $C_{27}H_{30}O_6$ calc.: C, 71.98; H, 6.71%).

(*b*) A solution of the *p*-methoxybenzyl ether **61** (see below) (150 mg, 0.27 mmol) and dichlorodicyanobenzoquinone (200 mg, 0.88 mmol) in CH_2Cl_2 (10 mL) and water (1 mL) was stirred at 20° and the reaction was monitored by t.l.c. (2:1 EtOAc–light petroleum). After 2 h, **61** (R_F 0.5) was converted into a major product (R_F 0.3) together with by-products (R_F 0.75 and 0.1). The mixture was diluted with CH_2Cl_2 (25 mL), and the organic layer was washed with aq. sodium metabisulphite and saturated aq. sodium hydrogen carbonate, dried (K_2CO_3), and concentrated. Column chromatography (1:1 ether–light petroleum followed by ether) of the residue gave **40** (93 mg), m.p. 104–106°, $[\alpha]_D^{25}$ −26° (*c* 1, $CHCl_3$), identical with the material described in (*a*), thus establishing the absolute configurations of **60** and **61** described below.

1D-2,4,5-Tri-O-benzyl-myo-*inositol* (**44**). — The diol **37** (regenerated from **38**) was converted into the triol **44** as described for the conversion of the enantiomer **32** into the triol **40**. The triol **44** had m.p. 104–106° (from 10:1 light petroleum–EtOAc), $[\alpha]_D^{25}$ +25° (*c* 1, $CHCl_3$), and a ^{1}H-n.m.r. spectrum identical with that of the enantiomer **40**.

1D-2,5,6-Tri-O-benzyl-myo-inositol 1,3,4-tris[di(2-cyanoethyl) phosphate] (**41**). — The chiral triol **40** was treated with bis(2-cyanoethoxy)diisopropylaminophosphine (**20**) and the trisphosphite produced was oxidised[1] with *m*-chloroperoxybenzoic acid. Column chromatography (15:1 $CHCl_3$–MeOH) of the product gave **41**, isolated as a syrup (55%), $[\alpha]_D^{25}$ −2.3° (*c* 1, $CHCl_3$). ^{31}P-N.m.r. data: δ −3.30, −3.10, −2.49 (Found: C, 52.23; H, 5.24; N, 8.56; P, 9.38. $C_{45}H_{51}N_6O_{15}P_3$ calc.: C, 53.57; H, 5.10; N, 8.33; P, 9.21%).

1D-2,4,5-Tri-O-benzyl-myo-inositol 1,3,6-tris(dibenzyl phosphate) (**45**). — The triol **44** was treated[1] with bis(benzyloxy)diisopropylaminophosphine (**21**). T.l.c. (15:1 $CHCl_3$–MeOH) showed conversion of **44** (R_F 0.7) into the trisphosphite (R_F 1.0), which was oxidised[1] with *m*-chloroperoxybenzoic acid to give crude **45** (R_F 0.4). Column chromatography (ether followed by EtOAc) gave **45** (85%), isolated as a syrup, $[\alpha]_D^{25}$ −5.8° (*c* 1, $CHCl_3$). ^{31}P-N.m.r. data: δ −1.88, −1.41, −1.28 (Found: C, 66.45; H, 5.79; P, 7.33. $C_{69}H_{69}O_{15}P_3$ calc.: C, 67.31; H, 5.65; P, 7.55%); no data given in refs. 23 and 24 for the enantiomer.

A solution of **45** (375 mg, 0.3 mmol) and sodium iodide (637 mg, 4.25 mmol) in acetone (30 mL) was heated under reflux for 5 h. During this time, small portions of the solution were added to M HCl in saturated aq. KCl and the mixture was extracted with ether. T.l.c. (90:10:1 $CHCl_3$–MeOH–acetic acid) of the extracts showed rapid conversion of **45** (R_F 0.8) into products (R_F 0.5 and 0.25) and more slowly into a product (R_F 0) assumed to be the acid **47**. The solution was cooled and concentrated to give a crystalline mixture of the trisodium salt **46** and sodium iodide, which was triturated with light petroleum to remove benzyl iodide. The mixture of **46** and sodium iodide was acidified and the free acid **47** was extracted as described above. A solution of **47** and 3 equiv. of NaOAc in MeOH was concentrated, and toluene and EtOH were evaporated from the residue to remove acetic acid, leaving the trisodium salt **46**, m.p. 268–271° (dec.) (from 1:5 EtOH–acetone), $[\alpha]_D^{25}$ −8.4° (*c* 1, MeOH). ^{31}P-N.m.r. data (D_2O, in the presence of the disodium salt of EDTA): δ −0.81 (1 P), −0.54 (2 P) (Found: C, 54.48; H, 4.98; P, 8.66; Na, 6.16. $C_{48}H_{48}Na_3O_{15}P_3 \cdot 2H_2O$ calc.: C, 54.24; H, 4.93; P, 8.74; Na, 6.49%).

(±)-2,5,6-Tri-O-benzyl-3,4-O-isopropylidene-1-O-p-methoxybenzyl-myo-inositol (**50**). — A mixture of racemic 2,4,5-tri-*O*-benzyl-*myo*-inositol[1,8] (2 g), 2,2-dimethoxypropane (6 mL), and toluene *p*-sulphonic acid (20 mg) in acetone (20 mL) was stirred for 5 h at 20°. T.l.c. (1:1 ether–light petroleum) then showed almost complete conversion of the starting material (R_F 0) into a product (R_F 0.6) which was isolated in the usual way. Column chromatography (1:1 ether–light petroleum) gave the *O*-isopropylidene derivative **49** (1.86 g, 85%), isolated as a syrup which was treated with an excess of *p*-methoxybenzyl chloride and sodium hydride in *N,N*-dimethylformamide. The product was isolated in the usual way to give **50**, m.p. 119–120° (from 1:5 EtOAc–light petroleum). ^{1}H-N.m.r. data: δ 1.43, 1.46 (2 s, 6 H, 2 CMe), 3.78 (s, 3 H, OMe) (Found: C, 75.45; H, 6.96. $C_{38}H_{42}O_7$ calc.: C, 74.73; H, 6.93%).

(±)-2,5,6-Tri-O-benzyl-1-O-p-methoxybenzyl-myo-inositol (**51**). — A mixture of **50** (1.45 g) and 1:3:7 M HCl–acetone–MeOH (50 mL) was kept for 1 h at 20°. An excess

of sodium hydrogencarbonate was added and the solvents were evaporated. Extraction of the residue with CH_2Cl_2 gave **51** (1.19 g), m.p. 172–174° (from EtOH). ^{1}H-N.m.r. data: δ 2.28 (d, 1 H, *J* 7.9 Hz, OH), 2.47 (d, 1 H, *J* 2 Hz, OH), 3.80 (s, 3 H, OMe), 4.59–5.10 (m, 8 H, 4 C*H*$_2$Ph), 6.79–7.32 (m, 19 H, aromatic) (Found: C, 73.65; H, 6.82. $C_{35}H_{38}O_7$ calc.: C, 73.66; H, 6.71%).

The diacetate (**52**) of **51** had m.p. 95–96° (from 1:5 ether–light petroleum). ^{1}H-N.m.r. data: δ 1.89, 1.95 (2 s, 6 H, 2 Ac), 3.81 (s, 3 H, OMe), 5.62 (t, 1 H, *J* 9.77 Hz, H-4) (Found: C, 71.54; H, 6.55. $C_{39}H_{42}O_9$ calc.: C, 71.54; H, 6.47%).

Bis-(−)-ω-camphanate (**60**) *of* 1D-*2,5,6-tri*-O-*benzyl-1*-O-p-*methoxybenzyl*-myo-*inositol* (**61**). — The racemic diol **51** (400 mg) was converted into the mixture of diastereoisomeric bis-(−)-ω-camphanates **53** (644 mg) in the usual way (see above). ^{1}H-N.m.r. data: δ 0.75 (3 H), 0.83 (3 H), 0.90 (9 H), 0.95 (6 H), 0.99 (3 H), 1.02 (6 H), 1.07 (6 H), (7 s, 12 CMe of the camphanate portions). Crystallisation of the mixture from 1:1 light petroleum–EtOAc gave **60** (286 mg, 88% of this diastereoisomer), m.p. 198–200°, $[\alpha]_D^{26}$ − 3.8° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 0.75 (3 H), 0.90 (6 H), 0.98 (3 H), 1.02 (3 H), 1.07 (3 H), (5 s, 6 CMe of the camphanate portion) (Found: C, 70.80; H, 6.72. $C_{55}H_{62}O_{13}$ calc.: C, 70.95; H, 6.71%).

1D-*2,5,6-Tri*-O-*benzyl-1*-O-p-*methoxybenzyl*-myo-*inositol* (**61**). — The bis-camphanate **60** was saponified with NaOH in MeOH to give **61**, m.p. 154–155° (from 1:3 EtOAc–light petroleum), $[\alpha]_D^{25}$ − 14° (*c* 1, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of the racemate **51** (Found: C, 73.40; H, 6.49. $C_{35}H_{38}O_7$ calc.: C, 73.66; H, 6.71%).

Removal of the *O-p*-methoxybenzyl group from **61** gave 1D-2,5,6-tri-*O*-benzyl-*myo*-inositol (**40**), as described above, thus establishing the absolute configurations of **60** and **61**.

(±)-*6*-O-*Acetyl-1,2,4,5-tetra*-O-*benzyl-3*-O-p-*methoxybenzyl*-myo-*inositol* (**56**). — A mixture of **51** (1 g, 1.75 mmol), dibutyltin oxide (473 mg, 1.9 mmol), tetrabutylammonium bromide (565 mg, 1.75 mmol), benzyl bromide (1 mL, 8.4 mmol), and acetonitrile (50 mL) was heated under reflux with a Soxhlet apparatus containing molecular sieve 3 Å. The reaction was monitored by t.l.c. (2:1 ether–light petroleum). After 20 h, **51** (R_F 0) was converted into a major (**55**, R_F 0.8) and a minor product (R_F 0.75) which was not further investigated but was presumed to be the regioisomer **57**. The acetonitrile was evaporated and the residue was partitioned between ether (50 mL) and water (50 mL). The ether layer was separated and stirred with saturated aq. sodium hydrogencarbonate (200 mL) for 1 h, the mixture was filtered through Celite, and the ether layer was dried (K_2CO_3) and concentrated. Column chromatography (5:1 light petroleum ether followed by 3:1) of the residue gave **55**, isolated as a syrup (R_F 0.8, 880 mg, 76%), and **57** (R_F 0.75, 220 mg). The acetate (**56**) of **55** had m.p. 122–124° (from light petroleum). ^{1}H-N.m.r. data: δ 1.91 (s, 3 H, Ac), 3.19–3.53 (m, 3 H, H-1,3,5), 3.81 (s, 3 H, OMe), 4.45–4.86 (m, 10 H, 5 C*H*$_2$Ph), 5.63 (t, 1 H, *J* 9.77 Hz, H-6), 6.79–7.28 (m, 24 H, aromatic) (Found: C, 75.23; H, 6.58. $C_{44}H_{46}O_8$ calc.: C, 75.19; H, 6.60%.

Removal of the *O-p*-methoxybenzyl group from **55** (using dichlorodicyanobenzoquinone as described above) gave racemic 1,2,4,5-tetra-*O*-benzyl-*myo*-inositol (**71**)

identical with the material described below and which gave an acetate identical with **72** described below, thus establishing the structure of **55**.

1D-2,3,5,6-Tetra-O-*benzyl-1*-O-p-*methoxybenzyl*-myo-*inositol* (**63**). — The benzylation described in the previous section was repeated with the dibutylstannylene derivative **62** of the chiral diol **61** to give, as the major product, **63**, m.p. 62–64°, $[\alpha]_D^{25}$ + 8.5° (*c* 1, $CHCl_3$) (Found: C, 74.38; H, 6.67. $C_{42}H_{44}O_7 \cdot H_2O$ calc.: C, 74.31; H, 6.83%).

Removal of the *O-p*-methoxybenzyl group from **63** gave 1D-2,3,5,6-tetra-*O*-benzyl-*myo*-inositol (**82**) as described below.

(±)-*1,2,4,5-Tetra*-O-*benzyl-3,6-di*-O-(cis-*prop-1-enyl)*-myo-*inositol* (**70**). — Racemic 1,4-di-*O*-allyl-*myo*-inositol[13] (**67**) was treated with an excess of benzyl bromide and sodium hydride in *N,N*-dimethylformamide in the usual way to give the tetrabenzyl ether **69** as a syrup (R_F 0.6; 1:2 ether–light petroleum). This product was treated[14] with potassium *tert*-butoxide in dry Me_2SO and the reaction was monitored by t.l.c. (as above), which showed conversion of **69** into monoallyl-mono(prop-1-enyl) ethers (R_F 0.65) and **70** (R_F 0.7). The product was isolated in the usual way to give **70**, m.p. 95–97° (from light petroleum containing a little triethylamine). ^{1}H-N.m.r. data: δ 1.59 – 1.70 (m, 6 H, 2 =CH*Me*), 3.28–3.59 (m, 3 H, H-1,3,5), 3.94–4.51 (m, 5 H, 2 =C*H*Me and H-2,4,6), 4.59, 4.75, 4.77, 4.83 (4 s, 8 H, 4 CH_2Ph), 6.08, 6.26 (2 dd, 2 H, *J* 1.83 and 6.10 Hz, 2 OCH=) (Found: C, 77.43; H, 7.26. $C_{40}H_{44}O_6$ calc.: C, 77.39; H, 7.15%).

(±)-*3,6-Di*-O-*acetyl-1,2,4,5-tetra*-O-*benzyl*-myo-*inositol* (**72**). — Compound **70** was treated with 1:9 M HCl–acetone at reflux for 30 min. An excess of sodium hydrogencarbonate was added, the solvents were evaporated, and the syrupy **71** was extracted from the residue with ether. ^{1}H-N.m.r. data: δ 2.27 (d, 1 H, *J* 6.1 Hz, OH), 2.52 (d, 1 H, *J* 1.8 Hz, OH), 3.22–4.28 (m, 6 ring protons), 4.63–5.00 (m, 8 H, 4 CH_2Ph), 7.32 (s, 20 H, aromatic).

The diacetate (**72**) of **71** had m.p. 128–129° (from 1:25 EtOAc–light petroleum). ^{1}H-N.m.r. data: δ 1.91 (s, 6 H, 2 Ac), 3.37–3.58 (m, 2 H, H-1,5), 4.03–4.24 (m, 2 H, H-2,4), 4.50–4.93 (m, 9 H, 4 CH_2Ph and H-3), 5.63 (t, 1 H, *J* 10.0 Hz, H-6), 7.27, 7.29 (2 s, 20 H, aromatic) (Found: C, 73.26; H, 6.47. $C_{38}H_{40}O_8$ calc.: C, 73.06; H, 6.45%).

1D- (**76**) *and 1L-* (**80**) *1,2,4,5-Tetra*-O-*benzyl-3,6-di*-O-[(−)-*ω-camphanoyl]*-myo-*inositol*. — The racemic diol **71** (regenerated from **72**) was converted into the mixture of diastereoisomeric bis-(−)-*ω*-camphanates **73** and the products were isolated in the usual way (see above). ^{1}H-N.m.r. data: δ 0.73 (3 H), 0.76 (3 H), 0.83 (3 H), 0.88 (3 H), 0.94 (9 H), 0.99 (3 H), 1.03 (6 H), 1.07 (6 H), (8 s, 12 CMe of the camphanate portions). The mixture **73** (370 mg) was crystallised from EtOAc–light petroleum to give **76** (123 mg, 66% of this diastereoisomer), m.p. 234–236°, $[\alpha]_D^{25}$ + 1.1° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 0.76, 0.89, 0.93, 0.99, 1.04, 1.08 (6 s, 18 H, 6 CMe of the camphanate portion), 3.58–3.79 (m, 2 H, H-1,5), 4.15–4.36 (m, 2 H, H-2,4), 5.84 (t, 1 H, *J* 9.76 Hz, H-6), 7.23, 7.25, 7.29 (3 s, 20 H, aromatic) (Found: C, 71.46; H, 6.41. $C_{54}H_{60}O_{12}$ calc.: C, 71.98; H, 6.71%).

Recrystallisation of the material in the mother liquors (as above) gave a mixture of diastereoisomers (from n.m.r.) and further recrystallisation of the material remaining in these mother liquors, from MeOH, gave **80** (90 mg, 48% of this diastereoisomer), m.p. 192–194°, $[\alpha]_D^{25}$ − 7.7° (*c* 1, $CHCl_3$). ^{1}H-N.m.r. data: δ 0.73 (3 H), 0.83 (3 H), 0.95 (6

H), 1.03 (3 H), 1.07 (3 H), (5 s, 6 CMe of the camphanate portion) (Found: C, 71.86; H, 6.79%).

1D-1,2,4,5-Tetra-O-*benzyl*-myo-*inositol* (**77**). — Saponification of **76** with NaOH in MeOH gave **77**, m.p. 105–107° (from ethyl acetate–light petroleum), $[\alpha]_D^{25}$ −4.3° (*c* 1, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of the racemate **71** (Found: C, 75.83; H, 6.78. $C_{34}H_{36}O_6$ calc.: C, 75.53; H, 6.71%).

The diacetate (**78**) of **77** had m.p. 132–133°, $[\alpha]_D^{25}$ +23.5° (*c* 1, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of the racemate **72** (Found: C, 73.22; H, 6.35. $C_{38}H_{40}O_8$ calc.: C, 73.06; H, 6.45%).

Comparison of **77** and **78** with the enantiomers **82** and **83**, prepared as described below from 1D-2,3,5,6-tetra-*O*-benzyl-1-*O*-*p*-methoxybenzyl-*myo*-inositol (**63**), established the absolute configurations of these compounds.

1D-2,3,5,6-Tetra-O-*benzyl-1,4-di*-O-[(+)-*ω*-*camphanoyl]*-myo-*inositol* (**81**). — The contents of the mother liquors obtained above, after the first crystallisation of **76** from the mixture **73**, were saponified with NaOH in MeOH, and the diol **71** (2 g, enriched in the enantiomer **82**) was converted into the mixture of (+)-*ω*-camphanates **74** (enriched with **81**) in the usual way. Crystallisation of the product (3 g) from 1:8 EtOAc–MeOH gave **81** (2 g), m.p. 229–231°, $[\alpha]_D^{25}$ −1.9° (*c* 1, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of its enantiomer **76** (Found: C, 71.84; H, 6.58. $C_{54}H_{60}O_{12}$ calc.: C, 71.98; H, 6.71%).

1D-2,3,5,6-Tetra-O-*benzyl*-myo-*inositol* (**82**). — (*a*) Saponification of **81** with NaOH in MeOH gave **82**, m.p. 105–107°, $[\alpha]_D^{25}$ +3.9° (*c* 1, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of the racemate **71** described above (Found: C, 75.37; H, 6.86. $C_{34}H_{36}O_6$ calc.: C, 75.53; H, 6.71%).

The diacetate (**83**) of **82** had m.p. 132–133°, $[\alpha]_D^{25}$ −27° (*c* 1, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of its enantiomer **78** and racemate **72** (Found: C, 73.01; H, 6.49. $C_{38}H_{40}O_8$ calc.: C, 73.06; H, 6.45%).

(*b*) Treatment of **63** (146 mg) with dichlorodicyanobenzoquinone in CH_2Cl_2–water (as described above) and monitoring the reaction by t.l.c. (1:1 EtOAc–light petroleum) showed conversion of **63** (R_F 0.5) into a major product (R_F 0.4) and less polar by-products. Column chromatography (1:1 ether–light petroleum followed by 2:1) of the mixture gave **82** (94 mg), m.p. 101–103° (from light petroleum), $[\alpha]_D^{25}$ +4.6° (*c* 0.55, $CHCl_3$), with a ^{1}H-n.m.r. spectrum identical with that of the racemate **71** described above (Found: C, 75.36; H, 7.04. $C_{34}H_{36}O_6$ calc.: C, 75.53; H, 6.71%).

The diacetate (**83**) of **82** had properties identical with those described in (*a*).

1D-1,2,4,5-Tetra-O-*benzyl-3,6-di*-O-*octyl*-myo-*inositol* (**79**). — A mixture of **77** (370 mg, 0.68 mmol), sodium hydride (200 mg), and octyl bromide (500 mg, 2.6 mmol) in *N,N*-dimethylformamide was stirred at 20° for 20 h when t.l.c. (1:2 ether–light petroleum) showed conversion of **77** (R_F 0.1) into a product (R_F 0.75). Methanol was added to destroy the excess of sodium hydride, the solution was diluted with water and extracted with ether, and the extract was dried (K_2CO_3) and concentrated. Column chromatography (1:4 ether–light petroleum) of the residue gave **79** (490 mg), m.p. 44–46° (from MeOH), $[\alpha]_D^{25}$ −9.8° (*c* 1, $CHCl_3$) (Found: C, 78.76; H, 9.30. $C_{50}H_{68}O_6$ calc.: C, 78.49; H, 8.96%).

*1D-3,6-Di-O-octyl-*myo*-inositol* (**86**). — A solution of **79** (400 mg) in EtOH (10 mL) was stirred with Pd/C (10% Fluka, 300 mg) under hydrogen at atmospheric pressure for 24 h, then filtered, and the solvent evaporated. Recrystallisation of the product (199 mg, 96%) from EtOAc gave **86**, $[\alpha]_D^{25}$ +14.1° (*c* 1, MeOH) (Found: C, 65.63; H, 10.87. $C_{22}H_{44}O_6$ calc.: C, 65.31; H, 10.96%).

This material showed liquid crystalline behaviour with the crystals 'melting' at 130–132° to liquid crystals which changed to a clear liquid at 168–170°. These figures were confirmed[25] by differential scanning calorimetry and polarisation microscopy which also showed a phase change in the crystals around 64°.

*(±)-1,2:4,5-Di-O-isopropylidene-3,6-di-O-octyl-*myo*-inositol* (**66**). — A mixture of racemic 1,2:4,5-di-*O*-isopropylidene-*myo*-inositol[15] (**65**; 2 g, 7.7 mmol), octyl bromide (4 g, 20.7 mmol), and sodium hydride (500 mg, 20.8 mmol) in *N,N*-dimethylformamide (30 mL) was stirred for 16 h at 20°. T.l.c. (1:2 ether–light petroleum) then showed a major product (R_F 0.75). Methanol was added to destroy the excess of sodium hydride, the solution was diluted with water, the crystalline product was collected, and a solution in ether was dried (K_2CO_3) and passed through basic alumina in ether to remove polar contaminants. Evaporation of the solvent gave **66**, m.p. 84–85° (from light petroleum). ^{1}H-N.m.r. data: δ 0.81–0.93 (m, 6 H, 2 CH_2*Me*), 1.27 (s, 24 H, CH_2 of the octyl chain), 1.37 (3 H), 1.44 (6 H), 1.55 (3 H), (3 s, 2 CMe_2), 3.18–4.11 (m, 10 H, ring protons and 2 OCH_2-), 4.47 (t, 1 H, *J* 4.6 Hz, H-2) (Found: C, 69.50; H, 10.33. $C_{28}H_{52}O_6$ calc.: C, 69.38; H, 10.81%).

*(±)-3,6-Di-O-octyl-*myo*-inositol*[16] (**68**). — Compound **66** was heated for 1 h at 100° with 4:1 acetic acid–water. The solvents were evaporated and toluene was evaporated from the residue which was recrystallised from EtOAc to give **68**. This showed liquid crystalline behaviour[16] with crystals 'melting' at 141° to liquid crystals which changed to a clear liquid at 171° (Found: C, 65.42; H, 10.75. $C_{22}H_{44}O_6$ calc.: C, 65.31; H, 10.96%).

*(±)-1,2,4,5-Tetra-O-benzyl-*myo*-inositol 3,6-bis[di(2-cyanoethyl) phosphate]* (**75**). — The racemic diol **71** was treated with bis-(2-cyanoethoxy)diisopropylaminophosphine (**20**) and the bisphosphite produced was oxidised[1] to the bisphosphate with *m*-chloroperoxybenzoic acid to give a major product (R_F 0.6; 15:1 $CHCl_3$–MeOH). Column chromatography (same solvent system) gave **75** (59%), m.p. 96–98° (from EtOAc–ether). ^{31}P-N.m.r. data: δ −3.10, −2.42 (Found: C, 60.53; H, 5.51; N, 6.16; P, 6.87. $C_{46}H_{50}N_4O_{12}P_2$ calc.: C, 60.52; H, 5.52; N, 6.14; P, 6.79%).

*1D-2,3,5,6-Tetra-O-benzyl-*myo*-inositol 1,4-bis(dibenzyl phosphate)* (**85**). — The diol **82** was treated[1] with bis(benzyloxy)diisopropylaminophosphine (**21**). T.l.c. (1:1 ether–light petroleum) showed conversion of **82** (R_F 0.3) into the bisphosphite **84** (R_F 0.95) which was oxidised[1] with *m*-chloroperoxybenzoic acid to give **85** (R_F 0.5, ether). Column chromatography (ether) gave **85** (64%), m.p. 79–81° (from ether–light petroleum), $[\alpha]_D^{25}$ +4.4° (*c* 1, $CHCl_3$). ^{31}P-N.m.r. data: δ −1.55 (Found: C, 69.98; H, 5.48; P, 6.03. $C_{62}H_{62}O_{12}P_2$ calc.: C, 70.18; H, 5.89; P, 5.84%).

*2,4,5,6-Tetra-O-benzyl-1,3-di-O-(*cis*-prop-1-enyl)-*myo*-inositol* (**90**). — Treatment of racemic 1,3-di-*O*-allyl-2,6-di-*O*-benzyl-*myo*-inositol[1] (**88**) or 1,3-di-*O*-allyl-*myo*-inositol[5] (**87**) with an excess of benzyl bromide and sodium hydride in *N,N*-

dimethylformamide and isolation of the products in the usual way gave 1,3-di-*O*-allyl-2,4,5,6-tetra-*O*-benzyl-*myo*-inositol (**89**) as a syrup. This product was treated with potassium *tert*-butoxide in dry Me_2SO for 3 h at 50°. A small portion of the mixture was added to saturated aq. KCl and the mixture was extracted with ether. T.l.c. (1:2 ether–light petroleum) of the extract showed a product (R_F 0.6) which co-migrated with **89**. The contents of the ether extract were treated with 1:10 M HCl–acetone at reflux for 15 min. T.l.c. (as above) showed complete conversion of the product (R_F 0.6) into a new product (R_F 0), indicating that the conversion of **89** into **90** was complete. The mixture was diluted with semi-saturated aq. KCl and the product was extracted with ether to give **90**, m.p. 80–81° (from light petroleum containing a little triethylamine). ^{1}H-N.m.r. data: δ 1.67 (dd, 6 H, *J* 1.83 and 6.71 Hz, 2 =CH*Me*), 3.44 (t, 1 H, *J* 9.15 Hz, H-5), 3.58 (dd, 2 H, *J* 2.44 and 9.86 Hz, H-1,3), 3.98–4.19 (m, 3 H, H-2,4,6), 4.77 (2 H), 4.80 (2 H), 4.84 (4 H), (3 s, 8 H, 4 C*H*$_2$Ph), 6.10 (dd, 2 H, *J* 1.83 and 6.1 Hz, 2 OCH =), 7.21–7.72 (m, 20 H, aromatic) (Found: C, 77.66; H, 7.46. $C_{40}H_{44}O_6$ calc.: C, 77.39; H, 7.15%).

*1,3-Di-*O*-benzoyl-2,4,5,6-tetra-*O*-benzyl-*myo*-inositol* (**93**). — Compound **90** was heated under reflux in 1:10 M HCl–acetone for 30 min. An excess of sodium hydrogencarbonate was added, the solvents were evaporated, and the residue was extracted with CH_2Cl_2 to give the diol **91** as a syrup. ^{1}H-N.m.r. data: δ 2.28 (d, 2 H, *J* 5.5 Hz, 2 OH), 3.36–3.92 (m, 5 H, H-1,3,4,5,6), 3.99 (t, 1 H, *J* 2.44 Hz, H-2), 4.80 (s, 2 H, C*H*$_2$Ph), 4.84 (ABq, 2 H, C*H*$_2$Ph), 4.87 (s, 4 H, 2 C*H*$_2$Ph), 7.30, 7.32 (2 s, 20 H, aromatic).

The diacetate (**92**) of **91** was a syrup. ^{1}H-N.m.r. data: δ 1.91 (s, 6 H, 2 Ac), 3.58 (t, 1 H, *J* 9.8 Hz, H-5), 3.95–4.17 (m, 3 H, H-2,4,6), 4.62–4.98 (m, 10 H, 4 C*H*$_2$Ph and H-1,3), 7.28, 7.32 (2 s, 20 H, aromatic).

The dibenzoate (**93**) of **91** had m.p. 122–123° (from MeOH). ^{1}H-N.m.r. data: δ 3.73 (t, 1 H, *J* 9.15 Hz, H-5), 4.18–4.40 (m, 3 H, H-2,4,6), 4.66 (2 H), 4.80 (4 H), 4.90 (2 H), (3 s, 8 H, 4 C*H*$_2$Ph), 5.30 (dd, 2 H, *J* 9.76 and 2.44 Hz, H-1,3), 7.14, 7.19, 7.29, 7.40, 7.49, 7.58, 7.94, 7.96, 8.03 (m, 30 H, aromatic) (Found: C, 76.55; H, 6.00. $C_{48}H_{44}O_8$ calc.: C, 76.98; H, 5.92%).

*2,4,5,6-Tetra-*O*-benzyl-*myo*-inositol 1,3-bis(dibenzyl phosphate)* (**95**). — The diol **91** was treated[1] with bis(benzyloxy)diisopropylaminophosphine (**21**). The reaction was monitored by t.l.c. (1:1 ether–light petroleum) which showed conversion of **91** (R_F 0.1) into the bisphosphite **94** (R_F 0.95). The bisphosphite was oxidised[1] with *m*-chloroperoxybenzoic acid to give **95** (R_F 0.7, ether) which was isolated in the usual way[1]. Column chromatography (4:1 ether–light petroleum followed by ether) gave **95** (78%) as a syrup. ^{31}P-N.m.r. data: δ −1.48 (Found: C, 69.74; H, 5.89; P, 5.45. $C_{62}H_{62}O_{12}P_2$ calc.: C, 70.18; H, 5.89; P, 5.84%).

*2,4,5,6-Tetra-*O*-benzyl-*myo*-inositol 1,3-bis(sodium benzyl phosphate)* (**96**). — A solution of **95** (629 mg) and sodium iodide (1.24 g) in acetone (30 mL) was heated under reflux for 4 h. T.l.c. (90:10:1 $CHCl_3$–MeOH–acetic acid) of portions of the solution acidified and extracted as described above showed conversion of **95** (R_F 0.7) through an intermediate product (R_F 0.3) into a product (R_F 0.1). The solution was cooled and the product (329 mg), which crystallised out, was washed with cold acetone, and had m.p. 239–242°. ^{31}P-N.m.r. data (D_2O): δ −0.47 (Found: C, 56.41; H, 5.54; P, 5.88; Na, 5.40. $C_{48}H_{48}Na_2O_{12}P_2 \cdot 5H_2O$ calc.: C, 56.80; H, 5.76; P, 6.10; Na, 4.53%).

2,5-Di-O-benzyl-myo-*inositol 1,3,4,6-tetrakis(dibenzyl phosphate)* (**98**). — 2,5-Di-*O*-benzyl-*myo*-inositol[1] was treated[1] with bis(benzyloxy)diisopropylaminophosphine (**21**). T.l.c. (15:1 $CHCl_3$–MeOH) showed conversion of the starting material (R_F 0) into the tetrakisphosphite (R_F 0.95), which was oxidised[1] with *m*-chloroperoxybenzoic acid to give **98** (R_F 0.3). The product was isolated in the usual way[1] and column chromatography (ether followed by ethyl acetate) gave **98** (70%), isolated as a syrup. ^{31}P-N.m.r. data: δ −1.82, −1.28 (Found: C, 64.90; H, 5.57; P, 8.35. $C_{76}H_{76}O_{18}P_4$ calc.: C, 65.14; H, 5.47; P, 8.84%).

2,5-Di-O-benzyl-myo-*inositol 1,3,4,6-tetrakis(sodium benzyl phosphate)* (**99**). — A solution of **98** (1.34 g) and sodium iodide (2 g) in acetone (50 mL) was heated under reflux for 4 h. During this time, portions of the solution were acidified and extracted as described above, and t.l.c. (90:10:1 $CHCl_3$–MeOH–acetic acid) of the extracts showed conversion of **98** (R_F 0.7) through intermediate products (R_F 0.5, 0.4, and 0.2) into a product (R_F 0). The solution was cooled, and the product **99** which crystallised out (1.04 g) was collected and washed with cold acetone, and had m.p. 313–316° (dec.) (from 4:1 EtOH–water). ^{31}P-N.m.r. data (D_2O): δ −0.40 (Found: C, 49.73; H, 4.70; P, 9.85; Na, 8.07. $C_{48}H_{48}Na_4O_{18}P_4{\cdot}2H_2O$ calc.: C, 49.49; H, 4.50; P, 10.64; Na, 7.90%).

1D-2,6-Di-O-benzyl-myo-*inositol 1,3,4,5-tetrakis(sodium benzyl phosphate)* (**101**). — A solution of syrupy 1D-2,6-di-*O*-benzyl-*myo*-inositol-1,3,4,5-tetrakis(dibenzyl phosphate)[1] (**100**, 456 mg) and sodium iodide (666 mg) in dry acetone (20 mL) was heated under reflux for 3.5 h. T.l.c. (90:10:1 $CHCl_3$–MeOH–acetic acid) of acidified samples (prepared as described above) showed conversion of **100** (R_F 0.7) through intermediate products (R_F 0.6, 0.5 and 0.2) into **101** (R_F 0), which had crystallised from the mixture. The hygroscopic crystals (333 mg, 97%), which were collected and washed with cold acetone, had m.p. 297–300° (dec.) (from EtOH–acetone), $[\alpha]_D^{25}$ +3.8° (*c* 1, MeOH). ^{31}P-N.m.r. data (D_2O): δ −0.40 (3 P), −0.20 (1 P) (Found: C, 48.67; H, 4.60; P, 10.15; Na, 7.48. $C_{48}H_{48}Na_4O_{18}P_4{\cdot}3H_2O$ calc.: C, 48.74; H, 4.60; P, 10.47; Na, 7.78%).

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