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The preparation of racemic and enantiomerically pure *myo*-inositol derivatives as intermediates for the synthesis of phosphatidylinositol 3-, 3,4-bis-, and 3,4,5-tris-phosphates and for the synthesis of analogues of 1D-*myo*-inositol 1,3,4,5-tetrakisphosphate [1]

Trupti Desai, Jill Gigg, Roy Gigg *, Eloisa Martín-Zamora [2]

Division of Lipid and General Chemistry, National Institute for Medical Research, Mill Hill, London NW7 1AA, UK

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Abstract

Details of the products obtained by the tin-mediated allylation and benzylation of 1,2-*O*-isopropylidene-*myo*-inositol, which were previously described in a preliminary communication, are provided here. Some of the products from these reactions, particularly 3,4,6-tri-*O*-allyl- and 3,5,6-tri-*O*-allyl-1,2-*O*-isopropylidene-*myo*-inositol, have been used to prepare intermediates for the synthesis of the title compounds. The syntheses of the following are described: 1L-2,4,5,6-tetra-*O*-benzyl-1-*O*-*p*-methoxybenzyl-*myo*-inositol (an intermediate for phosphatidylinositol 3-phosphate), 1L-2,4,5-tri-*O*-benzyl-*myo*-inositol 1,6-bis(dibenzyl phosphate) and 1L-2,4,5-tri-*O*-benzyl-1,6-di-*O*-*p*-methoxybenzyl-*myo*-inositol (intermediates for phosphatidylinositol 3,4-bisphosphate), 1L-2,4-di-*O*-benzyl-*myo*-inositol 1,5,6-tris(dibenzyl phosphate) and (±)-2,4-di-*O*-benzyl-1,5,6-tri-*O*-*p*-methoxybenzyl-*myo*-inositol (intermediates for phosphatidylinositol 3,4,5-trisphosphate). Some of the intermediates used in the above preparations were also used for the synthesis of

* Corresponding author.

[1] The Allyl Group for Protection in Carbohydrate Chemistry, Part 32. For Part 31, see ref. [1]. Presented in part at the Royal Society of Chemistry, Carbohydrate Group (Exeter, April 20–22, 1994) and Lipid Group (Bangor, September 15–16, 1994) and at EUROCARB VIII, the VIIIth European Symposium on Carbohydrates, Seville, Spain, July 2–7, 1995 (Abstract AO-1). Part of this work is described in a Thesis [2]. For Preliminary communications see refs. [3–5].

[2] Visiting scientist from the University of Seville, Spain.

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myo-inositol derivatives suitable for the preparation of analogues of 1D-*myo*-inositol 1,3,4,5-tetrakisphosphate. Thus 1L-2,4-di-*O*-benzyl-5-*O*-*p*-methoxybenzyl-*myo*-inositol (for a 5-phosphorothioate analogue), crystalline 1L-2,4-di-*O*-benzyl-1-*O*-*p*-methoxybenzyl-*myo*-inositol 3,5,6-tris(dibenzyl phosphate), and crystalline 1D-2,6-di-*O*-benzyl-*myo*-inositol 1,4,5-tris(dibenzyl phosphate) (for a 3-phosphorothioate analogue) were prepared. The possibilities of using the latter compound in syntheses of tritium-labelled 1D-*myo*-inositol 1,4,5-trisphosphate and 1,3,4,5-tetrakisphosphate are discussed. © 1996 Elsevier Science Ltd.

Keywords: Phosphatidylinositol 3-, 3,4-bis-, and 3,4,5-tris-phosphates; Chiral *myo*-inositol derivatives; Tin-mediated alkylations; Allyl ethers; *p*-Methoxybenzyl ethers; 1D-*myo*-Inositol 1,3,4,5-tetrakisphosphate analogues

1. Introduction

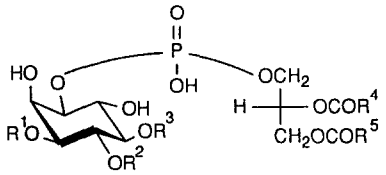
The phosphatidylinositols **1–3** were discovered by Folch and Woolley [6] in the 1940s and their structures were established by Ballou and Brown and their co-workers [7] in the 1960s (see ref. [8] for reviews). In the 1950s the Hokins [9] discovered that there was a rapid biological turnover of **1** in the presence of various hormones and eventually in 1983 Berridge and his co-workers [10] showed that phosphatidylinositol 4,5-bisphosphate (**3**) was the precursor of a new second messenger 1D-*myo*-inositol 1,4,5-trisphosphate (IP_3, **7**) which was produced by the action of a phospholipase C on **3**. The resultant extensive biological interest has led to intensive chemical studies [11] during the last decade on the synthesis of the many inositol phosphates (and analogues) which are metabolites of **7** (Scheme 1).

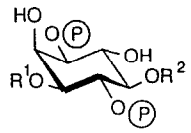
In 1987 new phosphatidylinositols, which were produced only after the interaction of cells with growth factors and other agonists, were discovered by Cantley [12] and Traynor-Kaplan [13] and their co-workers. Subsequently these were characterised as the 3-phosphorylated phosphatidylinositols **4–6** which were produced after the activation of a phosphatidylinositol 3-kinase (PI-3-kinase) by the growth factors. The possibility that these lipids **4–6**, which were not hydrolysed by phospholipase C, might act as novel second messengers has stimulated a considerable amount of biological work concerning the function of the lipids **4–6** and of the PI-3-kinase, and this has been the subject of numerous reviews; the more recent ones are listed in refs. [14–16].

Because of this intense biological interest in the 3-phosphorylated lipids [particularly in phosphatidylinositol 3,4-bis- (**5**) and 3,4,5-tris-phosphate (**6**)] synthetic work in this area has also flourished [4,14,17,18]. For our work in this area [4] many chiral inositol derivatives were required and we describe here our approach to these.

2. Results and discussion

*Tin-mediated alkylation of 1,2-*O*-isopropylidene-*myo*-inositol* (**11**).—We have been able to prepare several of the enantiomerically pure *myo*-inositol derivatives required for this work from the products obtained by the tin-mediated allylation of (±)-1,2-*O*-isopropylidene-*myo*-inositol (**11**), which we have described in a preliminary communication





* **1** $R^1 = R^2 = R^3 = H$

2 $R^1 = R^3 = H$; $R^2 = (P)$

3 $R^1 = H$; $R^2 = R^3 = (P)$

4 $R^1 = (P)$; $R^2 = R^3 = H$

5 $R^1 = R^2 = (P)$; $R^3 = H$

6 $R^1 = R^2 = R^3 = (P)$

7 $R^1 = H$; $R^2 = (P)$

8 $R^1 = R^2 = (P)$

9 $R^1 = PS(OH)_2$; $R^2 = (P)$

10 $R^1 = (P)$; $R^2 = PS(OH)_2$

R^4 and R^5 = long-chain alkyl

(P) = $PO(OH)_2$

* In the formulae, racemic inositol derivatives are indicated with (±) in the ring; enantiopure 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.

All = CH_2-CH=CH_2; Bn = CH_2Ph; pMB = CH_2Ph(*p*OMe); Crot = CH_2-CH=CH-Me

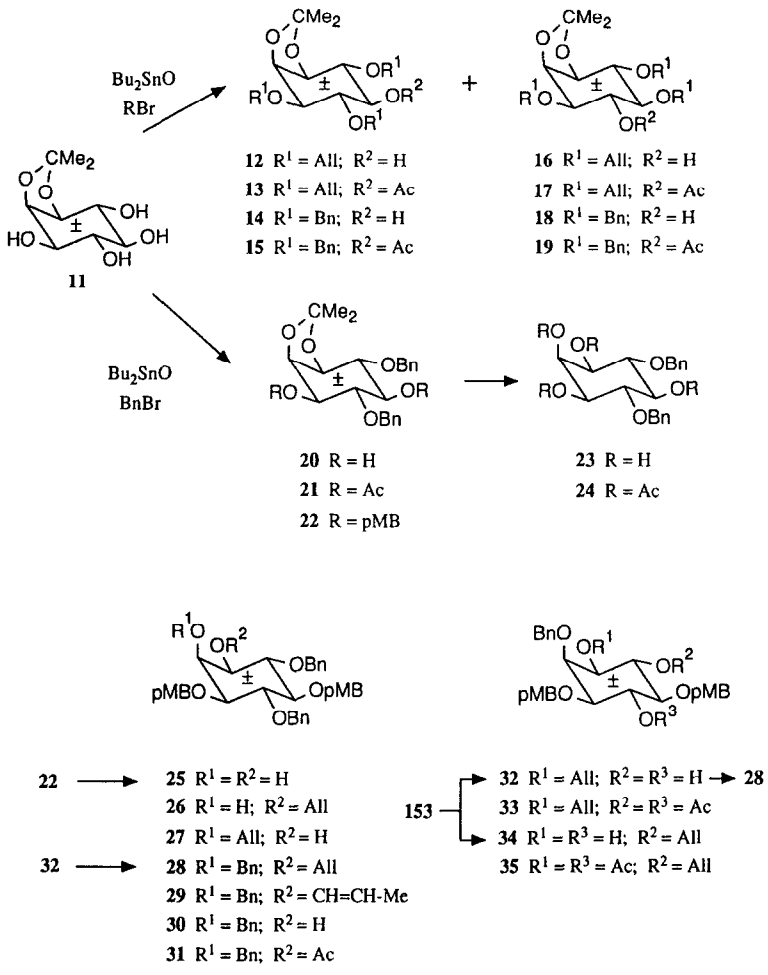
Scheme 1.

[3], and details of this work are given here. The two major products obtained in this reaction using allyl bromide were **12** and **16**, and these have been key intermediates in this work. When benzyl bromide was used in the tin-mediated alkylation of **11** the major products were **14** and **18**, and in this reaction a minor product **20** was isolated and characterised. Compounds **14** and **18**, which were identical with the products obtained by the tin-mediated benzylation of racemic 1,4-di-*O*-benzyl-2,3-*O*-isopropylidene-*myo*-inositol **57** [19], were used to establish the structure of **12** and for that reason are described here (Scheme 2).

The triallyl ethers **16** and **12** were characterised as follows: acid hydrolysis of **16** gave the known [20] crystalline triol **36** which gave the known triacetate **37**. Methylation of **36** gave **38** and this, on deallylation with Pd–C [21], gave the triol **40** which was characterised as the triacetate **41**. Similar treatments of **12** gave **47** via **42**, **44**, and **46** (Scheme 3).

The tin-mediated alkylation of **11** was repeated with crotyl bromide in place of allyl bromide to give similar results and the corresponding crystalline triols **51** and **55** were obtained from the major products after acid hydrolysis.

For characterisation of the tribenzyl ethers **14** and **18** the process of acid hydrolysis, methylation, and hydrogenolysis gave **41** from **18** (via **58**, **61**, and **40**) which established the structure of **18** by correlating **58** with the known **36**. The other product must therefore have structure **14** (because it was obtained together with **18** from **57**) and

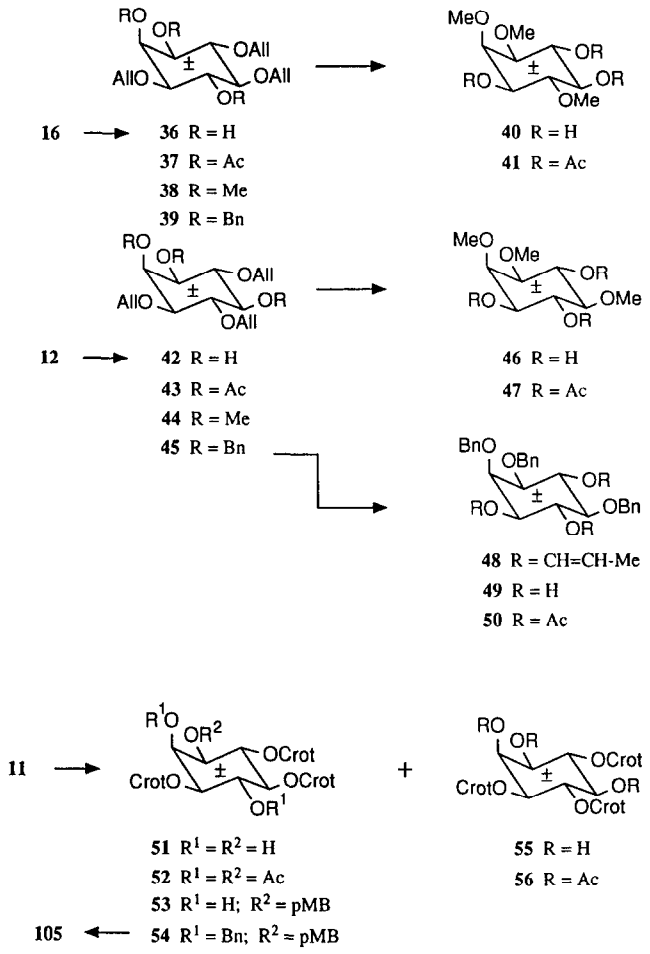


Scheme 2.

because the conversion of **14** (via **62**, **65**, and **46**) gave **47**, this also established the structure of **12** (Scheme 4).

The minor product **20** from the tin-mediated benzylation of **11** was converted into the tetraol **23** and the ^{1}H NMR spectrum of the derived tetraacetate **24** indicated its symmetrical structure. Compound **20** is the only dibenzyl ether available from **11** which on hydrolysis would give a symmetrical tetraol such as **23**.

For purposes other than those in the title, the alcohol **30** was required and a route to this from **20** was investigated. *p*-Methoxybenzylation of **20** gave **22** and this gave the crystalline diol **25** on acid hydrolysis. Tin-mediated allylation of **25** gave crystalline **26** which was benzylated to give **28**. Since **20** was not available in quantity from the tin-mediated benzylation described above, a further route to **28**, from a more readily available starting material (**153**, see below), was investigated. Tin-mediated allylation of

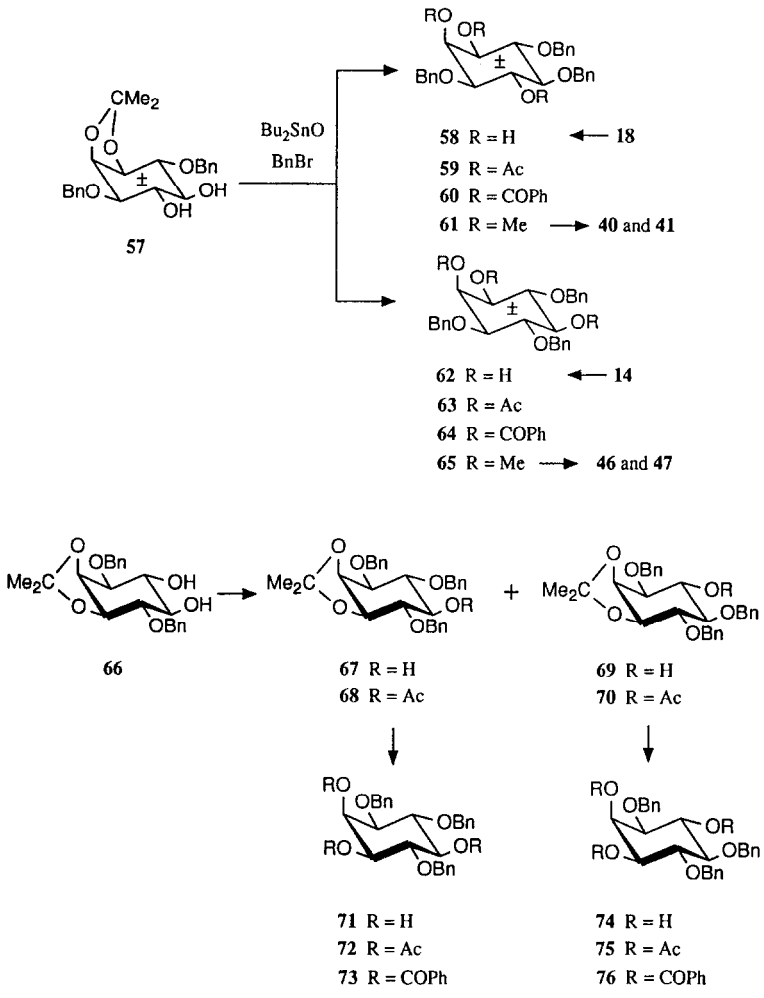


Scheme 3.

153 gave an inseparable mixture of **32** and **34** but the corresponding diacetates **33** and **35** could be separated by column chromatography. Saponification of **33** (the major product) gave **32** which was benzylated to give **28** identical with the material prepared from **20**.

The allyl group was removed from **28** by isomerisation to the crystalline *cis*-prop-1-enyl ether **29**; subsequent acid hydrolysis gave the required alcohol **30** and this was purified via the crystalline acetate **31**.

Tin-mediated benzylation of 1D-*1,4-di-*O*-benzyl-2,3-*O*-isopropylidene*-myo-*inositol* (**66**).—Tin-mediated benzylation of enantiopure **66** [19] gave the mixture of alcohols **67** and **69** which were separated as described for the corresponding racemic mixtures **14** and **18**. These were hydrolysed with acid to give the triols **71** and **74** (corresponding to the racemic mixtures **62** and **58**) and these were converted into the acetates **72** and **75**,

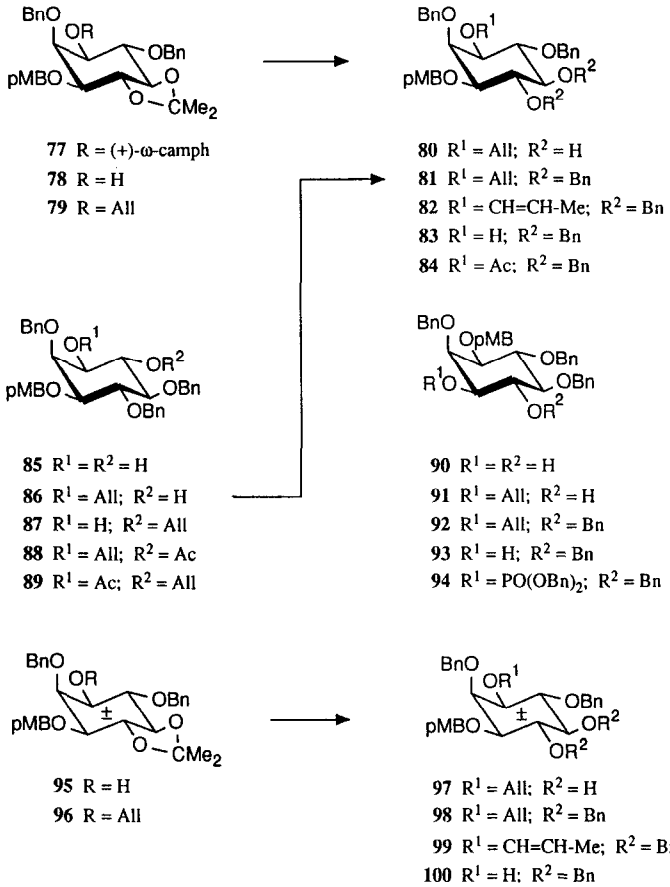


Scheme 4.

and benzoates **73** and **76**, respectively. These compounds will be used for the purposes described in the preliminary communication [3].

Intermediates for the synthesis of phosphatidylinositol 3-phosphate (**4**).—The (+)-ω-camphanate **77** [22] was saponified to give **78** and this was converted into the allyl ether **79**. Acid hydrolysis of **79** gave the crystalline diol **80** which was benzylated to give crystalline **81**. Isomerisation [23] of the allyl group with potassium *tert*-butoxide in dimethyl sulfoxide gave the *cis*-(prop-1-enyl) ether **82** and this on acid hydrolysis gave the crystalline alcohol **83** which gave a crystalline acetate **84** (Scheme 5).

Initial experiments for this route were carried out with racemic material and the constants for the products are recorded in the Experimental section together with those of the corresponding enantiopure products. For the racemic compounds the starting



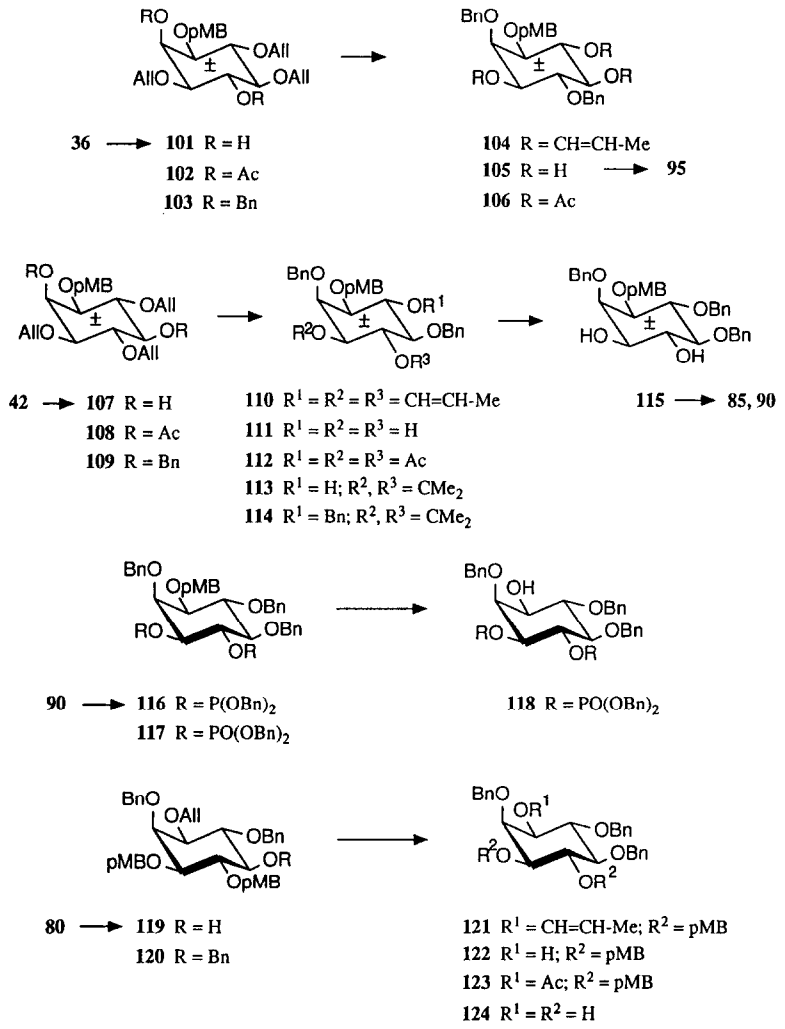
Scheme 5.

material was the alcohol **95** [22] which was taken through the same sequence of reactions via **96–99** to give **100**.

As an alternative approach to **83**, the enantiopure diol **85** (see Experimental section) was subjected to tin-mediated allylation to give, as the major product, crystalline **86** which gave a crystalline acetate **88**. Benzylation of **86** gave **81** identical with the material described above and this was converted into **83** as described above.

Compound **83** is suitable for coupling to a phosphorylated diglyceride to give an intermediate for the synthesis of **4**. Application of the above route to the enantiomer **90** [24] of **85** will give **93** (the enantiomer of **83**) which could be converted into the dibenzyl phosphate **94** which is another potential intermediate for the synthesis of **4**.

The routes described above to **83** and **93** (and some of the routes described below) made use of the racemic analogues **95** and **115** of the enantiopure compounds **78** and **85**, respectively. With compounds **12** and **16** available from the tin-mediated allylation of **11**, as described above, new syntheses of **95** and **115**, preferable to those described previously [22,24], were developed.



Scheme 6.

Tin-mediated *p*-methoxybenzylation of the triol **36** gave **101** which was benzylated to give **103**. Deallylation of the latter gave the triol **105** which was converted into the required racemic isopropylidene derivative **95** [22] and this was resolved via the (+)- and (−)-ω-camphanates as described previously [22] to give **78** and its enantiomer (Scheme 6).

Tin-mediated *p*-methoxybenzylation of the triol **42** gave **107** which was benzylated to give **109**. Deallylation of the latter gave the triol **111** which for purification was converted into the isopropylidene derivative **113** and this was benzylated to give **114** identical with the material described previously [24]. Acid hydrolysis of **114** gave the required racemic diol **115** [24] which was resolved via the (+)- and (−)-ω-camphanates, as described previously for the (−)-ω-camphanate [24], to give **85** and **90**.

Intermediates for the synthesis of phosphatidylinositol 3,4-bisphosphate (**5**).—The enantiopure diol **90** [24] described above is a suitable intermediate for the synthesis of **5**. Phosphitylation of **90** with bis(benzyloxy)diisopropylaminophosphine (see ref. [25]) in the presence of 1*H*-tetrazole gave the bisphosphite **116** which was oxidised with *tert*-butyl hydroperoxide to give the bisphosphate **117**. Removal of the *p*-methoxybenzyl group from **117** with ammonium cerium(IV) nitrate [26] gave the alcohol **118** suitable for condensation with a phosphorylated diglyceride to give a protected derivative of **5**.

In another approach to an intermediate for the synthesis of **5** the enantiopure diol **80** was subjected to tin-mediated *p*-methoxybenzylation to give predominantly the derivative **119**. This was benzylated to give **120**, which on deallylation gave syrupy **122** and this gave a crystalline acetate **123**. De-*p*-methoxybenzylation of **122** gave the known [24] 1L-2,4,5-tri-*O*-benzyl-*myo*-inositol **124**, thus confirming the substitution pattern of **122**. Initial experiments for this route were carried out with racemic material and the constants for the products are recorded in the Experimental section together with those of the corresponding enantiopure products. For the racemic compounds, the starting material was the diol **97** which was converted through **125**, **126**, and **129** to **130** (Scheme 7).

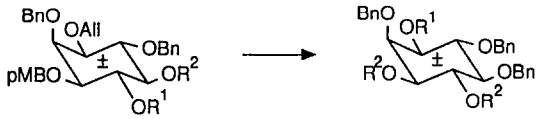
Intermediates for the synthesis of phosphatidylinositol 3,4,5-trisphosphate (**6**).—The enantiopure derivative **78** is a suitable intermediate for the synthesis of **6** as we have described [4].

In a further approach to an intermediate for the synthesis of **6** initial work was carried out with racemic derivatives. When the racemic diol **134** [25] was treated with 1.2 equiv of dichlorodicyanobenzoquinone (DDQ) ([27], see also ref. [28]), the major product (50%) was the triol **135** and the other minor products were starting material **134**, 2,4-di-*O*-benzyl-*myo*-inositol **139** [25], and 2,4-di-*O*-benzyl-5-*O*-*p*-methoxybenzyl-*myo*-inositol (the racemic analogue of **166**, see below). Phosphorylation of **135** using phosphoramidite methodology gave **137** and this was treated with dichlorodicyanobenzoquinone [27,28] to give **138**.

Because of the success of this route it was repeated with the enantiopure diol **140** [25] to give **145** via **142** and **144**. In the Experimental section the constants for both enantiopure and racemic compounds are described together. As **145** is a useful intermediate for the synthesis of **6** new routes to the starting diol **140** were investigated.

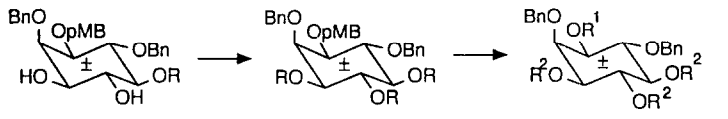
The racemic alcohol **12** was converted into the *p*-methoxybenzyl ether **146** which on acid hydrolysis gave the diol **147**. Tin-mediated *p*-methoxybenzylation of **147** gave **149** and this was benzylated to give **151**. Isomerisation [23] of the allyl groups gave the tris(prop-1-enyl) ether **152** and acid hydrolysis of this gave the triol **153** which for purification was converted into the nicely crystalline isopropylidene derivative **155** by the action of 2,2-dimethoxypropane and an acid catalyst. Benzylation of **155** gave the known [25] crystalline **156** and acid hydrolysis of this gave the required diol **134** which was resolved as described [25] to give **140**.

In another approach to **140** the enantiopure diol **157** [24] was subjected to tin-mediated benzylation to give a mixture of **159** and **162** which were best separated as the acetates **158** and **161**, respectively, and these were then saponified. Deallylation of **159** using Pd–C [21] in refluxing ethanol gave the known 1L-2,4-di-*O*-benzyl-*myo*-inositol (**188**) [25], thus proving the substitution pattern in **159**. *p*-Methoxybenzylation of **159**



125 R^1 = pMB; R^2 = H
126 R^1 = pMB; R^2 = Bn
127 R^1 = pMB; R^2 = Ac
128 R^1 = Ac; R^2 = pMB

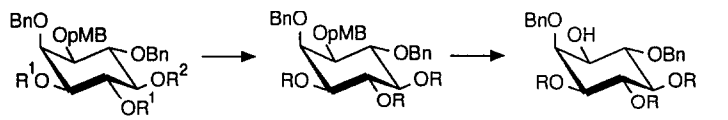
129 R^1 = CH=CH-Me; R^2 = pMB
130 R^1 = H; R^2 = pMB
131 R^1 = Ac; R^2 = pMB
132 R^1 = R^2 = H
133 R^1 = R^2 = Ac



134 R = pMB
135 R = H

136 R = Ac
137 R = $PO(OBn)_2$

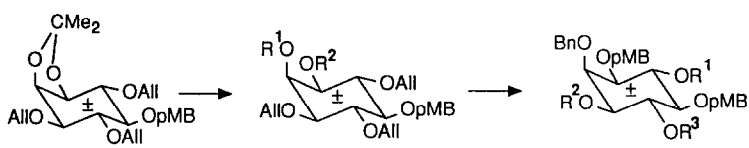
138 R^1 = H; R^2 = $PO(OBn)_2$
139 R^1 = R^2 = H



140 R^1 = H; R^2 = pMB
141 R^1 = Bn; R^2 = pMB
142 R^1 = R^2 = H

143 R = Ac
144 R = $PO(OBn)_2$

145 R = $PO(OBn)_2$



12 → **146**

147 R^1 = R^2 = H
148 R^1 = R^2 = Ac
149 R^1 = H; R^2 = pMB
150 R^1 = Ac; R^2 = pMB
151 R^1 = Bn; R^2 = pMB

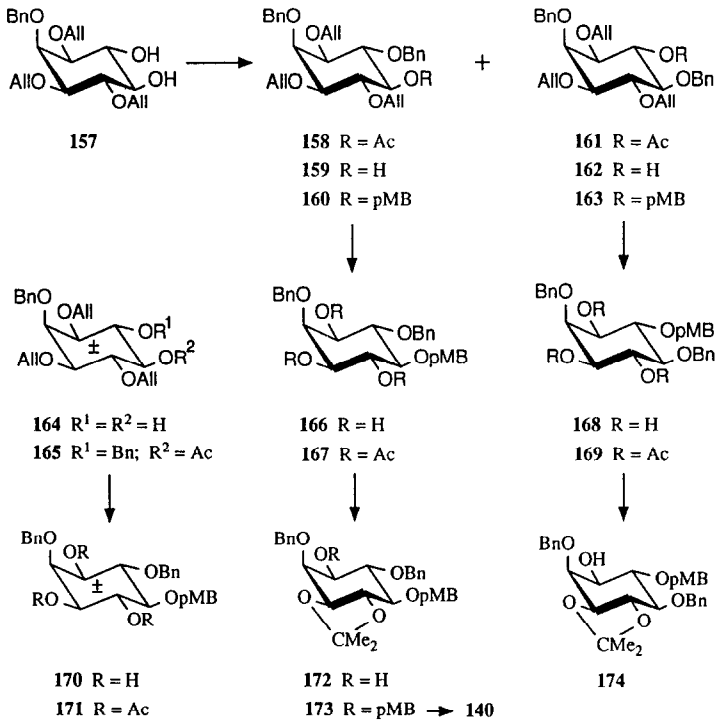
152 R^1 = R^2 = R^3 = CH=CH-Me
153 R^1 = R^2 = R^3 = H
154 R^1 = R^2 = R^3 = Ac
155 R^1 = H; R^2, R^3 = CMe_2
156 R^1 = Bn; R^2, R^3 = CMe_2

↓

134

Scheme 7.

gave **160** and the allyl groups were removed with Pd–C [21] to give the triol **166** that was converted into the crystalline isopropylidene derivative **172**, which is itself a potential intermediate for the synthesis of **6**. *p*-Methoxybenzylation of **172** gave **173** which on acid hydrolysis gave the required, known [25] enantiopure diol **140**. For other purposes **140** was also benzylated to give 1D-2,3,4,6-tetra-*O*-benzyl-1,5-di-*O*-*p*-methoxybenzyl-*myo*-inositol (**141**). Initial experiments had been conducted with the



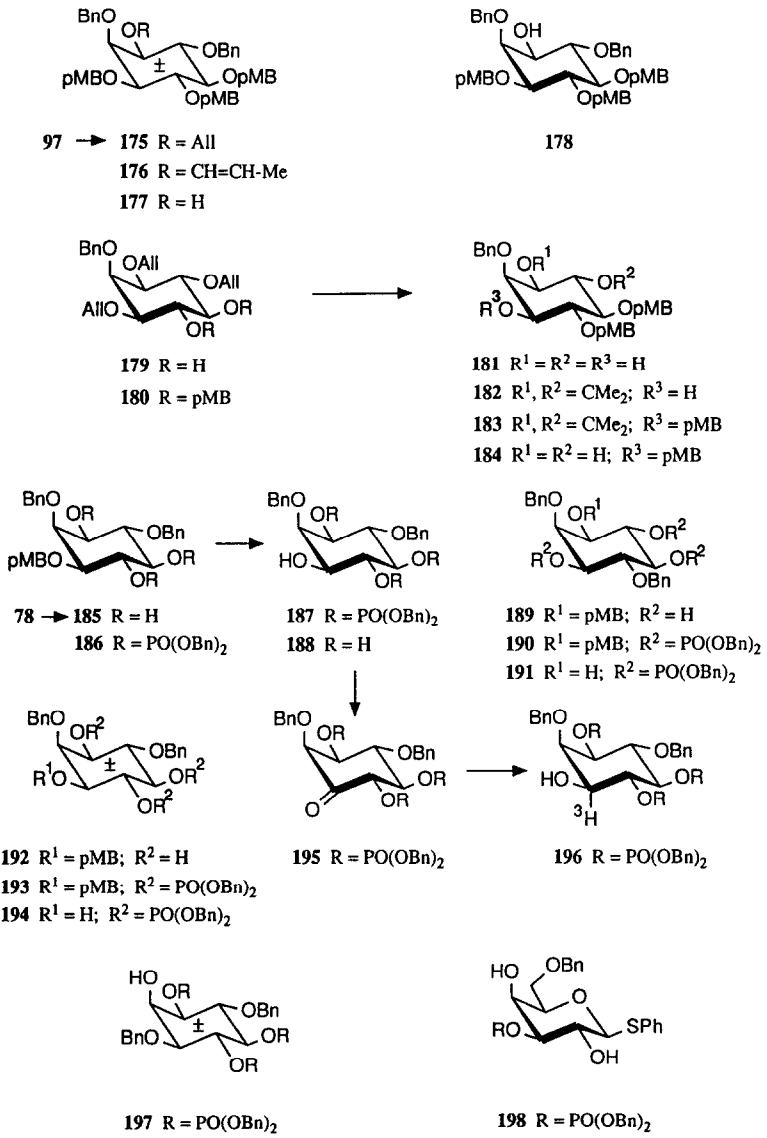
Scheme 8.

racemic diol **164** [24] which gave racemic **170** and its triacetate **171**, and the constants for these are recorded with those of the enantiopure materials. Similar treatment of the alcohol **162** gave the isopropylidene derivative **174** via **163** and the triol **168** (Scheme 8).

A further potential intermediate for the synthesis of **6** is the tris(*p*-methoxybenzyl) ether **178** and the synthesis of racemic **177** was investigated. *p*-Methoxybenzylation of the racemic diol **97** gave **175** and the allyl group was isomerised to give the *cis*-prop-1-enyl ether **176** which on mild acid hydrolysis gave the racemic alcohol **177** (Scheme 9).

With the enantiopure diol **179** available [24] (but before **78**, which would be a better intermediate for **178**, was available), the synthesis of another potential intermediate **184** (suitable for the preparation of **178** after a tin-mediated alkylation reaction) was investigated. *p*-Methoxybenzylation of **179** gave **180** and deallylation of the latter gave the crystalline triol **181** which was converted into the isopropylidene derivative **182**. *p*-Methoxybenzylation of the latter gave **183**, which on acid hydrolysis gave the enantiopure diol **184**. Because other routes gave more suitable intermediates for the synthesis of **6**, the conversion of **184** into **178** was not investigated further.

Intermediates for the synthesis of myo-*inositol 1,3,4,5-tetrakisphosphate and analogues.*—The phosphate substitution pattern of the *myo*-inositol in phosphatidylinositol 3,4,5-trisphosphate (**6**) is the same as that in 1D-*myo*-inositol 1,3,4,5-tetrakisphosphate (**8**) and some of the compounds described above are suitable intermediates for the



Scheme 9.

synthesis of derivatives of **8** which would be useful for biological studies with this compound. The biological function of **8** is the subject of some dispute [11,16] but it is known to be metabolised by both 3- and 5-phosphatases. The racemic analogue of the 5-phosphorothioate **10** [29] and the racemic analogue of **9** [30] and the enantiopure [31] 3-phosphorothioate **9** (analogues of **8**) have been prepared for biological investigations concerning these enzymes, and compound **166** should be a suitable intermediate for a synthesis of enantiopure **10**.

We describe here the synthesis of the phosphorylated intermediate **187** suitable for the synthesis of **9**. Acid hydrolysis of **78** gave the triol **185** which was phosphorylated using phosphoramidite methodology to give crystalline **186**, and the *p*-methoxybenzyl group was removed with dichlorodicyanobenzoquinone [27,28] to give the required crystalline intermediate **187**. The latter is also being investigated as an intermediate for the synthesis of tritiated IP_3 (**7**) by conversion via the ketone **195** and subsequent reduction with tritiated borohydride into **196** which on hydrogenolysis would give a tritiated **7**. Similarly phosphorylation of **196** and subsequent hydrogenolysis would give a tritiated derivative of **8**.

A similar approach to a tritiated analogue of IP_3 (**7**) has been reported [32] via (±)-3,6-di-*O*-benzyl-*myo*-inositol 1,4,5-tris(dibenzyl phosphate) (**197**) which has a *cis*-hydroxyl group vicinal to the dibenzyl phosphate group allowing facile cyclic phosphate formation [33], although a very recent report [34] discusses the stability of phenyl 6-*O*-benzyl-3-*O*-dibenzyloxyphosphoryl-1-thio-β-D-galactopyranoside (**198**) and related compounds which also have *cis*-hydroxyl groups vicinal to the dibenzyl phosphate group. Nevertheless, compound **187** should be more stable than **197** since it has a *trans*-hydroxyl group vicinal to the dibenzyl phosphate group. The enantiomer **191** of **187** and the racemic mixture **194** were prepared in a similar way to **187** and their constants are recorded in the Experimental section together with those of **187**.

3. Experimental

General.—The light petroleum used for chromatography (column and thin layer) had bp 40–60 °C; otherwise the fraction used had bp 60–80 °C. TLC was carried out on Silica Gel G (E. Merck) and column chromatography was performed on silica gel. Extracts were concentrated under reduced pressure. ^1H NMR spectra (selected data) were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Jeol FX90Q Fourier-transform spectrometer and ^{31}P NMR spectra were recorded, on the same instrument, in $CDCl_3$ with an external aqueous phosphoric acid reference (4% in a capillary tube inside the NMR tube). Optical rotations were performed at ambient temperature (25–30 °C) on a Bendix Automatic or Perkin–Elmer polarimeter.

*Tin-mediated allylation of (±)-1,2-*O*-isopropylidene-*myo*-inositol* (**11**) *with excess reagents* [3].—A mixture of **11** [19] (2.2 g, 10 mmol), Bu_2SnO (8.2 g, 33 mmol), and Bu_4NBr (9 g, 28 mmol) in allyl bromide (50 mL) was heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 7 h. The mixture was concentrated and toluene was evaporated from the residue to remove the last trace of allyl bromide. The residue was distributed between ether (100 mL) and water (100 mL), and the ether layer was separated and stirred with satd aq $NaHCO_3$ (50 mL) and $NaHCO_3$ (10 g) for 1 h. The ether layer was separated, dried (K_2CO_3), and concentrated. TLC (3:1 ether–light petroleum) showed two major products (R_f 0.8 and 0.7) with minor products (R_f 0.95, 0.65, 0.4, and 0.25). Column chromatography (2:1 ether–light petroleum) gave the two major products as syrups which were characterised as described below.

*(±)-1,4,5-Tri-*O*-allyl-*myo*-inositol* (**36**) [20], *the triacetate* (**37**) [20], *and the corresponding tri(but-2-enyl) ether* (**51**).—The more polar major product (R_f 0.7, 784 mg,

23%) from the tin-mediated allylation described above [which gave a syrupy acetate **17**; ^{1}H NMR data: δ 1.36, 1.55 (2 s, each 3 H, CMe_2), 2.08 (s, 3 H, Ac), 3.27 (t, 1 H, *J* 8.8 Hz)] was treated with 10:1 MeOH–M HCl (20 mL) at reflux for 30 min. An excess of $NaHCO_3$ was added, the solution was concentrated, and the product (400 mg) was extracted with CH_2Cl_2; mp 132–134 °C (from EtOAc–light petroleum); identical with **36** described previously [20]. This was acetylated to give the triacetate **37**; mp 90–92 °C (from light petroleum); identical (NMR, TLC) with the material described previously [20]. Therefore the major product (R_f 0.7) from the tin-mediated allylation reaction was (±)-1,4,5-tri-*O*-allyl-2,3-*O*-isopropylidene-*myo*-inositol (**16**).

The more polar major product from a similar tin-mediated alkylation of **11** with crotyl bromide was hydrolysed as described for **16** to give the triol **51**; mp 115–116 °C. Anal. Calcd for $C_{18}H_{30}O_6$: C, 63.13; H, 8.83. Found: C, 63.65; H, 9.02. This gave a syrupy triacetate **52**; ^{1}H NMR data: δ 1.70 (d, 9 H, *J* 4.9 Hz, 3 × =CH*Me*), 2.04, 2.09, 2.11 (3 s, each 3 H, 3 × Ac), 3.30 (t, 1 H, *J* 10.4 Hz, H-5), 3.37 (dd, 1 H, *J* 3.1 and 10.4 Hz, H-1), 3.73 (t, 1 H, *J* 10.4 Hz, H-4), 4.76 (dd, 1 H, *J* 3.1 and 10.4 Hz, H-3), 5.25 (t, 1 H, *J* 10 Hz, H-6).

(±)-1,4,5-Tri-O-*acetyl-2,3,6-tri*-O-*methyl*-myo-*inositol* (**41**).—(*a*) The triol **36** was treated with MeI and NaH in DMF and the product isolated in the usual way to give the trimethyl ether **38** as a syrup. TLC (ether) showed conversion of **36** (R_f 0.1) into **38** (R_f 0.9). ^{1}H NMR data: (for **38**) δ 2.90–3.20 (m, 3 H, H-1,3,5), 3.41–3.63 (m, 2 H, H-4,6), 3.49 (s, 3 H, OMe), 3.60 (s, 6 H, 2 × OMe), 3.77 (t, 1 H, *J* 2.4 Hz, H-2), 4.14–4.32 (m, 6 H, 3 × OCH_2), 5.09–5.39 (m, 6 H, 3 × $=CH_2$), 5.75–6.21 (m, 3 H, 3 × CH=).

A mixture of **38** (300 mg), Pd–C (350 mg, 10%), and toluene-*p*-sulfonic acid (60 mg) in 19:1 EtOH–water (20 mL) was heated under reflux for 16 h. TLC (4:1 $CHCl_3$–MeOH) then showed a single product **40** (R_f 0.5). An excess of $NaHCO_3$ was added and the mixture was concentrated. EtOH and toluene were evaporated from the residue (to remove water). The total residue was treated with acetic anhydride–pyridine at 60 °C for 5 h and the product was isolated in the usual way to give the triacetate **41** (200 mg, 79%); mp 157–159 °C (from 1:10 EtOAc–light petroleum); ^{1}H NMR data: δ 2.04, 2.06, 2.15 (3 s, each 3 H, 3 × Ac), 3.27 (dd, 1 H, *J* 2.4 and 9.8 Hz, H-3), 3.41, 3.45, 3.55 (3 s, each 3 H, 3 × OMe), 3.74 (t, 1 H, *J* 10.4 Hz, H-6), 3.92 (t, 1 H, *J* 2.4 Hz, H-2), 4.72 (dd, 1 H, *J* 2.4 and 10.4 Hz, H-1), 4.97 (t, 1 H, *J* 9.8 Hz, H-5), 5.37 (t, 1 H, *J* 9.8 Hz, H-4). Anal. Calcd for $C_{15}H_{24}O_9$: C, 51.72; H, 6.95. Found: C, 51.50; H, 7.15.

(*b*) The tribenzyl ether **58** (see below) was methylated as above to give the trimethyl ether **61**; mp 67–69 °C; ^{1}H NMR data: δ 3.05 (dd, 1 H, *J* 2.4 and 9.8 Hz), 3.48, 3.62, 3.66 (3 s, each 3 H, 3 × OMe), 4.73–4.83 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.73, 4.80, and 4.83) (TLC: R_f 0.6 in 1:1 ether–light petroleum). Anal. Calcd for $C_{30}H_{36}O_6$: C, 73.14; H, 7.37. Found: C, 72.52; H, 7.25. This was treated with hydrogen over Pd–C in AcOH at atmospheric temperature and pressure for 15 h to give the triol **40** which was acetylated as described in (*a*) to give the triacetate **41**; mp 156–158 °C; identical with the material described in (*a*).

(±)-1,4,5-Tri-O-*allyl-2,3,6-tri*-O-*benzyl*-myo-*inositol* (**39**) [20,35].—The triol **36** was treated with benzyl bromide and NaH in DMF and the product isolated in the usual way to give **39**; mp 52–54 °C (from light petroleum); identical with the material described previously [20,35].

*(±)-1,4,6-Tri-*O*-allyl-*myo*-inositol* (**42**) *and the corresponding tri(but-2-enyl) ether* (**55**).—The less polar major product from the tin-mediated allylation described above (R_f 0.8, 900 mg, 26%) [which gave a syrupy acetate **13**; ^{1}H NMR data: δ 1.36, 1.55 (2 s, each 3 H, CMe_2), 2.08 (s, 3 H, Ac)] was hydrolysed (as described above in the preparation of **36**) to give **42**; mp 120–122 °C (from EtOAc–light petroleum). Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.98; H, 8.06. Found: C, 59.75; H, 7.94. This gave a syrupy triacetate **43**; ^{1}H NMR data: δ 2.03, 2.10, 2.15 (3 s, each 3 H, 3 × Ac), 4.83 (dd, 1 H, *J* 3.1 and 10.4 Hz, H-3), 5.59 (t, 1 H, *J* 2.4 Hz, H-2).

The less polar major product from a similar tin-mediated alkylation of **11** with crotyl bromide was hydrolysed similarly to give the triol **55**; mp 80–81 °C (from EtOAc–light petroleum). Anal. Calcd for $C_{18}H_{30}O_6$: C, 63.13; H, 8.83. Found: C, 63.13; H, 8.65. This gave a syrupy triacetate **56**; ^{1}H NMR data: δ 1.69 (d, 9 H, *J* 4.9 Hz, 3 × =CH*Me*), 2.02, 2.11, 2.14 (3 s, each 3 H, 3 × Ac), 3.35–3.80 (m, 3 H, with major peaks at 3.49, 3.58, 3.69, and 3.80, H-1,4,6), 4.79 (dd, 1 H, *J* 3.0 and 10.4 Hz, H-3), 4.97 (t, 1 H, *J* 9.2 Hz, H-5).

*(±)-1,4,6-Tri-*O*-acetyl-2,3,5-tri-*O*-methyl-*myo*-inositol* (**47**).—(*a*) The triallyl ether **42** was methylated (as described above for the preparation of **38**) to give the trimethyl ether **44** as a syrup (TLC: 1:1 ether–light petroleum, R_f 0.5); ^{1}H NMR data: δ 3.48, 3.58, 3.60 (3 s, each 3 H, 3 × OMe). This was deallylated (as described above for the preparation of **40**) and, after 16 h, TLC (4:1 $CHCl_3$–MeOH) showed a single product **46** (R_f 0.6). This was treated with acetic anhydride–pyridine (as described above for the preparation of **41**) to give the triacetate **47**; mp 161–163 °C (from EtOAc–light petroleum); ^{1}H NMR data: δ 2.06, 2.09, 2.11 (3 s, each 3 H, 3 × Ac), 3.22 (dd, 1 H, *J* 2.4 and 10.1 Hz, H-3), 3.31 (t, 1 H, *J* 9.4 Hz, H-5), 3.38, 3.41, 3.56 (3 s, each 3 H, 3 × OMe), 3.90 (t, 1 H, *J* 2.4 Hz, H-2), 4.77 (dd, 1 H, *J* 2.4 and 10.4 Hz, H-1), 5.31–5.61 (m, 2 H, H-4,6). Anal. Calcd for $C_{15}H_{24}O_9$: C, 51.72; H, 6.95. Found: C, 51.96; H, 6.98.

(*b*) The tribenzyl ether **62** (see below) was methylated (as described above for the preparation of **61**) to give the trimethyl ether **65** (TLC: 1:1 ether–light petroleum, R_f 0.5); mp 83–84 °C; ^{1}H NMR data: δ 3.48 (s, 3 H, OMe), 3.65 (s, 6 H, 2 × OMe), 4.72 (s, 2 H, CH_2Ph), 4.81–4.84 (m, 4 H, 2 × CH_2Ph). Anal. Calcd for $C_{30}H_{36}O_6$: C, 73.14; H, 7.37. Found: C, 73.76; H, 7.43. This was hydrogenolysed (as described above for the treatment of **61**) and the product **46** was acetylated (as above) to give **47** identical with the material described in (*a*).

*(±)-1,4,6-Tri-*O*-allyl-2,3,5-tri-*O*-benzyl-*myo*-inositol* (**45**).—The triol **42** was treated with benzyl bromide and NaH in DMF and the product isolated in the usual way to give **45** as a syrup; ^{1}H NMR data: δ 3.09–3.43 (m, 3 H, H-1,3,5, with major peaks at 3.09, 3.12, 3.21, 3.23, 3.32, and 3.43), 3.73–4.35 (m, 9 H, H-2,4,6 and 3 × OCH_2CH=), 4.56–4.82 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.62, 4.63, and 4.82). Anal. Calcd for $C_{36}H_{42}O_6$: C, 75.76; H, 7.42. Found: C, 75.45; H, 7.45.

*(±)-1,2,5-Tri-*O*-benzyl-*myo*-inositol* (**49**).—The triallyl ether **45** was treated with potassium *tert*-butoxide in Me_2SO and the product isolated in the usual way [23]. TLC (1:2 ether–light petroleum) showed conversion of **45** (R_f 0.6) into a product **48** (R_f 0.9). A solution of the tri(prop-1-enyl) derivative **48** in 9:1 acetone–M HCl was heated under reflux for 40 min after which time TLC (ether) showed conversion of **48** (R_f 1.0)

into the triol **49** (R_f 0.2). Column chromatography (4:1 EtOAc–light petroleum) gave **49**; mp 158–160 °C (from EtOAc–light petroleum); ^{1}H NMR data: δ 4.51–5.03 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.59, 4.64, 4.67, 4.71, 4.84, and 4.90). Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.99; H, 6.77. This gave a syrupy triacetate **50**; ^{1}H NMR data: δ 1.93 (s, 3 H, Ac), 1.95 (s, 6 H, 2 × Ac), 3.35–3.68 (m, 2 H, H-3,5), 4.08 (t, *J* 2.4 Hz, H-2), 4.40–5.00 (m, 7 H, 3 × CH_2Ph and H-1), 5.71 (t, 2 H, H-4,6), 7.26–7.29 (m, 15 H, aromatic).

*Tin-mediated benzylation of (±)-1,2-*O*-isopropylidene-*myo*-inositol* (**11**) *with excess reagents* [3].—A mixture of **11** (2.2 g, 10 mmol), Bu_2SnO (11.3 g, 45 mmol), Bu_4NBr (9 g, 28 mmol), benzyl bromide (15 mL, 126 mmol), and MeCN (50 mL) was heated under reflux with 3 Å molecular sieve in a Soxhlet apparatus for 50 h. The Soxhlet was removed, NEt_3 (15 mL) was added, and refluxing was continued for 1 h to destroy the excess of benzyl bromide. The product was isolated as described above for the product of the tin-mediated allylation reaction. TLC (2:1 ether–light petroleum) showed two major products (R_f 0.7 and 0.8) and minor products (R_f 0.95, 0.6, 0.5, 0.2, and 0.1) [TLC (ether) resolved the minor polar products (R_f 0.2 and 0.1 above) into three components (R_f 0.6, 0.5, and 0.4)]. Column chromatography (1:1 ether–light petroleum) gave the products R_f 0.8 (40%), 0.7 (30%), and 0.5 (4%) which were characterised as described below and were shown to be identical with the products obtained when the tin-mediated benzylation was carried out starting with 1,4-di-*O*-benzyl-2,3-*O*-isopropylidene-*myo*-inositol (**57**). The minor product (R_f 0.6 in 2:1 ether–light petroleum) was shown to be a mixture [3] and was not further investigated; neither were the products with R_f 0.2 and 0.1.

*(±)-1,4,5-Tri-*O*-benzyl-2,3-*O*-isopropylidene-*myo*-inositol* (**18**).—The more polar major product (R_f 0.7) from the tin-mediated benzylation of **11** had mp 60–61 °C (from 1:20 EtOAc–light petroleum) and was shown to be **18** after methylation studies of the derived triol **58** (see above); ^{1}H NMR data: δ 1.34, 1.48 (2 s, each 3 H, CMe_2), 2.65 (d, 1 H, OH), 3.18–4.39 (m, 6 H, ring protons), 4.55–4.98 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.65, 4.73, 4.79, and 4.83). Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.36; H, 6.99. This gave a syrupy acetate **19**; ^{1}H NMR data: δ 1.34, 1.51 (2 s, each 3 H, CMe_2), 1.94 (s, 3 H, Ac), 3.41 (t, 1 H, *J* 8.5 Hz), 3.65 (dd, 1 H, *J* 3.7 and 8.6 Hz), 3.80–4.39 (m, 3 H with major peaks at 3.80, 3.87, 3.97, 4.09, 4.16, 4.23, and 4.33), 4.28–5.10 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.63, 4.69, 4.72, 4.74, and 4.79), 5.44 (t, 1 H, *J* 8.5 Hz, H-6).

*(±)-1,4,5-Tri-*O*-benzyl-*myo*-inositol* (**58**), *the triacetate* (**59**), *and the tribenzoate* (**60**).—Compound **18** was treated with 9:1 MeOH–M HCl at reflux for 1 h. An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated, and the residue extracted with CH_2Cl_2 to give **58**; mp 119–120 °C (EtOAc–light petroleum); ^{1}H NMR data: δ 2.49 (s, 3 H, 3 × OH), 3.23–4.24 (m, 6 H, ring protons with major peaks at 3.23, 3.27, 3.37, 3.46, 3.72, 3.82, and 4.21), 4.70–5.01 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.70, 4.80, 4.86, and 4.88). Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.73; H, 7.03.

Acetylation of **58** with Ac_2O–pyridine at 60 °C for 5 h gave the triacetate **59**; mp 112–113 °C; ^{1}H NMR data: δ 1.93, 1.96, 2.14 (3 s, each 3 H, 3 × Ac), 3.38–3.60 (m, 2

H, H-1,5), 3.99 (t, 1 H, *J* 9.2 Hz, H-4), 5.43 (t, 1 H, *J* 9.8 Hz, H-6), 5.70 (t, 1 H, *J* 2.4 Hz, H-2). Anal. Calcd for $C_{33}H_{36}O_9$: C, 68.73; H, 6.29. Found: C, 68.60; H, 6.18.

Benzoylation of **58** with benzoyl chloride in pyridine gave the tribenzoate **60**; mp 146–147 °C (from ether–light petroleum); ^{1}H NMR data: δ 3.70–3.95 (m, 2 H, H-1,5), 4.25–5.01 (m, 7 H, 3 × CH_2Ph and H-4), 5.36 (dd, 1 H, *J* 2.8 and 10.0 Hz, H-3), 5.91 (t, 1 H, *J* 9.8 Hz, H-6), 6.15 (t, 1 H, *J* 2.8 Hz, H-2). Anal. Calcd for $C_{48}H_{42}O_9$: C, 75.57; H, 5.55. Found: C, 75.56; H, 5.46.

*(±)-1,4,6-Tri-*O*-benzyl-2,3-*O*-isopropylidene-*myo*-inositol* (**14**).—The less polar product (R_f 0.8) from the tin-mediated benzylation of **11**, which had mp 80–81 °C (from 1:20 EtOAc–light petroleum), was **14** and was correlated with **12** by the methylation studies described above; ^{1}H NMR data: δ 1.35, 1.51 (2 s, each 3 H, CMe_2), 2.65 (d, 1 H, *J* 1.8 Hz, OH), 3.40–4.38 (m, 6 H, ring protons, with major peaks at 3.60, 3.67, 3.71, 3.74, 3.83, 4.09, 4.16, and 4.25), 4.62–4.98 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.75, 4.80, and 4.84). Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.30; H, 7.05. This gave a syrupy acetate **15**; ^{1}H NMR data: δ 1.35, 1.52 (2 s, each 3 H, CMe_2), 1.93 (s, 3 H, Ac), 3.61–4.39 (m, 5 H, H-1 to 4 and H-6, with major peaks at 3.61, 3.68, 3.71, 3.77, 3.82, 3.86, 3.90, 4.10, 4.17, 4.24, 4.29, 4.33, and 4.36), 4.56–5.12 (m, 7 H, 3 × CH_2Ph and H-5, with major peaks at 4.56, 4.70, 4.75, 4.77, 4.90, and 5.03), 7.25–7.32 (m, 15 H, aromatic, with major peaks at 7.25, 7.28, 7.30 and 7.32).

*(±)-1,4,6-Tri-*O*-benzyl-*myo*-inositol* (**62**), *the triacetate* (**63**), *and the tribenzoate* (**64**).—Compound **14** was hydrolysed, as described for **18**, to give the triol **62** as a monohydrate; mp 83–84 °C (from 1:20 EtOAc–light petroleum); ^{1}H NMR data: δ 2.62–2.72 (m, 3 H, 3 × OH), 3.34–3.95 (m, 5 H, 5 ring protons), 4.18 (t, 1 H, H-2), 4.68–5.03 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.68, 4.80, 4.82, 4.89, 4.91, 5.01, and 5.03). Anal. Calcd for $C_{27}H_{30}O_6 \cdot H_2O$: C, 69.21; H, 6.89. Found: C, 69.07; H, 6.93.

Acetylation as described above for the preparation of **59** gave the triacetate **63**; mp 85–86 °C (from 1:20 ether–light petroleum); ^{1}H NMR data: δ 1.87, 1.97, 2.17 (3 s, each 3 H, 3 × Ac), 3.55–4.01 (m, 3 H, H-1,4,6), 4.63 (ABq, 4 H, 2 × CH_2Ph), 4.54, 4.80 (AB, 2 H, *J* 11 Hz, CH_2Ph), 4.91 (dd, 1 H, *J* 2.4 and 9.8 Hz, H-3), 5.16 (t, 1 H, *J* 11 Hz, H-5), 5.74 (t, 1 H, *J* 2.4 Hz, H-2). Anal. Calcd for $C_{33}H_{36}O_9$: C, 68.73; H, 6.29. Found: C, 68.72; H, 6.25.

Benzoylation with benzoyl chloride in pyridine gave the tribenzoate **64**; mp 129–130 °C (from ether–light petroleum); ^{1}H NMR data: δ 3.90–4.91 (m, 9 H, 3 × CH_2Ph and H-1,4,6), 5.40 (dd, 1 H, *J* 2.4 and 10.3 Hz, H-3), 5.72 (t, 1 H, *J* 9.2 Hz, H-5), 6.18 (t, 1 H, *J* 2.4 Hz, H-2). Anal. Calcd for $C_{48}H_{42}O_9$: C, 75.57; H, 5.55. Found: C, 75.16; H, 5.83.

*(±)-4,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-*myo*-inositol* (**20**) *and the diacetate* (**21**). —The fraction (R_f 0.5) from the tin-mediated benzylation of **11** (see above) had mp 97–98 °C (from light petroleum); ^{1}H NMR data: δ 1.40, 1.53 (2 s, each 3 H, CMe_2), 2.55, 2.65 (2 s, each 1 H, 2 × OH). Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 69.06; H, 6.95.

Diol **20** gave a diacetate **21**; mp 110–111 °C (from EtOAc–light petroleum); ^{1}H NMR data: δ 1.33, 1.50 (2 s, each 3 H, CMe_2), 1.93, 2.07 (2 s, each 3 H, 2 × Ac),

3.63–3.97 (m, 2 H), 4.30 (t, 1 H, *J* 6.1 Hz), 4.48–4.60 (m, 1 H), 4.65 (s, 2 H, CH_2Ph), 4.73, 4.75 (AB, 2 H, *J* 12 Hz, CH_2Ph), 5.12 (t, 1 H, *J* 7.0 Hz), 5.29 (dd, 1 H, *J* 3.7 and 8.5 Hz). Anal. Calcd for $C_{27}H_{32}O_8$: C, 66.93; H, 6.66. Found: C, 67.33; H, 6.71.

4,6-Di-O-benzyl-myo-*inositol* (**23**) *and the tetraacetate* (**24**).—Acid hydrolysis of the diol **20**, as described for the hydrolysis of **18**, gave the tetraol **23**; mp 138–140 °C (from EtOAc). Anal. Calcd for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71. Found: C, 66.43; H, 6.66.

Acetylation of **23** (as described above for the preparation of **59**) gave the tetraacetate **24**; mp 189–190 °C (from EtOAc–light petroleum); ^{1}H NMR data (indicating the symmetrical structure): δ 1.89 (3 H), 1.95 (6 H), 2.17 (3 H), (3 s, 4 × Ac), 3.88 (t, 2 H, *J* 10 Hz, H-4,6), 4.61 (s, 4 H, 2 × CH_2Ph), 5.06 (dd, 2 H, *J* 2.4 and 10.4 Hz, H-1,3), 5.23 (t, 1 H, *J* 9.8 Hz, H-5), 5.56 (t, 1 H, *J* 2.4 Hz, H-2). Anal. Calcd for $C_{28}H_{32}O_{10}$: C, 63.63; H, 6.10. Found: C, 63.31; H, 6.02.

(±)-4,6-Di-O-benzyl-1,5-di-O-p-methoxybenzyl-myo-*inositol* (**25**).—The diol **20** was treated with *p*-methoxybenzyl chloride and NaH in DMF and the product isolated in the usual way. TLC (1:1 ether–light petroleum) showed conversion of **20** (R_f 0.5) into a product (R_f 0.8) together with less polar byproducts. Column chromatography (same solvent) gave **22** (90%) as a syrup; ^{1}H NMR data: δ 1.35, 1.51 (2 s, each 3 H, CMe_2), 3.26–4.28 (m, 6 H, ring protons), 3.78, 3.79 (2 s, each 3 H, 2 × OMe), 4.64–4.95 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.70, 4.77, and 4.82), 6.75–7.33 (m, 18 H, aromatic, with major peaks at 6.75, 6.82, 6.85, 6.89, 7.15, 7.25, and 7.33). This was treated with 9:1 MeOH–M HCl at reflux for 20 min. An excess of $NaHCO_3$ was added, the mixture was concentrated, and the product was extracted from the residue with CH_2Cl_2. TLC (ether) showed conversion of **22** (R_f 1.0) into the diol **25** (R_f 0.5) together with a trace byproduct (R_f 0.1), probably due to acidic de-*p*-methoxybenzylation. Column chromatography (9:1 ether–CH_2Cl_2) gave **25** (80%); mp 115–117 °C (from EtOAc–light petroleum); ^{1}H NMR data: δ 2.43 (d, 1 H, OH), 2.50 (s, 1 H, OH), 3.39–4.16 (m, 6 H, ring protons), 3.79 (s, 6 H, 2 × OMe), 4.63–5.03 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.63, 4.79, 4.88, and 4.90), 6.76–7.32 (m, 18 H, aromatic, with major peaks at 6.78, 6.85, 6.88, 7.15, 7.20, 7.25, and 7.32). Anal. Calcd for $C_{36}H_{40}O_8$: C, 71.98; H, 6.71. Found: C, 72.06; H, 6.78.

(±)-1-O-Allyl-4,6-di-O-benzyl-3,5-di-O-p-methoxybenzyl-myo-*inositol* (**26**).—A mixture of the diol **25** (475 mg, 0.79 mmol), Bu_2SnO (250 mg, 1 mmol), Bu_4NBr (240 mg, 0.74 mmol), allyl bromide (8 mL, 92.5 mmol), and MeCN (16 mL) was heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 6 h and the crystalline product was isolated in the usual way. TLC (1:1:1 ether–light petroleum–CH_2Cl_2) showed a major product **26** (R_f 0.7) and a trace product (R_f 0.75, probably **27**) together with other, more polar, trace products. Column chromatography (same solvent) gave **26** (430 mg, 85%); mp 110–111 °C (from ether–light petroleum). Anal. Calcd for $C_{39}H_{44}O_8$: C, 73.10; H, 6.92. Found: C, 73.22; H, 6.98.

(±)-1-O-Allyl-2,4,6-tri-O-benzyl-3,5-di-O-p-methoxybenzyl-myo-*inositol* (**28**).—(*a*) The alcohol **26** was treated with benzyl bromide and NaH in DMF and the product isolated in the usual way. TLC (1:1 ether–light petroleum) showed the product at R_f 0.75. Column chromatography (same solvent) gave **28** as a syrup (95%); ^{1}H NMR data: δ 3.24 (dd, 1 H, *J* 2.2 and 9.4 Hz, H-1 or -3), 3.36 (dd, 1 H, *J* 2.4 and 9.1 Hz, H-3 or -1), 3.44 (t, 1 H, *J* 8.5 Hz, H-5), 3.74, 3.76 (2 s, each 3 H, 2 × OMe), 3.91–4.14 (m, 5

H, OCH_2CH= and H-2,4,6), 4.56 (s, 2 H, CH_2Ph), 4.72–4.99 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.80, 4.84, and 4.87), 5.08–5.39 (m, 2 H, =CH_2), 5.71–6.12 (m, 1 H, CH=), 6.74–7.49 (m, 23 H, aromatic, with major peaks at 6.74, 6.78, 6.84, 6.87, 7.16, 7.18, 7.30, and 7.38). Anal. Calcd for $C_{46}H_{50}O_8$: C, 75.59; H, 6.90. Found: C, 75.63; H, 6.87.

(*b*) The triol **153** (see below) (1 g, 1.96 mmol), Bu_2SnO (700 mg, 2.8 mmol), Bu_4NBr (650 mg, 2.02 mmol), and allyl bromide (50 mL) were heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 5 h and the products isolated in the usual way. TLC (ether) showed conversion of **153** (R_f 0.1) into a major product (R_f 0.75) with no separation of the expected products (**32** and **34**). The crude product was acetylated in the usual way and TLC (2:1 ether–light petroleum) showed conversion of the mixed diols (**32** and **34**, R_f 0.3) into minor (R_f 0.6) and major (R_f 0.5) products. Column chromatography (same solvent) gave the minor product **35** (R_f 0.6, 277 mg, 22% from **153**) as a syrup; ^{1}H NMR data: δ 1.95, 2.01 (2 s, each 3 H, 2 × Ac), 3.39 (t, 1 H, *J* 9.5 Hz, H-5), 3.39 (dd, 1 H, *J* 1.8 and 9.7 Hz, H-1), 3.76, 3.77 (2 s, each 3 H, 2 × OMe), 3.86–4.30 (m, 4 H, OCH_2CH= and H-2,4), 4.43–4.91 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.43, 4.49, 4.58, 4.67, and 4.79), 5.55 (t, 1 H, *J* 10 Hz, H-6), 5.67–6.06 (m, 1 H, CH=), 6.80–7.30 (m, 13 H, aromatic, with major peaks at 6.80, 6.89, 6.90, 7.15, 7.24, and 7.30). This was followed by the major product **33** (R_f 0.5, 615 mg, 50% from **153**) obtained as a syrup which slowly crystallised; ^{1}H NMR data: δ 1.98, 1.99 (2 s, each 3 H, 2 × Ac), 3.22, 3.30 (2 dd, each 1 H, each *J* 1.8 and 9.5 Hz, H-1,3), 3.51 (t, 1 H, *J* 9.2 Hz, H-5), 3.73, 3.76 (2 s, each 3 H, 2 × OMe), 3.86–3.99 (m, 3 H, OCH_2CH= and H-2), 4.39, 4.43 (AB, 2 H, *J* 11.6 Hz, CH_2Ph), 4.50, 4.83 (2 s, each 2 H, 2 × CH_2Ph), 5.09–5.29 (m, 2 H, =CH_2), 5.63, 5.65 (2 t, each 1 H, each *J* 9.5 Hz, H-4,6), 5.52–5.95 (m, 1 H, CH=), 6.76–7.41 (m, 13 H, aromatic, with major peaks at 6.76, 6.79, 6.86, 6.89, 7.10, 7.12, 7.20, 7.22, 7.28, and 7.34).

The diacetate **33** was saponified with NaOH in MeOH and the product isolated in the usual way to give the diol **32**; ^{1}H NMR data: δ 2.77 (s, 2 H, 2 × OH), 3.73, 3.75 (2 s, each 3 H, 2 × OMe), 4.52, 4.76, 4.81 (3 s, each 2 H, 3 × CH_2Ph), 6.78–7.35 (m, 13 H, aromatic, with major peaks at 6.79, 6.87, 6.89, 7.19, 7.25, 7.28, 7.31, and 7.35). The diol **32** was treated with benzyl bromide and NaH in DMF and the product isolated in the usual way to give **28** identical with the material described in (*a*).

(±)-2,4,6-Tri-O-*benzyl-3,5-di*-O-p-*methoxybenzyl-1*-O-*(*cis-*prop-1-enyl)*-myo-*inositol* (**29**).—The allyl ether **28** was treated with KOBu^t in Me_2SO at 50 °C for 2 h in the usual way. TLC (1:1 ether–light petroleum) did not separate **28** from the product **29** (R_f 0.75) but acid hydrolysis of a portion of the product (as described below, to give the alcohol **30** from **29**) showed when the isomerisation was completed. The product was isolated in the usual way and after column chromatography (same solvent) gave **29** (95%); mp 93.5–95 °C (from light petroleum containing a little NEt_3); ^{1}H NMR data: δ 1.67 (dd, 3 H, *J* 1.4 and 7.0 Hz, =CH*Me*), 3.32–3.60 (m, 3 H, H-1,3,5), 3.73, 3.75 (2 s, each 3 H, 2 × OMe), 3.95–4.57 (m, 4 H, MeC*H*= and H-2,4,6), 4.54 (s, 2 H, CH_2Ph), 4.60–5.01 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.80, 4.86, and 4.88), 6.09 (dd, 1 H, *J* 1.3 and 6.1 Hz, OCH=), 6.75–7.40 (m, 23 H, aromatic, with major peaks at 6.75, 6.77, 6.85, 6.87, 7.16, 7.17, 7.27, 7.29, and 7.38). Anal. Calcd for $C_{46}H_{50}O_8$: C, 75.59; H, 6.90. Found: C, 75.64; H, 6.52.

(±)-1-O-Acetyl-2,4,6-tri-O-benzyl-3,5-di-O-p-methoxybenzyl-myo-inositol (**31**).—A solution of the prop-1-enyl ether **29** in 3:6:1 acetone–MeOH–M HCl was heated under reflux for 20 min after which time TLC (1:1 ether–light petroleum) showed conversion of **29** (R_f 0.75) into a major product (R_f 0.25) together with a trace of more polar product (R_f 0.1, probably due to acidic de-*p*-methoxybenzylation). An excess of NEt_3 and $NaHCO_3$ was added and the syrupy alcohol **30** (90%) was isolated in the usual way. This was acetylated in the usual way to give the acetate **31** as a syrup which crystallised slowly; mp 73–75 °C (from MeOH); ^{1}H NMR data: δ 1.89 (s, 3 H, Ac), 3.35–3.65 (m, 2 H, H-3,5), 3.75, 3.77 (2 s, each 3 H, 2 × OMe), 3.95–4.20 (m, 3 H, H-2,4,6), 4.58–5.05 (m, 11 H, 5 × CH_2Ph and H-1, with major peaks at 4.59, 4.69, 4.74, 4.87, and 4.90), 6.74–7.30 (m, 23 H, aromatic, with major peaks at 6.74, 6.78, 6.84, 6.88, 7.14, 7.19, 7.29, and 7.30). Anal. Calcd for $C_{45}H_{48}O_9$: C, 73.75; H, 6.60. Found: C, 73.62; H, 6.41.

Tin-mediated benzylation of 1D-1,4-di-O-benzyl-2,3-O-isopropylidene-myo-inositol (**66**) *to give 1D-1,4,6-tri-O-benzyl-* (**67**) *and 1D-1,4,5-tri-O-benzyl-2,3-O-isopropylidene-myo-inositol* (**69**).—A mixture of the enantiopure diol **66** [19] (3.25 g, 8.11 mmol), Bu_2SnO (4.2 g, 16.9 mmol), Bu_4NBr (3 g, 9.3 mmol), and benzyl bromide (3 mL, 25 mmol) in MeCN (100 mL) was heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 35 h. TLC (3:2 ether–light petroleum) showed conversion of **66** into **67** (R_f 0.8) and **69** (R_f 0.7) (which co-chromatographed with the racemic materials **14** and **18**, respectively, described above) together with minor less polar products (R_f 0.9 and 0.95). The products were isolated in the usual way (see above) and column chromatography (3:2 followed by 2:1 ether–light petroleum and ether) gave **67** as a syrup (1.5 g, 38%); $[\alpha]_D$ +5.9° (*c* 1.25, $CHCl_3$); with a ^{1}H NMR spectrum identical with that of racemic **14**. Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.50; H, 6.91.

This was followed by **69** (1.1 g, 28%); mp 57–58 °C; $[\alpha]_D$ +23.2° (*c* 1, $CHCl_3$); with a ^{1}H NMR spectrum identical with that of racemic **18**. Anal. Calcd for $C_{30}H_{34}O_6 \cdot 0.5H_2O$: C, 72.12; H, 7.06. Found: C, 72.09; H, 7.40.

Compounds **67** and **69** gave syrupy acetates **68** and **70**, respectively, with ^{1}H NMR spectra identical with those of racemic **15** and **19**, respectively.

1D-1,4,6-Tri-O-benzyl-myo-inositol (**71**) and the tribenzoate (**73**).—The isopropylidene derivative **67** was hydrolysed, as described for racemic **14**, to give **71**; mp 70–71 °C (from EtOAc–light petroleum); $[\alpha]_D$ −11.3° (*c* 1, CH_2Cl_2); with a ^{1}H NMR spectrum identical with that of racemic **62**. Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.91; H, 6.62.

Compound **71** gave a syrupy triacetate **72** with a ^{1}H NMR spectrum identical with that of racemic **63**, and a syrupy tribenzoate **73**; $[\alpha]_D$ +38° (*c* 1, CH_2Cl_2); with a ^{1}H NMR spectrum identical with that of racemic **64**. Anal. (for **73**), Calcd for $C_{48}H_{42}O_9$: C, 75.57; H, 5.55. Found: C, 75.42; H, 5.55.

1D-1,4,5-Tri-O-benzyl-myo-inositol (**74**) *and the tribenzoate* (**76**).—The isopropylidene derivative **69** was hydrolysed, as described for racemic **18**, to give **74**; mp 106–107 °C (from EtOAc–light petroleum); $[\alpha]_D$ −3.3° (*c* 1, CH_2Cl_2); with a ^{1}H NMR spectrum as described for racemic **58**. Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.89; H, 6.67.

Triol **74** gave a syrupy triacetate **75** with a ^{1}H NMR spectrum identical with that of racemic **59**, and a syrupy tribenzoate **76**; $[\alpha]_D$ +4.1° (*c* 1, CH_2Cl_2); with a ^{1}H NMR spectrum identical with that of racemic **60**. Anal. (for **76**), Calcd for $C_{48}H_{42}O_9$: C, 75.57; H, 5.55. Found: C, 75.94; H, 5.46.

1L-3-O-Allyl-2,4-di-O-benzyl-1-O-p-methoxybenzyl-myo-inositol (**80**) *and racemic* **97**.—Saponification of the (+)-ω-camphanate **77** [22] gave the alcohol **78** as a syrup and this was converted into the syrupy allyl ether **79**. Acid hydrolysis of the isopropylidene group (as described for the enantiomer [22]) gave the diol **80**; mp 120–122 °C (from EtOAc–light petroleum); $[\alpha]_D$ +21° (*c* 1, $CHCl_3$) {ref. [22] for the enantiomer; mp 121–122 °C; $[\alpha]_D$ −22° (*c* 1, $CHCl_3$)}; with a ^{1}H NMR spectrum as described for the enantiomer [22]. Anal. Calcd for $C_{31}H_{36}O_7$: C, 71.51; H, 6.97. Found: C, 71.70; H, 6.94.

For the preparation of racemic **97**, the alcohol **95** [22] was converted into the allyl ether **96** which was hydrolysed to the diol **97**; mp 100–102 °C. Anal. Found: C, 71.87; H, 7.09.

1D-1-O-Allyl-2,4,5,6-tetra-O-benzyl-3-O-p-methoxybenzyl-myo-inositol (**81**) *and racemic* **98**.—(*a*) Treatment of **80** with benzyl bromide and NaH in DMF and isolation of the product in the usual way gave **81**; mp 88–90 °C (from 1:20 EtOAc–light petroleum); $[\alpha]_D$ +1.5° (*c* 2.2, $CHCl_3$); ^{1}H NMR data: δ 3.23 (dd, 1 H, *J* 1.8 and 9.7 Hz, H-1 or 3), 3.34 (dd, 1 H, *J* 1.9 and 9.6 Hz, H-3 or 1), 3.43 (t, 1 H, *J* 9.1 Hz, H-5), 3.80 (s, 3 H, OMe), 3.93–4.11 (m, 5 H, OCH_2CH= and H-2,4,6), 4.57 (s, 2 H, CH_2Ph), 4.86 (s, 8 H, 4 × CH_2Ph), 5.08–5.36 (m, 2 H, $=CH_2$), 5.71–6.13 (m, 1 H, CH=), 6.78–7.38 (m, 24 H, aromatic). Anal. Calcd for $C_{45}H_{48}O_7$: C, 77.12; H, 6.90. Found: C, 76.93; H, 6.81.

(*b*) Benzylation of the alcohol **86** (see below) in the usual way gave **81** identical with the material described in (*a*).

Racemic **98** was prepared from the racemic diol **97** as described for the enantiopure material in (*a*) and had mp 82–84 °C. Anal. Found: C, 76.77; H, 6.74.

1D-2,4,5,6-Tetra-O-benzyl-3-O-p-methoxybenzyl-myo-inositol (**83**), *the acetate* (**84**), *and the racemic alcohol* (**100**).—Treatment of the allyl ether **81** with KOBu^t in Me_2SO at 50 °C for 3 h gave the prop-1-enyl ether **82**. TLC (1:1 ether–light petroleum) did not separate **81** and **82** (R_f 0.75) and the course of the isomerisation was followed by hydrolysis of a portion of the reaction mixture (as described below) to give the alcohol **83** (R_f 0.1) from **82**. Crude **82** [^{1}H NMR data: δ 1.68 (dd, 3 H, *J* 1.8 and 6.7 Hz, =CH*Me*), 3.69 (s, 3 H, OMe), 4.50 (s, 2 H, CH_2Ph), 4.77–4.87 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.77, 4.80, and 4.87), 6.09 (dd, 1 H, *J* 1.9 and 6.1 Hz, OCH=), 6.75–7.45 (m, 24 H, aromatic)] was isolated in the usual way and treated with 3:7:1 acetone–MeOH–M HCl at 50 °C for 30 min. An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated, and the product extracted with CH_2Cl_2. Column chromatography (2:1 ether–light petroleum) gave **83** (87%); mp 91–93 °C (from 1:20 EtOAc–light petroleum); $[\alpha]_D$ −7.9° (*c* 1.9, $CHCl_3$); ^{1}H NMR data: δ 2.19 (d, 1 H, *J* 6.1 Hz, OH), 3.35–4.14 (m, 6 H, ring protons), 3.79 (s, 3 H, OMe), 4.61 (s, 2 H, CH_2Ph), 4.66–5.06 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.74, 4.78, 4.88, 4.89, and 4.93), 6.78–7.32 (m, 24 H, aromatic). Anal. Calcd for $C_{42}H_{44}O_7$: C, 76.34; H, 6.71. Found: C, 76.29; H, 6.20.

The racemic alcohol **100** was prepared similarly from the racemic allyl ether **98** via **99** and had mp 89–90 °C. Anal. Found: C, 75.98; H, 6.60.

The chiral alcohol **83** gave an acetate **84**; mp 92–94 °C (from 1:20 ether–light petroleum); $[\alpha]_D$ −26.5° (*c* 2.6, $CHCl_3$); ^{1}H NMR data: δ 1.90 (s, 3 H, Ac), 3.41–3.61 (m, 2 H, H-3,5), 3.79 (s, 3 H, OMe), 3.95–4.16 (m, 3 H, H-2,4,6), 4.59 (s, 2 H, CH_2Ph), 4.55–5.00 (m, 9 H, 4 × CH_2Ph and H-1, with major peaks at 4.69, 4.73, 4.78, 4.85, and 4.88), 6.79–7.31 (m, 24 H, aromatic). Anal. Calcd for $C_{44}H_{46}O_8$: C, 75.19; H, 6.60. Found: C, 75.13; H, 6.70.

1D-1-O-Allyl-2,4,5-tri-O-benzyl-3-O-p-methoxybenzyl-myo-inositol (**86**).—The diol **85** was prepared from racemic **115** via the bis-(+)-ω-camphanate as described for the enantiomer **90** which was obtained from the bis-(−)-ω-camphanate [24]. A mixture of **85** (2.44 g, 4.28 mmol), Bu_2SnO (1.5 g, 6.03 mmol), Bu_4NBr (1.3 g, 4.03 mmol), allyl bromide (30 mL), and MeCN (30 mL) was heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 10 h. The course of the reaction was followed by TLC (1:1 ether–light petroleum) which showed conversion of **85** (R_f 0) into major (R_f 0.6) and minor (R_f 0.5) products which were isolated in the usual way (see above). Column chromatography (same solvent) gave the crystalline major product **86** (1.62 g, 62%) [^{1}H NMR data: δ 2.54 (s, 1 H, OH), 3.08 (dd, 1 H, *J* 2.4 and 9.8 Hz, H-1 or 3), 3.25–3.46 (m, 2 H, H-3 or 1 and H-5), 3.79 (s, 3 H, OMe), 3.93–4.20 (m, 5 H, OCH_2CH= and H-2,4,6), 4.58 (s, 2 H, CH_2Ph), 4.42–4.99 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.82, 4.85, and 4.87)] and the syrupy minor product **87** (480 mg, 18%); [^{1}H NMR data: δ 2.43 (d, 1 H, *J* 5.0 Hz, OH), 3.33–3.71 (m, 3 H, ring protons), 3.73 (s, 3 H, OMe), 3.90–4.33 (m, 5 H, OCH_2CH= and 3 ring protons), 4.59 (s, 2 H, CH_2Ph), 4.64–5.06 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.78, 4.84, 4.88, and 4.93). Compound **86** had mp 76–78 °C (from 1:2 ether–light petroleum at 0 °C); $[\alpha]_D$ +9.5° (*c* 2.2, $CHCl_3$). Anal. Calcd for $C_{38}H_{42}O_7$: C, 74.73; H, 6.93. Found: C, 74.44; H, 6.53.

Compound **86** gave an acetate **88**; mp 103–105 °C; ^{1}H NMR data: δ 1.94 (s, 3 H, Ac), 3.19 (dd, 1 H, *J* 2.4 and 10.4 Hz, H-1 or 3), 3.26–3.54 (m, 2 H, H-3 or 1 and H-5), 3.79 (s, 3 H, OMe), 3.88–4.23 (m, 4 H, OCH_2CH= and H-2,4), 4.55 (s, 2 H, CH_2Ph), 4.67–4.99 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.67, 4.78, 4.81, and 4.85), 5.58 (t, 1 H, *J* 10.4 Hz, H-6).

Compound **87** gave a syrupy acetate **89**; ^{1}H NMR data: δ 2.01 (s, 3 H, Ac), 3.34–3.54 (m, 2 H, H-3,5), 3.79 (s, 3 H, OMe), 3.82–4.22 (m, 5 H, OCH_2CH= and H-2,4,6), 4.59 (s, 2 H, CH_2Ph), 4.62–4.99 (m, 7 H, 3 × CH_2Ph and H-1, with major peaks at 4.70, 4.80, 4.83, and 4.87).

(±)-1,4,5-Tri-O-allyl-3-O-p-methoxybenzyl-myo-inositol (**101**) *and the corresponding tri(but-2-enyl) ether* (**53**).—A mixture of the triallyl ether **36** (1 g, 3.33 mmol), Bu_2SnO (1.66 g, 6.67 mmol), and Bu_4NBr (2.14 g, 6.64 mmol) in MeCN (50 mL) was heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 3 h. *p*-Methoxybenzyl chloride (2.1 g, 13.4 mmol) was added and refluxing was continued for 4 h after which time TLC (ether) showed complete conversion of **36** (R_f 0.2) into a major product (R_f 0.8). The mixture was concentrated and processed as described above for similar reactions, and column chromatography (2:1 ether–light petroleum) gave **101** (1.23 g, 85%); mp 53–55 °C (from ether–light petroleum); ^{1}H NMR data: δ 2.4, 2.53 (2

s, each 1 H, 2 × OH), 3.03–3.91 (m, 6 H, ring protons), 3.81 (s, 3 H, OMe), 4.64 (s, 2 H, CH_2Ph), 6.83–7.34 (m, 4 H, aromatic). Anal. Calcd for $C_{23}H_{32}O_7$: C, 65.69; H, 7.67. Found: C, 65.92; H, 7.84. This gave a syrupy diacetate **102**; ^{1}H NMR data: δ 2.07, 2.11 (2 s, each 3 H, 2 × Ac), 3.79 (s, 3 H, OMe), 4.50, 4.58 (AB, 2 H, *J* 12 Hz, CH_2Ph), 5.10–5.33 (m 7 H, 3 × =CH_2 and H-6), 5.69 (t, H-2), 6.91–7.21 (AB, 4 H, *J* 8.5 Hz, aromatic).

When the tri(but-2-enyl) ether **51** was subjected to similar tin-mediated *p*-methoxybenzylation, the *p*-methoxybenzyl ether **53** was obtained as a syrup; ^{1}H NMR data: δ 1.68–1.74 (m, 9 H, 3 × =CH*Me*), 2.37, 2.50 (2 s, each 1 H, 2 × OH), 3.01–3.41 (m, 3 H, H-1,3,5), 3.65–4.48 (m, 9 H, 3 × OCH_2CH= and H-2,4,6), 3.81 (s, 3 H, OMe), 4.65 (s, 2 H, CH_2Ph), 5.65–5.85 (m, 6 H, 3 × CH=CH), 6.93–7.26 (AB, 4 H, *J* 8.5 Hz, aromatic).

(±)-1,4,5-Tri-O-*allyl-2,6-di*-O-*benzyl-3*-O-p-*methoxybenzyl*-myo-*inositol* (**103**) *and the corresponding tri(but-2-enyl) ether* (**54**).—The diol **101** was treated with NaH and benzyl bromide in DMF and the product isolated in the usual way. TLC (1:1 ether–light petroleum) showed conversion of **101** (R_f 0) into **103** (R_f 0.8) together with trace byproducts. Column chromatography (1:2 ether–light petroleum) gave **103**; mp 55–57 °C (from light petroleum at 0 °C); ^{1}H NMR data: δ 3.11–3.33 (m, 3 H), 3.81 (s, 3 H, OMe), 4.54 (s, 2 H, CH_2Ph), 4.80, 4.82 (AB, 2 H, *J* 11 Hz, CH_2Ph), 4.84 (s, 2 H, CH_2Ph), 6.81–7.34 (m, 14 H, aromatic). Anal. Calcd for $C_{37}H_{44}O_7$: C, 73.97; H, 7.38. Found: C, 73.68; H, 7.41.

Similar benzylation of the diol **53** gave **54** as a syrup; ^{1}H NMR data: δ 1.61–1.72 (m, 9 H, 3 × =CH*Me*), 3.09–3.30 (m, 3 H, H-1,3,5), 3.80 (s, 3 H, OMe), 3.72–4.46 (m, 9 H, 3 × OCH_2CH= and H-2,4,6), 4.56 (s, 2 H, CH_2Ph), 4.80–4.84 (m, 4 H, 2 × CH_2Ph), 5.50–5.78 (m, 6 H, 3 × CH=CH), 6.81–7.42 (m, 14 H, aromatic). Anal. Calcd for $C_{40}H_{50}O_7$: C, 74.74; H, 7.84. Found: C, 74.68; H, 7.86.

(±)-2,4-Di-O-*benzyl-1*-O-p-*methoxybenzyl*-myo-*inositol* (**105**) *and the triacetate* (**106**).—(*a*) The triallyl ether **103** was treated with KOBu^t in Me_2SO at 50 °C for 9 h and the product isolated in the usual way. TLC (1:2 ether–light petroleum) showed conversion of **103** (R_f 0.5) into a major product **104** (R_f 0.75). The crude product was treated with 9:1 acetone–M HCl at 50 °C for 40 min after which time TLC (ether) showed conversion of **104** (R_f 1.0) into a major product (R_f 0.4). An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated, and the crude product was extracted with ether. Column chromatography (ether) gave **105** (77%); mp 124–125 °C (from EtOAc); ^{1}H NMR data: δ 2.36 (d, 1 H, *J* 6.1 Hz, OH), 2.71 (m, 2 H, 2 × OH), 3.25 (dd, 1 H, *J* 2.4 and 8.5 Hz), 3.45–4.05 (m, 5 H, ring protons), 3.79 (s, 3 H, OMe), 4.53, 4.57 (AB, 2 H, *J* 11 Hz, CH_2Ph), 4.75, 4.87 (AB, 2 H, *J* 11 Hz, CH_2Ph), 4.84 (s, 2 H, CH_2Ph), 6.81–7.33 (m, 14 H, aromatic). Anal. Calcd for $C_{28}H_{32}O_7$: C, 69.98; H, 6.71. Found: C, 70.22; H, 6.74.

Triol **105** gave a triacetate **106**; mp 127–128 °C (from ether–light petroleum); ^{1}H NMR data: δ 1.91 (6 H), 1.98 (3 H), (2 s, 3 × Ac), 3.53 (dd, 1 H, *J* 2.4 and 9.8 Hz, H-3), 3.79 (s, 3 H, OMe), 4.01–4.22 (m, 2 H, H-2,4), 4.47–4.80 (m, 6 H, 3 × CH_2Ph), 5.05 (t, 1 H, *J* 9.8 Hz, H-5), 5.53 (t, 1 H, *J* 9.8 Hz, H-6), 6.81–7.32 (m, 14 H, aromatic). Anal. Calcd for $C_{34}H_{38}O_{10}$: C, 67.31; H, 6.31. Found: C, 67.48; H, 6.20.

(*b*) The tri(but-2-enyl) ether **54** (400 mg, 0.62 mmol) was treated with $KOBu^t$ (1 g, 8.2 mmol) in Me_2SO (10 mL) at 50 °C for 1 h. TLC (1:2 ether–light petroleum) showed conversion of **54** (R_f 0.5) into a product (R_f 0) [TLC (ether) R_f 0.5]. Semi-satd aq KCl (20 mL) was added and the product was extracted with ether and purified as in (*a*) to give **105** (200 mg, 67%) identical with that described in (*a*).

*(±)-2,4-Di-*O*-benzyl-5,6-*O*-isopropylidene-1-*O*-*p*-methoxybenzyl*-myo-*inositol* (**95**) [22].—A solution of the triol **105** (1 g) and toluene-*p*-sulfonic acid (30 mg) in acetone (20 mL) and 2,2-dimethoxypropane (10 mL) was kept at 20 °C for 2 h. TLC (1:1 ether–light petroleum) showed conversion of **105** (R_f 0) into a major product (R_f 0.7). Triethylamine (1 mL) and $NaHCO_3$ (1 g) were added and the mixture was concentrated. Column chromatography (same solvent) gave syrupy **95** (89%) identical with the material described previously [22].

*(±)-2,5-Di-*O*-acetyl-1,4,6-tri-*O*-allyl-3-*O*-*p*-methoxybenzyl*-myo-*inositol* (**108**).—A mixture of the triol **42** (8.3 g, 27.6 mmol), Bu_2SnO (10.3 g, 41.4 mmol), Bu_4NBr (13.4 g, 41.6 mmol), and MeCN (220 mL) was heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 4 h. After cooling, *p*-methoxybenzyl chloride (7.5 mL, 55.3 mmol) was added and refluxing was continued for 12 h. TLC (5:1 ether–light petroleum) showed conversion of **42** (R_f 0) into a major product (R_f 0.45) together with traces of less polar products and these were isolated in the usual way (see above). Column chromatography (same solvent) gave **107** (10.6 g, 91%) as a syrup; ^1H NMR data: δ 2.53, 2.70 (2 s, each 1 H, 2 × OH), 3.12–3.69 (m, 5 H, ring protons), 3.79 (s, 3 H, OMe), 4.09–4.35 (m, 7 H, 1 ring proton and 3 × OCH_2CH=), 4.63 (s, 2 H, CH_2Ph), 5.10–5.35 (m, 6 H, 3 × =CH_2), 5.72–6.16 (m, 3 H, 3 × CH=), 6.82–7.34 (m, 4 H, aromatic).

A portion of **107** was treated with 1:2 Ac_2O–pyridine at 50 °C for 8 h and the diacetate **108**, isolated in the usual way, had mp 99–101 °C (from 1:2 ether–light petroleum); ^1H NMR data: δ 2.09, 2.13 (2 s, each 3 H, 2 × Ac), 3.26–3.71 (m, 4 H, H-1,3,4,6), 3.79 (s, 3 H, OMe), 3.93–4.26 (m, 6 H, 3 × OCH_2CH=), 4.48, 4.58 (AB, 2 H, *J* 10.4 Hz, CH_2Ph), 4.95 (t, 1 H, *J* 9.2 Hz, H-5), 5.06–5.33 (m, 6 H, 3 × =CH_2), 5.65–6.05 (m, 3 H, 3 × CH=), 5.68 (t, 1 H, *J* 2.4 Hz, H-2), 6.81–7.30 (m, 4 H, aromatic). Anal. Calcd for $C_{27}H_{36}O_9$: C, 64.27; H, 7.19. Found: C, 64.27; H, 7.22.

*(±)-1,4,6-Tri-*O*-allyl-2,5-di-*O*-benzyl-3-*O*-*p*-methoxybenzyl*-myo-*inositol* (**109**).—The diol **107** was treated with benzyl bromide and NaH in DMF and the product isolated in the usual way. TLC (1:2 ether–light petroleum) showed conversion of **107** (R_f 0) into **109** (R_f 0.3) together with traces of less polar byproducts. Column chromatography (same solvent) gave **109** (98%); mp 51–53 °C (from light petroleum and a little ether at 0 °C); ^1H NMR data: δ 3.08–3.41 (m, 3 H, ring protons), 3.72–4.35 (m, 9 H, 3 ring protons and 3 × OCH_2CH=), 3.80 (s, 3 H, OMe), 4.55 (s, 2 H, CH_2Ph), 4.81 (s, 4 H, 2 × CH_2Ph), 5.07–5.35 (m, 6 H, 3 × =CH_2), 5.69–6.25 (m, 3 H, 3 × CH=), 6.81–7.32 (m, 14 H, aromatic). Anal. Calcd for $C_{37}H_{44}O_7$: C, 73.97; H, 7.38. Found: C, 73.93; H, 7.36.

*(±)-2,5-Di-*O*-benzyl-3,4-*O*-isopropylidene-1-*O*-*p*-methoxybenzyl*-myo-*inositol* (**113**).—A solution of **109** (18 g, 30 mmol) and $KOBu^t$ (11 g, 90 mmol) in dry Me_2SO (200 mL) was kept at 50 °C under anhydrous conditions and the progress of the isomerisation was followed by TLC (1:2 ether–light petroleum). For 4 h, **109** (R_f 0.3) was converted

through several intermediate products (R_f 0.3–0.7) into a major product **110** (R_f 0.7) together with more polar trace impurities. The solution was cooled and diluted with semi-satd aq KCl (300 mL) and the precipitated product was extracted with ether. The extract was dried (K_2CO_3) and concentrated to give crude **110** (17 g). This was treated with 3:7:1 acetone–MeOH–M HCl at reflux for 20 min after which time TLC (EtOAc) showed conversion of **110** (R_f 1.0) into a major product (R_f 0.6). An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated, and toluene was evaporated from the residue. The product was extracted from this residue with CH_2Cl_2 to give the crude triol **111** (12 g) as a solid which was soluble in EtOAc and acetone but did not recrystallise readily and was therefore purified via the isopropylidene derivative **113**.

The triol **111** gave a syrupy triacetate **112**; ^{1}H NMR data: δ 1.91 (s, 3 H, Ac), 1.94 (s, 6 H, 2 × Ac), 3.44 (dd, 1 H, H-3), 3.55 (t, 1 H, *J* 9.8 Hz, H-5), 3.76 (s, 3 H, OMe), 4.05 (t, 1 H, H-2), 4.41, 4.48 (AB, 2 H, *J* 11 Hz, CH_2Ph), 4.58 (s, 2 H, CH_2Ph), 4.66–4.93 (m, 3 H, CH_2Ph and H-1), 5.69 (t, 2 H, *J* 9.8 Hz, H-4,6), 6.81–7.29 (m, 14 H, aromatic).

A mixture of the crude triol **111** (12 g), toluene-*p*-sulfonic acid (1 g), acetone (200 mL), and 2,2-dimethoxypropane (200 mL) was stirred at 20 °C for 2 h after which time TLC (EtOAc) showed conversion of **111** (R_f 0.6) into a product (R_f 1.0) [TLC (2:1 ether–light petroleum) R_f 0.7]. An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated, and toluene was evaporated from the residue. The product was extracted from the residue with ether (containing a little NEt_3), the extract was concentrated, and the crystalline product recrystallised from light petroleum (containing a little NEt_3) to give **113** (7.36 g, 47% from **109**); mp 109–111 °C; ^{1}H NMR data: δ 1.44 (s, 6 H, CMe_2), 3.24–3.58 (m, 3 H), 3.79 (s, 3 H, OMe), 3.92–4.22 (m, 3 H), 4.47, 4.49 (AB, 2 H, *J* 11 Hz, CH_2Ph), 4.80 (s, 2 H, CH_2Ph), 4.75, 4.88 (AB, 2 H, *J* 11 Hz, CH_2Ph), 6.78–7.36 (m, 14 H, aromatic). Anal. Calcd for $C_{31}H_{36}O_7$: C, 71.52; H, 6.97. Found: C, 71.28; H, 6.97.

(±)-2,4,5-Tri-O-*benzyl-1,6*-O-*isopropylidene-3*-O-p-*methoxybenzyl*-myo-*inositol* (**114**) [24].—The alcohol **113** was treated with benzyl bromide and NaH in DMF and the product isolated in the usual way to give **114**. TLC (1:1 ether–light petroleum) showed conversion of **113** (R_f 0.4) into **114** (R_f 0.75). Column chromatography (same solvent) gave **114** with properties identical with those of the material described previously [24]; ^{1}H NMR data: δ 1.43, 1.46 (2 s, each 3 H, CMe_2), 3.28–3.94 (m, 4 H, ring protons), 3.79 (s, 3 H, OMe), 4.08 (t, 1 H, H-2), 4.27 (t, 1 H, *J* 9.8 Hz), 4.51 (s, 2 H, CH_2Ph), 4.65–5.00 (m, 9 H, 3 × CH_2Ph, with major peaks at 4.79, 4.83, and 4.86), 6.75–7.38 (m, 19 H, aromatic).

*1*D-*2,5,6-Tri*-O-*benzyl-1*-O-p-*methoxybenzyl*-myo-*inositol 3,4-bis(dibenzyl phosphate)* (**117**).—A solution of dry 1*H*-tetrazole (500 mg, 3.37 mmol) in dry MeCN (10 mL) was added to a solution of the enantiopure diol **90** (700 mg, 1.23 mmol) and bis(benzyloxy)diisopropylaminophosphine (1 g, 2.89 mmol) in dry CH_2Cl_2 (10 mL) at 20 °C. TLC (ether) showed conversion of **90** (R_f 0.5) into the bisphosphite **116** (R_f 1.0) and after 1 h the mixture was cooled to 0 °C and an aq solution of *tert*-butyl hydroperoxide (1 mL, 70%) was added. TLC (ether) showed conversion of **116** into the bisphosphate **117** (R_f 0.75). Toluene (20 mL) was added and the mixture was

concentrated to remove the MeCN. Dichloromethane (20 mL) and aq sodium metabisulfite (25 mL, 10%) were added and the organic layer was separated, washed (satd aq KCl), dried ($MgSO_4$), and concentrated. Column chromatography (ether) gave the syrupy bisphosphate **117** (1.03 g, 77%); $[\alpha]_D$ −0.6 ° (*c* 2.1, $CHCl_3$); ^{1}H NMR data: δ 3.78 (s, 3 H, OMe), 4.46 (s, 2 H, CH_2Ph), 4.67–5.06 (m, 14 H, 7 × CH_2Ph, with major peaks at 4.75, 4.82, 4.86, 4.91, 4.97, 5.00, and 5.06), 6.77–7.33 (m, 39 H, aromatic); ^{31}P NMR data: δ −2.02, −1.41; Anal. Calcd for $C_{63}H_{64}O_{13}P_2$: C, 69.35; H, 5.91; P, 5.68. Found: C, 68.72; H, 5.78; P, 6.31.

*1*D-*2,5,6-Tri*-O-*benzyl*-myo-*inositol 3,4-bis(dibenzyl phosphate)* (**118**).—A solution of ammonium cerium(IV) nitrate (1.89 g, 3.45 mmol) in 9:1 MeCN–water (12 mL) was added dropwise with stirring to a solution of **117** (940 mg, 0.86 mmol) in the same solvent (20 mL) during 15 min, after which time the dark-yellow colour of the reagent was no longer converted into a pale-yellow colour. TLC (ether) then showed complete conversion of **117** (R_f 0.75) into a product (R_f 0.3). Water (10 mL) was added, the solution was concentrated to remove MeCN, and the mixture was extracted with CH_2Cl_2. The organic layer was separated, washed (satd aq $NaHCO_3$), dried ($MgSO_4$), and concentrated. Column chromatography (ether) gave the syrupy alcohol **118** (585 mg, 70%); $[\alpha]_D$ +3.7° (*c* 2, $CHCl_3$); ^{1}H NMR data: δ 4.72–5.06 (m, 14 H, 7 × CH_2Ph, with major peaks at 4.72, 4.74, 4.79, 4.83, 4.87, 4.93, 4.97, 5.02, and 5.06); ^{31}P NMR data: δ −1.82, −1.28. Anal. Calcd for $C_{55}H_{56}O_{12}P_2$: C, 68.03; H, 5.81; P, 6.38. Found: C, 67.55; H, 5.70; P, 5.89.

*1*D-*1*-O-*Allyl-2,6-di*-O-*benzyl-3,4-di*-O-p-*methoxybenzyl*-myo-*inositol* (**119**) *and racemic* **125**.—A mixture of the diol **80** (1.8 g, 3.46 mmol), Bu_2SnO (2.58 g, 10.4 mmol), and Bu_4NBr (3.35 g, 10.4 mmol) in MeCN (50 mL) was heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 4 h. *p*-Methoxybenzyl chloride (2.7 g, 17.2 mmol) was added and refluxing was continued for 20 h. TLC (1:1 ether–light petroleum) showed conversion of **80** (R_f 0.05) into a major product (R_f 0.35) together with trace byproducts. The products were isolated in the usual way (see above) and column chromatography (same solvent) gave the crude product (which was a mixture of regioisomers, see racemic **125**). Crystallisation from EtOAc–light petroleum gave **119** (670 mg, 54%); mp 99–100 °C; $[\alpha]_D$ +2.2° (*c* 1, $CHCl_3$); ^{1}H NMR data: δ 2.47 (bs, 1 H, OH), 3.15–3.56 (m, 4 H), 3.79, 3.80 (2 s, each 3 H, 2 × OMe), 3.88–4.09 (m, 4 H), 4.56–4.99 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.56, 4.74, 4.80, and 4.86), 6.79–7.40 (m, 18 H, aromatic). Anal. Calcd for $C_{39}H_{44}O_8 \cdot 0.5H_2O$: C, 72.09; H, 6.98. Found: C, 72.18; H, 6.78.

Racemic **125**, prepared in the same way from the diol **97**, had mp 113–114 °C; with a ^{1}H NMR spectrum identical with that of **119**. Anal. Calcd for $C_{39}H_{44}O_8$: C, 73.10; H, 6.92. Found: C, 72.95; H, 6.93. A portion of crude racemic product acetylated before crystallisation showed two acetate peaks in the NMR spectrum, indicating the presence of **127** and **128** (approximately 3:2), but acetylation of the alcohol which crystallised gave only **127**.

*1*D-*1*-O-*Allyl-2,5,6-tri*-O-*benzyl-3,4-di*-O-p-*methoxybenzyl*-myo-*inositol* (**120**) *and racemic* **126**.—The alcohol **119** was treated with benzyl bromide and NaH in DMF and the product isolated in the usual way. TLC (1:1 ether–light petroleum) showed conversion of **119** (R_f 0.35) into **120** (R_f 0.6). Column chromatography (1:2 ether–light

petroleum) gave **120** (90%); mp 93–94 °C (from light petroleum); $[\alpha]_D$ +0.1° (*c* 1.1, $CHCl_3$); ^1H NMR data: δ 3.17–3.52 (m, 3 H, H-1,3,5), 3.78, 3.81 (2 s, each 3 H, 2 × OMe), 3.90–4.11 (m, 5 H, $OCH_2CH=$ and H-2,4,6), 4.58 (s, 2 H, CH_2Ph), 4.72–5.00 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.77, 4.80, 4.82, and 4.87), 5.10–5.43 (m, 2 H, $=CH_2$), 5.66–6.17 (m, 1 H, CH=), 6.74–7.38 (m, 23 H, aromatic). Anal. Calcd for $C_{46}H_{50}O_8$: C, 75.59; H, 6.90. Found: C, 75.05; H, 6.50.

Racemic **126**, prepared in the same way from **125**, had mp 81–82 °C (from light petroleum). Anal. Found: C, 75.27; H, 6.95.

1D-1-O-Acetyl-2,5,6-tri-O-benzyl-3,4-di-O-p-methoxybenzyl-myo-inositol (**123**) *and the racemic alcohol* (**130**).—The allyl ether **120** was treated with $KOBu^t$ in Me_2SO and the crystalline product **121** was isolated in the usual way. TLC (1:1 ether–light petroleum) showed no separation of **120** and **121** (R_f 0.7) but acid hydrolysis of a portion (see below) indicated when the isomerisation was complete. Hydrolysis of **121** with 7:3:1 MeOH–acetone–M HCl at 50 °C for 20 min and isolation of the product in the usual way gave **122** which was purified by column chromatography (2:1 ether–light petroleum). After crystallisation from EtOAc–light petroleum, **122** rapidly turned to a syrup (?hygroscopic) and was therefore converted into the acetate **123**; mp 109–110 °C (from light petroleum); $[\alpha]_D$ −26.4° (*c* 1.5, $CHCl_3$); ^1H NMR data: δ 1.90 (s, 3 H, Ac), 3.39–3.60 (m, 2 H, H-3,5), 3.77, 3.79 (2 s, each 3 H, 2 × OMe), 3.96–4.56 (m, 3 H, H-2,4,6), 4.55–4.94 (m, 11 H, 5 × CH_2Ph and H-1, with major peaks at 4.61, 4.70, 4.73, 4.78, 4.83, and 4.86), 6.75–7.32 (m, 23 H, aromatic). Anal. Calcd for $C_{45}H_{48}O_9$: C, 73.75; H, 6.60. Found: C, 73.24; H, 6.49.

De-*p*-methoxybenzylation of **122** (see below for racemate) gave the known [24] 1L-2,4,5-tri-*O*-benzyl-*myo*-inositol (**124**).

The racemic allyl ether **126** was treated in the same way to give the prop-1-enyl ether **129**; mp 103–104 °C (from light petroleum containing a little NEt_3); ^1H NMR data: δ 1.67 (dd, 3 H, *J* 1.2 and 6.7 Hz, =CH*Me*), 3.30–3.66 (m, 3 H, H-1,3,5), 3.77, 3.80 (2 s, each 3 H, 2 × OMe), 3.94–4.56 (m, 4 H, =C*H*Me and H-2,4,6), 4.56 (s, 2 H, CH_2Ph), 4.77 (d, 4 H, 2 × CH_2Ph), 4.86 (s, 4 H, 2 × CH_2Ph), 6.9 (dd, 1 H, *J* 1.8 and 6.1 Hz, OCH=), 6.74–7.39 (m, 23 H, aromatic). Compound **129** was hydrolysed as described above for the enantiopure material to give the racemic alcohol **130**; mp 78–79 °C (from EtOAc–light petroleum). Anal. Calcd for $C_{43}H_{46}O_8$: C, 74.76; H, 6.71. Found: C, 74.82; H, 6.76. A portion of this was converted into the acetate **131** which had a ^1H NMR spectrum identical with that of the enantiopure acetate **123**.

The alcohol **130** was treated with ammonium cerium(IV) nitrate in aq CH_2Cl_2 in the usual way (see above) to remove the *p*-methoxybenzyl groups. TLC (3:1 ether–light petroleum) showed conversion of **130** (R_f 0.5) through products (R_f 0.2) into a final product (R_f 0.1) which co-chromatographed with racemic 2,4,5-tri-*O*-benzyl-*myo*-inositol (**132**) prepared previously [35]. This was converted into the triacetate **133**; mp 134–135 °C (from ether–light petroleum); ^1H NMR data: δ 1.91 (s, 6 H, 2 × Ac), 1.97 (s, 3 H, Ac), 3.56 (t, 1 H, *J* 9.2 Hz, H-5), 4.02–4.24 (m, 2 H, H-2,4, with major peaks at 4.05, 4.07, and 4.13), 4.48–4.96 (m, 8 H, 3 × CH_2Ph and H-1,3, with major peaks at 4.63, 4.66, 4.73, and 4.77), 5.61 (t, 1 H, *J* 10 Hz, H-6), 7.24–7.32 (m, 15 H, aromatic). This spectrum was identical with that of the triacetate prepared from known **132**. Anal. Calcd for $C_{33}H_{36}O_9$: C, 68.73; H, 6.29. Found: C, 68.02; H, 6.30.

(±)-2,6-Di-O-benzyl-1-O-p-methoxybenzyl-myo-inositol (**135**), *the racemic triacetate* (**136**), *and 1D-2,6-di-O-benzyl-1-O-p-methoxybenzyl-myo-inositol* (**142**).—A solution of the racemic diol **134** [25] (2 g, 3.33 mmol) and DDQ (945 mg, 4.1 mmol, 1.25 equiv) in 20:1 CH_2Cl_2–water (100 mL) was stirred at 5 °C for 5 h and the solution was then washed with satd aq $NaHCO_3$ and dried (K_2CO_3). TLC (EtOAc) showed some starting material (R_f 0.8), a major product (R_f 0.4), and minor products (R_f 0.6 and 0.2). Column chromatography (EtOAc) gave **134** (148 mg), the product R_f 0.6 (47 mg), the major product **135** (R_f 0.4, 767 mg, 48%), and the product R_f 0.2 (100 mg). The minor product (R_f 0.6) had mp 116–117 °C (from EtOH); it co-chromatographed with, and had a ^{1}H NMR spectrum identical with that of, the enantiopure triol **166** (see below). The minor product (R_f 0.2) co-chromatographed with, and had a ^{1}H NMR spectrum identical with that of, 2,4-di-*O*-benzyl-*myo*-inositol (**139**) [25]. The major product **135** had mp 138–140 °C (from 1:10 EtOAc–light petroleum); ^{1}H NMR data: δ 2.51 (d, 1 H, *J* 7.9 Hz, OH), 2.80 (d, 1 H, *J* 1.8 Hz, OH), 3.07 (d, 1 H, *J* 1.7 Hz, OH), 3.43–3.98 (m, 6 H, ring protons, with major peaks at 3.35, 3.45, 3.48, 3.62, 3.73, and 3.98), 3.79 (s, 3 H, OMe), 4.60 (s, 2 H, CH_2Ph), 4.82, 4.87 (2 ABq, each 2 H, 2 × CH_2Ph), 6.79–7.32 (m, 14 H, aromatic). Anal. Calcd for $C_{28}H_{32}O_7$: C, 69.98; H, 6.71. Found: C, 69.97; H, 6.84.

The triol **135** gave a triacetate **136**; mp 141–143 °C (from 1:10 ether–light petroleum); ^{1}H NMR data: δ 1.90, 1.95, 1.98 (3 s, each 3 H, 3 × Ac), 3.56 (dd, 1 H, *J* 2.4 and 9.8 Hz, H-1), 3.81 (s, 3 H, OMe), 3.97–4.18 (m, 2 H, H-2,6, with a major peak at 4.07), 4.55–4.97 (m, 7 H, H-3 and 3 × CH_2Ph, with major peaks at 4.59, 4.68, 4.73, and 4.80), 5.07 (t, 1 H, *J* 9.4 Hz. H-5), 5.54 (t, 1 H, *J* 9.8 Hz, H-4), 6.80–7.34 (m, 14 H, aromatic, with major peaks at 6.89, 7.19 and 7.28). Anal. Calcd for $C_{34}H_{38}O_{10}$: C, 67.31; H, 6.31. Found: C, 67.24; H, 6.53.

The reaction was repeated with the enantiopure diol **140** [25] to give similar results with the major product being the triol **142** (57%); mp 136–137 °C (from 1:1 EtOAc–light petroleum); $[\alpha]_D$ −8.5° (*c* 1, $CHCl_3$); with a ^{1}H NMR spectrum identical with that of racemic **135**. Anal. Found: C, 69.47; H, 6.80.

Triol **142** gave a triacetate **143**; mp 138–139 °C (from 1:10 ether–light petroleum); with a ^{1}H NMR spectrum identical with that of racemic **136**. Anal. Found: C, 67.39; H, 6.52.

1D-2,6-Di-O-benzyl-1-O-p-methoxybenzyl-myo-inositol 3,4,5-tris(dibenzyl phosphate) (**144**) *and racemic* **137**.—A solution of dry 1*H*-tetrazole (623 mg, 8.9 mmol) in MeCN (15 mL) was added to a solution of the triol **142** (779 mg, 1.62 mmol) and bis(benzyloxy)diisopropylaminophosphine (1.85 g, 5.36 mmol) in CH_2Cl_2 (15 mL), and the solution was stirred at 20 °C for 1 h. The mixture was then cooled to 0 °C and a solution of 3-chloroperoxybenzoic acid (2.2 g, technical) in CH_2Cl_2 (5 mL) was added dropwise. After 2 h, TLC (EtOAc) showed conversion of **142** (R_f 0.4) into the trisphosphate **144** (R_f 0.9). TLC (ether) showed **144** (R_f 0.3) together with some less polar byproducts. The products were isolated in the usual way (see above) and column chromatography (ether to remove byproducts followed by EtOAc) gave **144** (1.3 g, 63%); $[\alpha]_D$ −10.2° (*c* 1.3, $CHCl_3$); ^{1}H NMR data: δ 3.4 (dd, 1 H, H-1), 3.76 (s, 3 H, OMe), 3.76–5.11 (m, 23 H, 9 × CH_2Ph, H-2 to 6, with major peaks at 4.39, 4.77, 4.81, 4.91, 4.95, 4.97, 5.00, 5.03, 5.05, and 5.11), 6.70–7.35 (m, 44 H, aromatic, with major peaks at 6.79, 7.01,

7.16, 7.18, 7.20, 7.24, 7.28, and 7.35). Anal. Calcd for $C_{70}H_{71}O_{16}P_3$: C, 66.66; H, 5.67; P, 7.37. Found: C, 66.24; H, 5.81; P, 7.64. ([14], no details).

In the same way, the racemic triol **135** was converted into the racemic trisphosphate **137** which had a ^{1}H NMR spectrum identical with that of **144**.

*(±)-2,4-Di-*O*-benzyl-*myo*-inositol 1,5,6-tris(dibenzyl phosphate)* (**138**) *and 1*L*-2,4-di-*O*-benzyl-*myo*-inositol 1,5,6-tris(dibenzyl phosphate)* (**145**).—A solution of ammonium cerium(IV) nitrate (553 mg, 1 mmol) in 9:1 MeCN–water (10 mL) was added dropwise to a solution of the racemic trisphosphate **137** (318 mg, 0.25 mmol) in 9:1 MeCN–water (7 mL) during 10 min. After 1 h at 20 °C, TLC (15:1 $CHCl_3$–MeOH) showed conversion of **137** (R_f 0.6) into a major product (R_f 0.5). Water (50 mL) was added and the mixture was concentrated to half volume to remove MeCN. The product was extracted with ether and the extract washed (satd aq $NaHCO_3$), dried ($MgSO_4$), and concentrated. Column chromatography (1:1:2 EtOAc–CH_2Cl_2–ether) gave **138** (400 mg, 80%) as a syrup; ^{31}P NMR data: δ −1.95, −1.34, −1.14. Anal. Calcd for $C_{62}H_{63}O_{15}P_3$: C, 65.76; H, 5.56; P, 8.14. Found: C, 65.25; H, 5.87; P, 7.94.

In the same way, the enantiopure trisphosphate **144** was converted into the alcohol **145** (70%) which was obtained as a syrup; $[\alpha]_D$ −5.8° (*c* 1.1, $CHCl_3$); with the same ^{31}P NMR spectrum as racemic **138** {[17] $[\alpha]_D$ −8.2° (*c* 1, $CHCl_3$); ^{31}P NMR data: δ −2.12, −1.55, −1.43; [14] ^{1}H NMR details only} Anal. Found: C, 65.49; H, 5.30; P, 8.44.

*(±)-1,4,6-Tri-*O*-allyl-2-*O*-benzyl-3,5-di-*O*-*p*-methoxybenzyl-*myo*-inositol* (**151**).—The alcohol **12** was treated with *p*-methoxybenzyl chloride and NaH in DMF and the product isolated in the usual way to give **146** as a syrup. TLC (2:1 ether–light petroleum) showed conversion of **12** (R_f 0.6) into **146** (R_f 0.8). The product was treated with 9:1 MeOH–M HCl at reflux for 20 min, an excess of NEt_3 and $NaHCO_3$ was added, and the mixture was concentrated. TLC (as above) showed the diol **147** with R_f 0.1. Column chromatography (2:1 ether–light petroleum followed by ether) gave **147** (70% from **12**) which formed a gel from most solvents. This gave a syrupy diacetate **148**; ^{1}H NMR data: δ 2.03, 2.08 (2 s, each 3 H, 2 × Ac), 3.30–4.35 (m, 10 H, H-1,4,5,6 and 3 × OCH_2CH=), 3.79 (s, 3 H, OMe), 4.75 (s, 2 H, CH_2Ph), 4.80 (dd, 1 H, H-3), 5.10–5.35 (m, 6 H, 3 × =CH_2), 5.55 (t, 1 H, H-2), 5.60–6.22 (m, 3 H, 3 × CH=), 6.83-7.35 (m, 4 H, aromatic).

A mixture of **147** (16.6 g, 39.5 mmol), Bu_2SnO (13 g, 52 mmol), Bu_4NBr (12.7 g, 39.4 mmol), and MeCN (400 mL) was heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 4 h, then *p*-methoxybenzyl chloride (10 mL, 73.7 mmol) was added, and refluxing was continued for 4 h. TLC (as above) showed a major product (R_f 0.5) and this was isolated in the usual way to give crude **149** as a syrup (20.2 g, 95%); ^{1}H NMR data: δ 3.80 (s, 6 H, 2 × OMe), 4.65, 4.74 (2 s, each 2 H, 2 × CH_2Ph).

A portion of **149** was acetylated to give the acetate **150** as a syrup; ^{1}H NMR data: δ 2.08 (s, 3 H, Ac), 3.23–4.34 (m, 11 H, 3 × OCH_2CH= and 5 ring protons), 3.79 (s, 6 H, 2 × OMe), 4.49, 4.59 (AB, 2 H, *J* 11 Hz, CH_2Ph), 4.75 (s, 2 H, CH_2Ph), 5.10–5.37 (m, 6 H, 3 × =CH_2), 5.67 (t, 1 H, H-2), 5.67–6.22 (m, 3 H, 3 × CH=), 6.81–7.36 (m, 8 H, aromatic).

The alcohol **149** (20 g) was treated with benzyl bromide and NaH in DMF and the product isolated in the usual way. TLC (1:1 ether–light petroleum) showed conversion of **149** (R_f 0.2) into **151** (R_f 0.7). Column chromatography (same solvent) gave **151** as a syrup (20 g, 86%). Anal. Calcd for $C_{38}H_{46}O_8$: C, 72.36; H, 7.35. Found: C, 72.29; H, 7.21.

*(±)-2-O-benzyl-3,4-O-isopropylidene-1,5-di-*O-p-*methoxybenzyl-*myo-*inositol* (**155**). —A solution of the triallyl ether **151** (10 g, 15.8 mmol) and $KOBu^t$ (7 g, 57 mmol) in dry Me_2SO (100 mL) was kept at 50 °C under N_2 for 3 h and the course of the isomerisation was followed by TLC (1:3 ether–light petroleum) which showed conversion of **151** (R_f 0.2) through intermediate products into a major product **152** (R_f 0.6). The product was isolated in the usual way (see above) and treated with 7:2:1 acetone–MeOH–M HCl (100 mL) at reflux for 20 min. An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated, and the crystalline product (7 g, 86%) was extracted from the residue with CH_2Cl_2. TLC (EtOAc) showed a major product (R_f 0.6) with minor less polar products. A portion was recrystallised from MeOH to give the triol **153**; mp 150–152 °C; ^{1}H NMR data: δ 2.1 (bs, 3 H, 3 × OH), 3.10–4.19 (m, 6 H, ring protons), 3.79, 3.81 (2 s, each 3 H, 2 × OMe), 4.59, 4.76, 4.80 (3 ABq, each 2 H, 3 × CH_2Ph), 6.82–7.31 (m, 13 H, aromatic, with major peaks at 6.82, 6.91, 7.21, 7.25, and 7.30). Anal. Calcd for $C_{29}H_{34}O_8 \cdot H_2O$: C, 65.89; H, 6.87. Found: C, 65.96; H, 6.71.

A portion of the triol **153** was acetylated to give **154** as a syrup; ^{1}H NMR data: δ 1.93 (s, 6 H, 2 × Ac), 1.96 (s, 3 H, Ac), 3.41 (dd, 1 H, *J* 1.8 and 10.4 Hz, H-1), 3.52 (t, 1 H, *J* 9.5 Hz, H-5), 3.73, 3.76 (2 s, each 3 H, 2 × OMe), 4.04 (t, 1 H, H-2), 4.40, 4.47 (AB, 2 H, *J* 11 Hz, CH_2Ph), 4.50 (s, 2 H, CH_2Ph), 4.70 (dd, 1 H, H-3), 4.72, 4.79 (AB, 2 H, *J* 11 Hz, CH_2Ph), 5.67 (t, 2 H, *J* 9.8 Hz, H-4,6), 6.76–7.28 (m, 13 H, aromatic).

The major portion (6 g) of the crude triol **153** in acetone (50 mL) and 2,2-dimethoxypropane (50 mL) containing toluene-*p*-sulfonic acid (200 mg) was kept at 20 °C for 2 h. An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated and the product extracted with CH_2Cl_2. TLC (ether) showed conversion of **153** (R_f 0.1) into a major product (R_f 0.9). Column chromatography (ether) gave **155** (5.2 g, 80% from **153**); mp 109–110 °C (from light petroleum containing a little NEt_3); ^{1}H NMR data: δ 1.44 (s, 6 H, CMe_2), 3.22–3.56 (m, 3 H, ring protons), 3.78 (s, 6 H, 2 × OMe), 3.90–4.31 (m, 3 H, ring protons), 4.47 (s, 2 H, CH_2Ph), 4.60–4.93 (m, 4 H, 2 × CH_2Ph, with major peaks at 4.74 and 4.80), 6.78–7.34 (m, 13 H, aromatic). Anal. Calcd for $C_{32}H_{38}O_8$: C, 69.80; H, 6.96. Found: C, 69.58; H, 6.89.

*(±)-2,6-Di-*O-*benzyl-3,4-*O-*isopropylidene-1,5-di-*O-p-*methoxybenzyl-*myo-*inositol* (**156**) [25].—The alcohol **155** was treated with benzyl bromide and NaH in DMF and the product isolated in the usual way to give **156**; mp 112–114 °C (from light petroleum containing a little NEt_3) identical with the material described previously [25]. Acid hydrolysis of **156** gave **134** identical with the material described previously [25].

*D-5-*O-*Acetyl-1,3,4-tri-*O-*allyl-2,6-di-*O-*benzyl-*myo-*inositol* (**158**).—A mixture of the enantiopure diol **157** [24] (5.1 g, 13.1 mmol), Bu_2SnO (3.9 g, 15.7 mmol), Bu_4NBr (5.1 g, 15.8 mmol), and benzyl bromide (10 mL, 84 mmol) in MeCN (150 mL) was heated under reflux with a Soxhlet apparatus containing 3 Å molecular sieve for 30 h.

TLC (1:1 ether–light petroleum) showed conversion of **157** (R_f 0) into two major products (R_f 0.45 and 0.5). Triethylamine (5 mL) was added and the mixture was heated under reflux for 1 h to destroy the excess of benzyl bromide. The products were isolated in the usual way (see above) and the mixture of products **159** and **162** was acetylated in the usual way to give a mixture of the acetates **158** and **161** (6.9 g). TLC (1:2 ether–light petroleum) showed the products at R_f 0.2 and 0.3. Column chromatography (same solvent) gave **161** (R_f 0.3, 2.57 g, 38%) as a syrup; ^{1}H NMR data: δ 1.95 (s, 3 H, Ac), 3.20 (dd, 2 H, J 2.4 and 9.7 Hz, H-1,3), 3.37 (t, 1 H, J 9.1 Hz, H-5), 3.82–4.38 (m, 8 H, 3 × OCH_2CH= and H-2,4), 4.67, 4.78 (AB, 2 H, J 12 Hz, CH_2Ph), 4.84 (s, 2 H, CH_2Ph), 5.05–5.45 (m, 6 H, 3 × =CH_2), 5.52 (t, 1 H, J 9.0 Hz, H-6), 5.62–6.25 (m, 3 H, 3 × CH=), 7.29–7.36 (m, 10 H, aromatic with major peak at 7.29).

Compound **158** (R_f 0.2, 2.54 g, 37%) was then eluted; mp 80–82 °C (from light petroleum); $[\alpha]_D$ +22.3° (c 1, $CHCl_3$); ^{1}H NMR data: δ 1.95 (s, 3 H, Ac), 3.16–3.40 (2 dd, each 1 H, H-1,3), 3.70–4.32 (m, 9 H, 3 × OCH_2CH= and H-2,4,6), 4.67, 4.78 (AB, 2 H, J 12 Hz, CH_2Ph), 4.86 (s, 2 H, CH_2Ph), 4.88–5.36 (m, 7 H, 3 × =CH_2 and H-5), 5.65–6.20 (m, 3 H, 3 × CH=), 7.28–7.40 (m, 10 H, aromatic, with a major peak at 7.28). Anal. Calcd for $C_{31}H_{38}O_7$: C, 71.24; H, 7.33. Found: C, 71.21; H, 7.49.

Deallylation of the alcohol **159** (obtained by saponification of **158**) as described below for the preparation of **172** gave the known 1L-2,4-di-*O*-benzyl-*myo*-inositol (**188**) [25], thus establishing the substitution pattern in **158**.

1D-1,3,4-Tri-O-allyl-2,6-di-O-benzyl-5-O-p-methoxybenzyl-myo-*inositol* (**160**).—The acetate **158** (2.5 g, 4.78 mmol) was saponified to give the alcohol **159** which was treated with *p*-methoxybenzyl chloride and NaH in DMF and the product isolated in the usual way. TLC (1:1 ether–light petroleum) showed conversion of **159** (R_f 0.45) into **160** (R_f 0.6). Column chromatography (1:2 ether–light petroleum) gave **160** (2.6 g, 90%); mp 54–56 °C (from EtOH); $[\alpha]_D$ +22.1° (c 1, $CHCl_3$); ^{1}H NMR data: δ 3.12–3.30 (2 dd, each 1 H, H-1,3), 3.35 (t, 1 H, J 9.1 Hz, H-5), 3.79 (s, 3 H, OMe), 3.86–4.36 (m, 9 H, 3 × OCH_2CH= and H-2,4,6), 4.71–5.00 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.76, 4.82, and 4.85), 5.09–5.37 (m, 6 H, 3 × =CH_2), 5.7–6.25 (m, 3 H, 3 × CH=), 6.78–7.39 (m, 14 H, aromatic, with major peaks at 6.78, 6.87, 7.20, 7.24, 7.32, and 7.37). Anal. Calcd for $C_{37}H_{44}O_7$: C, 73.97; H, 7.38. Found: C, 73.64; H, 7.52.

1D-2,6-Di-O-benzyl-3,4-O-isopropylidene-5-O-p-methoxybenzyl-myo-*inositol* (**172**). —A mixture of the triallyl ether **160** (760 mg), Pd–C (10%, 300 mg), and toluene-*p*-sulfonic acid (15 mg) in EtOH (95%, 25 mL) was stirred at 50 °C for 9 h, after which time TLC (15:1 $CHCl_3$–MeOH) showed a major product (R_f 0.4) and other minor products. An excess of NEt_3 and $NaHCO_3$ was added, the mixture was filtered through Celite which was washed with 15:1 $CHCl_3$–MeOH, and the filtrate was concentrated. Column chromatography (same solvent) gave the still crude triol **166** (375 mg, 61%). A solution of **166** in acetone (10 mL) and 2,2-dimethoxypropane (5 mL) containing toluene-*p*-sulfonic acid (20 mg) was kept at 20 °C for 3 h after which time TLC (as above) showed conversion of **166** into a major product (R_f 1.0) [TLC (1:1 ether–light petroleum), R_f 0.3]. An excess of NEt_3 and $NaHCO_3$ was added and the mixture was concentrated. The product was extracted from the residue with ether and column chromatography (1:1 ether–light petroleum) gave **172**; mp 104–106 °C (from light

petroleum containing a little NEt_3); $[\alpha]_D$ −6.7° (*c* 1, $CHCl_3$); ^1H NMR data: δ 1.46 (s, 6 H, CMe_2), 2.38–2.45 (m, 1 H, OH), 3.46 (dd, 1 H, *J* 1.8 and 9.8 Hz), 3.53–3.69 (m, 2 H), 3.79 (s, 3 H, OMe), 4.06–4.35 (m, 2 H with major peak at 4.16), 4.59–5.05 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.69, 4.71, 4.80, 4.81, 4.85, and 4.93), 6.78–7.34 (m, 14 H, aromatic, with major peaks at 6.88, 7.24, 7.31, and 7.34). Anal. Calcd for $C_{31}H_{36}O_7$: C, 71.52; H, 6.97. Found: C, 71.39; H, 7.06.

*1*D-*2,6-Di*-O-*benzyl-5*-O-p-*methoxybenzyl*-myo-*inositol* (**166**) *and* (±)-*1,3,4-tri*-O-*acetyl-2,6-di*-O-*benzyl-5*-O-p-*methoxybenzyl-myo-inositol* (**171**).—The alcohol **172** was treated with 7:3:1 MeOH–acetone–M HCl at 50 °C for 20 min and the product isolated in the usual way to give the triol **166**; mp 113–115 °C (from EtOH); $[\alpha]_D$ −21.8° (*c* 1, $CHCl_3$); ^1H NMR data: δ 2.32–2.55 (m, 3 H, 3 × OH, with major peaks at 2.32, 2.38, 2.47, 2.53, and 2.55), 3.20–4.15 (m, 6 H, ring protons), 3.78 (s, 3 H, OMe), 4.64–5.15 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.76, 4.81, and 4.88), 6.81–7.34 (m, 14 H, aromatic, with major peaks at 6.90, 7.22, 7.25, 7.32, and 7.34). Anal. Calcd for $C_{28}H_{32}O_7$: C, 69.98; H, 6.71. Found: C, 70.02; H, 6.88. This gave a crystalline triacetate **167**; mp 137–138 °C; ^1H NMR data: δ 1.90, 1.94, 1.98 (3 s, each 3 H, 3 × Ac), 3.54 (t, 1 H, *J* 9.5 Hz, H-5), 3.78 (s, 3 H, OMe), 4.00–4.25 (m, 2 H, H-2,6), 4.50–4.95 (m, 8 H, 3 × CH_2Ph and H-1,3), 5.59 (t, 1 H, *J* 9.8 Hz, H-4), 6.77–7.32 (m, 14 H, aromatic, with major peaks at 6.87, 7.10, 7.29, and 7.32).

The corresponding racemic triacetate **171**, prepared in the same way starting from the racemic diol **164** via **165** and **170**, had mp 138–140 °C (from EtOAc–light petroleum) with a ^1H NMR spectrum identical with that of **167**. Anal. Calcd for $C_{34}H_{38}O_{10}$: C, 67.31; H, 6.31. Found: C, 67.47; H, 6.49.

*1*D-*2,6-Di*-O-*benzyl-1,5-di*-O-p-*methoxybenzyl*-myo-*inositol* (**140**) [25] *and* *1*D-*2,3,4,6-tetra*-O-*benzyl-1,5-di*-O-p-*methoxybenzyl*-myo-*inositol* (**141**).—The alcohol **172** was treated with *p*-methoxybenzyl chloride and NaH in DMF and the product isolated in the usual way to give **173**. This was treated with 7:3:1 MeOH–acetone–M HCl at 50 °C for 20 min to give **140** identical with the material prepared previously [25].

Treatment of the diol **140** with benzyl bromide and NaH in DMF and isolation of the product in the usual way gave **141**; mp 88–90 °C (from light petroleum); $[\alpha]_D$ 0° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{50}H_{52}O_8$: C, 76.90; H, 6.71. Found: C, 76.70; H, 6.92.

*1*D-*2,5-Di*-O-*benzyl-3,4*-O-*isopropylidene-6*-O-p-*methoxybenzyl*-myo-*inositol* (**174**).—The acetate **161** obtained in the preparation of **158** (see above) was taken through a similar sequence of reactions as for **158**; thus **161** was saponified to give **162** which was converted into the *p*-methoxybenzyl ether **163**. Deallylation gave the triol **168** which gave a syrupy triacetate **169**; ^1H NMR data: δ 1.90, 1.94, 1.98 (3 s, each 3 H, 3 × Ac), 3.54 (t, 1 H, *J* 9.2 Hz, H-5), 3.79 (s, 3 H, OMe), 4.01–4.25 (m, 2 H, H-2,6, with major peaks at 4.01, 4.04, and 4.11), 4.51–5.00 (m, 8 H, 3 × CH_2Ph, H-1,3, with major peaks at 4.63, 4.66, 4.78, 4.80, 4.83, and 4.92), 5.61 (t, 1 H, *J* 9.8 Hz, H-4), 6.78–7.32 (m, 14 H, aromatic, with major peaks at 6.88, 7.13, 7.25, 7.28, and 7.32). For purification the triol **168** was converted into the isopropylidene derivative **174**; mp 93–95 °C (from light petroleum containing a little NEt_3); $[\alpha]_D$ −13.6° (*c* 1, $CHCl_3$); ^1H NMR data: δ 1.46 (s, 6 H, CMe_2), 3.46 (dd, 1 H, *J* 1.8 and 9.8 Hz), 3.60–3.64 (m, 2 H), 3.79 (s, 3 H, OMe), 4.16 (bs, 2 H), 4.60–5.01 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.73, 4.75,

4.78, 4.88, and 4.93), 6.78–7.34 (m, 14 H, aromatic, with major peaks at 6.88, 7.21, 7.25, and 7.34). Anal. Calcd for $C_{31}H_{36}O_7$: C, 71.52; H, 6.97. Found: C, 71.42; H, 7.16.

(±)-1-O-Allyl-2,6-di-O-benzyl-3,4,5-tri-O-p-methoxybenzyl-myo-inositol (**175**).—The diol **97** was treated with *p*-methoxybenzyl chloride and NaH in DMF and the product isolated in the usual way to give crude **175**. TLC (1:1 ether–light petroleum) showed conversion of **97** (R_f 0) into the product (R_f 0.5) together with minor byproducts (R_f 0.3, 0.8, and 0.9). Column chromatography (1:1 ether–light petroleum) gave **175** (70%); mp 72–74 °C (from light petroleum); ^{1}H NMR data: δ 3.17–3.54 (m, 3 H, H-1,3,5), 3.79 (s, 6 H, 2 × OMe), 3.81 (s, 3 H, OMe), 3.91–4.11 (m, 5 H, OCH_2CH= and H-2,4,6), 4.58 (s, 2 H, CH_2Ph), 4.70–5.01 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.80, 4.83, and 4.87), 5.12–5.45 (m, 2 H, $=CH_2$), 5.75–6.21 (m, 1 H, CH=), 6.78–7.38 (m, 22 H, aromatic, with major peaks at 6.78, 6.81, 6.87, 6,91, 7.19, 7.21, 7.25, 7,29, and 7.32). Anal. Calcd for $C_{47}H_{52}O_9$: C, 74.19; H, 6.89. Found: C, 74.11; H, 6.90.

(±)-2,6-Di-O-benzyl-3,4,5-tri-O-p-methoxybenzyl-1-O-(cis-prop-1-enyl)-myo-inositol (**176**).—The allyl ether **175** was treated with KOBu^t in Me_2SO and the product isolated in the usual way to give **176**. TLC (2:1 ether–light petroleum) showed no separation of **175** and **176** (R_f 0.8) and the course of the isomerisation was followed by acid hydrolysis of a portion of the reaction mixture to give the alcohol **177** (R_f 0.5, see below). Compound **176** had mp 85–86 °C (from light petroleum containing a little NEt_3); ^{1}H NMR data: δ 1.66 (dd, 3 H, *J* 1.2 and 6.7 Hz, =CH*Me*), 3.28–3.59 (m, 3 H, H-1,2,5), 3.78 (s, 6 H, 2 OMe), 3.80 (s, 3 H, OMe), 3.92–4.17 (m, 3 H, H-2,4,6), 4.36–4.58 (m, 2 H, =C*H*Me), 4.55 (s, 2 H, CH_2Ph), 4.65–4.90 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.78 and 4.85), 6.08 (dd, 1 H, *J* 1.2 and 6.1 Hz, OCH=), 6.76–7.50 (m, 22 H, aromatic). Anal. Calcd for $C_{47}H_{52}O_9$: C, 74.19; H, 6.89. Found: C, 73.84; H, 6.72.

(±)-2,4-Di-O-benzyl-1,5,6-tri-O-p-methoxybenzyl-myo-inositol (**177**).—The prop-1-enyl ether **176** was treated with 7:3:1 MeOH–acetone–M HCl at 50 °C for 50 min after which time TLC (2:1 ether–light petroleum) showed complete conversion of **176** (R_f 0.8) into the product **177** (R_f 0.5) together with traces of more polar byproducts (probably from acidic de-*p*-methoxybenzylation). An excess of NEt_3 and $NaHCO_3$ was added and the mixture was concentrated. The product was extracted from the residue with CH_2Cl_2 and column chromatography (same solvent) gave **177** (90%); mp 95–97 °C (from light petroleum); ^{1}H NMR data: δ 2.19 (d, 1 H, *J* 6.1 Hz, OH), 3.34–3.68 (m, 3 H), 3.79 (s, 6 H, 2 × OMe), 3.81 (s, 3 H, OMe), 3.81–4.11 (m, 3 H), 4.62 (s, 2 H, CH_2Ph), 4.66–5.05 (m, 8 H, 4 × CH_2Ph, with major peaks at 4.74, 4.78, 4.82, and 4.93), 6.80–7.32 (m, 22 H, aromatic). Anal. Calcd for $C_{44}H_{48}O_9$: C, 73.31; H, 6.71. Found: C, 72.93; H, 6.70.

1D-1,3,6-Tri-O-allyl-2-O-benzyl-4,5-di-O-p-methoxybenzyl-myo-inositol (**180**) (by Sheila Payne).—The enantiopure diol **179** [24] was treated with *p*-methoxybenzyl chloride and NaH in DMF and the product isolated in the usual way to give crude **180**. TLC (1:1 ether–light petroleum) showed conversion of **179** (R_f 0) into a major product (R_f 0.4) together with less polar byproducts (from the chloride). Column chromatography (1:2 ether–light petroleum followed by 1:1) gave **180**; mp 78–79 °C (from light petroleum); $[\alpha]_D$ −32.9° (*c* 1, $CHCl_3$); ^{1}H NMR data: δ 3.10–3.43 (m, 3

H, H-1,3,5), 3.75–4.36 (m, 9 H, 3 × OCH_2CH= and H-2,4,6), 3.79 (s, 6 H, 2 × OMe), 4.76 (s, 4 H, 2 × CH_2Ph), 4.84 (s, 2 H, CH_2Ph), 5.08–5.37 (m, 6 H, 3 × =CH_2), 5.71–6.22 (m, 3 H, 3 × CH=), 6.79–7.39 (m, 13 H, aromatic). Anal. Calcd for $C_{38}H_{46}O_8$: C, 72.35; H, 7.35. Found: C, 72.38; H, 7.54.

*1*D-*2-O-Benzyl-4,5-di*-O-p-*methoxybenzyl*-myo-*inositol* (**181**) (by Sheila Payne).—A mixture of **180** (3.2 g, 5.07 mmol), toluene-*p*-sulfonic acid (40 mg), and Pd–C (195 mg, 10%) in aq EtOH (50 mL, 95%) was stirred at 80 °C for 8 h. The course of the deallylation was followed by TLC (ether) which showed conversion of **180** (R_f 1.0), through several intermediate products, into a major product (R_f 0.2). An excess of $NaHCO_3$ was added, the mixture was concentrated, and the product extracted from the residue with CH_2Cl_2. Column chromatography (5:1 ether–EtOAc followed by 3:1) gave the crystalline triol **181** (1.24 g, 48%); mp 105–107 °C (from 1:7 EtOAc–light petroleum); $[\alpha]_D$ +25.8° (*c* 1, $CHCl_3$); ^{1}H NMR data: δ 2.26–2.47 (m, 3 H, 3 × OH), 3.20–4.03 (m, 6 H, ring protons), 3.79 (s, 6 H, 2 × OMe), 4.61–4.94 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.73, 4.79, and 4.82), 6.82–7.32 (m, 13 H, aromatic). Anal. Calcd for $C_{29}H_{34}O_8$: C, 68.22; H, 6.71. Found: C, 68.21; H, 6.79.

*1*D-*2-O-Benzyl-1,6*-O-*isopropylidene-4,5-di*-O-p-*methoxybenzyl*-myo-*inositol* (**182**) (by Sheila Payne).—A solution of the triol **181** (2.1 g, 4.1 mmol) and toluene-*p*-sulfonic acid (100 mg) in acetone (20 mL) and 2,2-dimethoxypropane (20 mL) was kept at 20 °C for 2 h after which time TLC (ether) showed almost complete conversion of **181** (R_f 0) into a product (R_f 0.9). An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated, and the product extracted with CH_2Cl_2. Column chromatography (1:2 ether–light petroleum followed by 1:1) gave **182** (2.04 g, 90%); mp 75–76 °C (from 1:50 EtOAc–light petroleum); $[\alpha]_D$ +6.2° (*c* 1, $CHCl_3$); ^{1}H NMR data: δ 1.46 (s, 6 H, CMe_2), 2.39 (d, 1 H, OH), 3.45 (dd, 1 H, *J* 1.2 and 9.8 Hz), 3.54–3.82 (m, 3 H, ring protons), 3.79 (s, 6 H, 2 × OMe), 4.16 (m, 2 H, ring protons), 4.59–5.05 (m, 6 H, 3 × CH_2Ph, with major peaks at 4.71, 4.72, 4.74, 4.79, and 4.93), 6.79–7.40 (m, 13 H, aromatic). Anal. Calcd for $C_{32}H_{38}O_8$: C, 69.80; H, 6.96. Found: C, 69.39; H, 7.12.

*1*D-*2-O-Benzyl-1,6*-O-*isopropylidene-3,4,5-tri*-O-p-*methoxybenzyl*-myo-*inositol* (**183**) (by Sheila Payne).—The alcohol **182** (2.3 g, 4.2 mmol) was treated with *p*-methoxybenzyl chloride and NaH in DMF and the product isolated in the usual way. TLC (1:1 ether–light petroleum) showed conversion of **182** (R_f 0.25) into **183** (R_f 0.5). Column chromatography (1:3 ether–light petroleum) gave **183** (2 g, 71%); mp 107–108 °C; $[\alpha]_D$ +3.7° (*c* 1, $CHCl_3$); ^{1}H NMR data: δ 1.42, 1.46 (2 s, each 3 H, CMe_2), 3.26–4.40 (m, 6 H, ring protons), 3.79 (s, 9 H, 3 × OMe), 4.51 (s, 2 H, CH_2Ph), 4.58–4.91 (m, 6 H, 2 × CH_2Ph, with major peaks at 4.71, 4.77, and 4.81), 6.78–7.36 (m, 17 H, aromatic). Anal. Calcd for $C_{40}H_{46}O_9$: C, 71.62; H, 6.91. Found: C, 71.77; H, 7.16.

*1*D-*2-O-Benzyl-3,4,5-tri*-O-p-*methoxybenzyl*-myo-*inositol* (**184**) (by Sheila Payne).—A solution of **183** (1.9 g, 2.8 mmol) in 9:1 MeOH–M HCl (50 mL) was kept at 30 °C for 15 min. TLC (EtOAc) showed conversion of **183** (R_f 1.0) into a product (R_f 0.7). An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated, and extraction of the residue with EtOAc gave **184** (1.6 g, 89%); mp 155–156 °C (from EtOH); $[\alpha]_D$ +9.6° (*c* 1, $CHCl_3$); ^{1}H NMR data: δ 2.24 (d, 1 H, *J* 7.3 Hz, OH), 2.38 (d, 1 H, *J* 2.4 Hz, OH), 3.17–4.12 (m, 6 H, ring protons), 3.79 (s, 6 H, 2 × OMe), 3.81 (s, 3 H, OMe),

4.58–5.14 (m, 8 H, $4 \times CH_2Ph$, with major peaks at 4.64, 4.71, 4.79, and 4.82), 6.78–7.32 (m, 17 H, aromatic). Anal. Calcd for $C_{37}H_{42}O_9$: C, 70.46; H, 6.71. Found: C, 70.40; H, 6.89.

*1D-2,6-Di-O-benzyl-3-O-p-methoxybenzyl-*myo*-inositol 1,4,5-tris(dibenzyl phosphate)* (**186**), *the enantiomer* (**190**), *and racemic* **193**.—The enantiopure alcohol **78** (782 mg, 1.5 mmol) prepared by saponification of the crystalline (+)-ω-camphanate **77** [22] was treated with 7:3:1 MeOH–acetone–M HCl at 20 °C for 30 min after which time TLC (ether) showed complete conversion of **78** (R_f 1.0) into the triol **185** (R_f 0.5). An excess of NEt_3 and $NaHCO_3$ was added, the mixture was concentrated, and the product **185** (690 mg, 96%) was extracted from the residue with CH_2Cl_2.

A solution of dry 1*H*-tetrazole (580 mg, 8.3 mmol) in dry MeCN (10 mL) was added to a solution of the triol **185** (690 mg, 1.4 mmol) and bis(benzyloxy)diisopropylaminophosphine (1.5 g, 4.3 mmol) in CH_2Cl_2 (10 mL). After 1 h at 20 °C, TLC (ether) showed complete conversion of **185** into a product (R_f 1.0). The reaction mixture was cooled to 0 °C and *tert*-butyl hydroperoxide (1.5 mL, 70% aq solution) was added dropwise for 5 min. After stirring for 1 h, TLC (ether) showed a major product (R_f 0.1). Toluene (10 mL) was added and the mixture was concentrated to remove MeCN. The residue was extracted with CH_2Cl_2 and the extract washed (aq 10% sodium metabisulfite), dried ($MgSO_4$), and concentrated. Column chromatography (ether followed by 1:1 ether–EtOAc) gave the trisphosphate **186** (983 mg, 54%); mp 88–90 °C (from 1:2 EtOAc–light petroleum); $[\alpha]_D$ −2.6° (*c* 1.85, $CHCl_3$); ^1H NMR data: δ 3.44 (dd, 1 H, H-3), 3.73 (s, 3 H, OMe), 4.08–5.03 (m, 23 H, $9 \times CH_2Ph$ and 5 ring protons, with major peaks at 4.17, 4.33, 4.42, 4.59, 4.63, 4.72, 4.77, 4.81, 4.86, 4.90, 4.95, 4.97, and 5.03), 6.70–7.26 (m, 44 H, aromatic, with major peaks at 6.70, 6.80, 7.00, 7.16, 7.22, 7.25, and 7.26); ^{31}P NMR data: δ −2.09, −1.82, −1.68. Anal. Calcd for $C_{70}H_{71}O_{16}P_3$: C, 66.66; H, 5.68; P, 7.37. Found: C, 66.27; H, 5.43; P, 7.42.

The enantiomeric trisphosphate **190** was prepared in a similar manner from the enantiopure triol **189** [22] and had mp 88–90 °C; $[\alpha]_D$ +2.3° (*c* 1.2, $CHCl_3$); with ^1H and ^{31}P NMR spectra identical with those of **186**. Anal. Found: C, 65.92; H, 5.57; P, 6.64.

The racemic trisphosphate **193** was prepared similarly (by Nathalie Schnetz, visiting scientist from the Faculté de Pharmacie, Université Louis Pasteur, Strasbourg, France) from the racemic triol **192** (obtained by hydrolysis of the isopropylidene derivative **95** [22]) and had mp 96–98 °C with NMR spectra identical with those of the enantiopure material. Anal. Found: C, 66.49; H, 5.58; P, 7.83.

*1D-2,6-Di-O-benzyl-*myo*-inositol 1,4,5-tris(dibenzyl phosphate)* (**187**), *the enantiomer* (**191**), *and racemic* **194**.—A solution of ammonium cerium(IV) nitrate (1.57 g, 2.86 mmol) in 9:1 MeCN–water (10 mL) was added dropwise to a solution of the *p*-methoxybenzyl ether **186** (900 mg, 0.71 mmol) in 9:1 MeCN–water (20 mL) at 20 °C and the course of the reaction was followed by TLC (4:1 ether–EtOAc) which showed conversion of **186** (R_f 0.6) into a product (R_f 0.4) after 1 h. Water (30 mL) was added and the solution concentrated to half volume to remove the MeCN. The product was extracted from the residue with 2:1 ether–CH_2Cl_2, and the extract was dried ($MgSO_4$) and concentrated. Column chromatography (4:1 ether–EtOAc) gave **187** (485 mg, 60%); mp 114–116 °C (from 1:1 EtOAc–light petroleum); $[\alpha]_D$ −24.7° (*c* 2, $CHCl_3$); ^1H

NMR data: δ 3.59–5.10 (m, 23 H, $8 \times CH_2Ph$, 6 ring protons and OH, with major peaks at 4.12, 4.23, 4.25, 4.42, 4.51, 4.63, 4.74, 4.78, 4.82, 4.85, 4.89, 4.91, 4.93, 4.95, 5.02, 5.05, and 5.10), 6.88–7.30 (m, 40 H, aromatic, with major peaks at 7.09, 7.19, 7.27, and 7.30); ^{31}P NMR data: δ −1.62, −1.41, +0.74. Anal. Calcd for $C_{62}H_{63}O_{15}P_3$: C, 65.26; H, 5.57; P, 8.14. Found: C, 64.84; H, 5.43; P, 7.61.

The enantiomer **191** prepared in the same way from **190** had mp 113–115 °C; $[\alpha]_D$ +23.4° (*c* 1.1, $CHCl_3$); and ^{1}H and ^{31}P NMR spectra identical with those of **187**. Anal. Found: C, 65.11; H, 5.27; P, 8.30.

Racemic **194** prepared in the same way from **193** (by Nathalie Schnetz) had mp 101–103 °C. Anal. Found: C, 64.90; H, 5.75; P, 8.90.

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