104. The Synthesis of DL-1-(Hexadecanoyloxy)methyl- and 1-*O*-Hexadecanoyl-inositols as Potential Inhibitors of Phospholipase C

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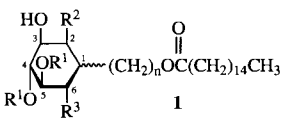
Dedicated to Dr. *O. Isler* on the occasion of his 80th birthday

(23.IV.90)

The synthesis of racemic analogues of phosphatidylinositol (PI) and phosphatidylinositol 4,5-bisphosphate (PIP_2) starting from *myo*-inositol is described. Inositol derivatives with and without homologation at C(1) and with and without ionic groups (phosphate or sulfate) at C(4) and C(5) were prepared as well as homologated derivatives with deoxy composition at C(2) and/or C(6). In all these compounds, palmitate ester groups were introduced in place of the diacylglyceryl group of PI or PIP_2.

Introduction. – *myo*-Inositol phosphates are key mediators of cellular metabolism, particularly through their function as second messengers [1–4]. Thus, it has been established in outline that an extracellular signal can trigger the hydrolysis of phosphatidylinositol 4,5-bisphosphate (PIP_2) to *myo*-inositol 1,4,5-trisphosphate (IP_3) and diacylglycerol (DG), a reaction which is catalysed by phospholipase C (PLC) in the cell membrane. Consequential upon these initial changes, a complex pattern of events occurs, much of it now elucidated [4]. It seems likely that there are associations with both inflammatory responses *via* the arachidonic-acid cascade [5] and the regulation of cell division [6]. These developments have stimulated intense worldwide interest in the chemical synthesis of inositol polyphosphates [7]. As part of a programme aimed at obtaining substances exerting control over the functions of inositol phosphates, we have synthesised a number of compounds, analogues of both PIP_2 and phosphatidylinositol (PI), as potential inhibitors of PLC.

The synthetic work here reported concerns primarily those PI and PIP_2 analogues having a C-atom replacing the O-atom at C(1), and attached to a lipid moiety *via* a carboxylate instead of a phosphate ester (see **1**). The function of PLC is to cleave a lipid/phosphate ester bond, and we were interested in finding out how *homologated* inositol palmitates would behave towards PLC, *i.e.* by replacing the inositol ring C(1)–O–PO_2O-lipid structure of PI and PIP_2 by an inositol ring C(1)–CH_2–OCO-lipid structure. An aspect of this question is to ascertain the importance of the PIP_2 phosphate groups at C(4) and C(5). Thus, we report the synthesis of C(1)-homologated inositol



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n = 0 or 1
R^1 = H or SO_3H or PO_3H_2
R^2 = H or OH
R^3 = H or OH

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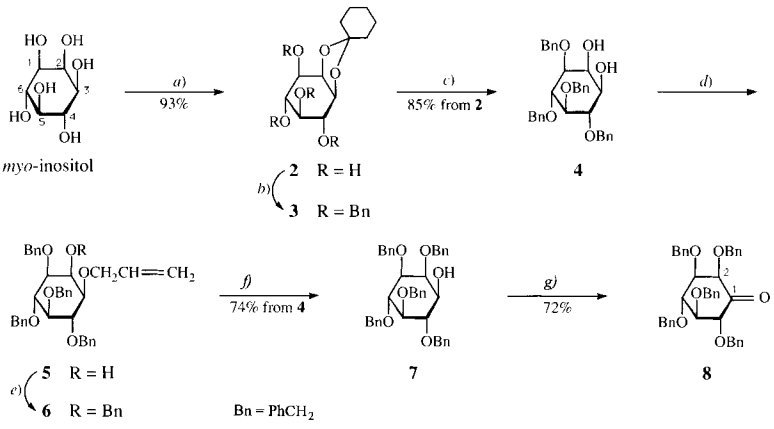
compounds both with and without ionic groups (phosphates or sulfates) at C(4) and C(5). Compounds with ionic groups at C(4) and C(5) but *without homologation* at C(1), were also prepared for comparison. All compounds synthesised are shown by the general formula **1**[2]).

Compounds of structure **1** in which $n = 1$, $R^1 = H$, and $R^2 = R^3 = OH$ are related to known compounds, *viz.* the parent hexols (and their hexa-acetates) of **14** and **15** *(Scheme 2)*, prepared by quite different methods [8] [9]. Compounds of structure **1** in which $n = 1$ and R^1 and either of R^2 or R^3 are a H-atom are derivatives of compounds known as pseudo-sugars, *i.e.* sugars in which the ring O-atom is replaced by CH_2 [10]. Thus, compounds **24** and **26** *(Scheme 5)* are esters of the pseudo-sugars related to DL-glucopyranose and DL-galactopyranose, respectively. The synthesis of these pseudo-sugars or their acetates by other routes has also been described [11–17].

Results and Discussion. – *Homologation at C(1) without Ionic Groups in the Molecule.* The initial target of this work was the homologation of inositol at C(1) without the introduction of ionic groups, *i.e.* structure **1** where $n = 1$ and $R^1 = H$. These compounds which are analogues of PI were prepared by the routes shown in *Schemes 1* and *2* ($R^1 = H$, $R^2 = R^3 = OH$) and in *Schemes 4* and *5* ($R^1 = H$, $R^2 = H$ or OH, $R^3 = H$ or OH).

The first objective was to prepare ketone **8** according to *Scheme 1*. The initial step, the synthesis of monocyclohexylidene-*myo*-inositol **2**, was achieved in 93% yield. This yield was rather better than those so far reported [20–26] and the method employed very simple. Thus, *myo*-inositol was reacted with excess cyclohexanone in DMF, catalysed by TsOH. By using toluene as co-solvent, H_2O of condensation was removed azeotropically

Scheme 1



a) 1) Cyclohexanone, TsOH, DMF/toluene, 144°, 9 h; 2) EtOH, TsOH, 25°, 1 h. *b*) $PhCH_2Cl$, KOH, 100–140°, 1 h. *c*) 80% AcOH, 80–100°, 1½ h. *d*) 1) Bu_2SnO, toluene, 110°, 1 h; 2) CH_2=$CHCH_2Br$, DMF, 80°, 4 h. *e*) $PhCH_2Br$, NaH, DMF, 40°, 4 h. *f*) 5% Pd/C, TsOH, EtOH/H_2O, reflux, 22 h. *g*) Pyridinium chlorochromate, CH_2Cl_2, 25°, 48 h.

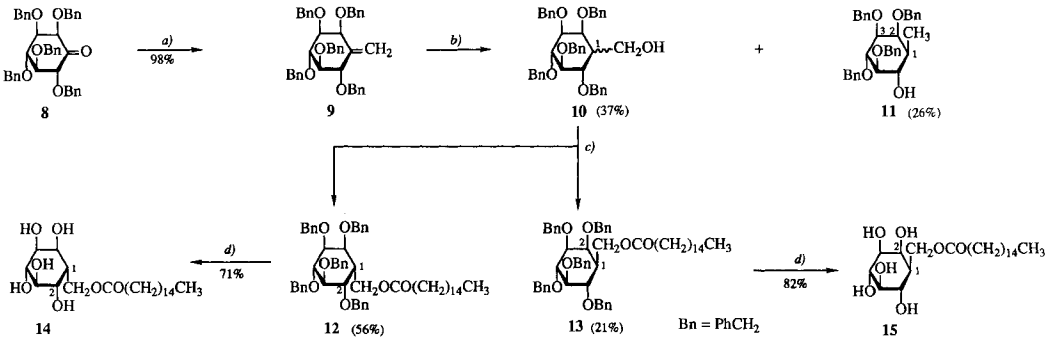
[2]) It should be noted that all the compounds described are either *meso* or racemic mixtures. In the latter case the structures portrayed here correspond, for convenience, to one enantiomer, but the DL-form is implied. Numbering and nomenclature are in accordance with IUPAC conventions [18], except for the abbreviations PI, PIP_2, IP_3, and DG which are based on the 1984 Clifton Conference system [19].

to give a clear reaction mixture indicating that little or no free *myo*-inositol was present. After removal of solvents by evaporation and the addition of EtOH product **2** crystallised from the solution. In this last stage, soluble polycyclohexylidene-inositols were converted to the insoluble monocyclohexylidene compound **2** which was collected by filtration[3]).

Benzylation of **2** yielded the tetrabenzyl compound **3** which was used in the next step without purification. Removal of the cyclohexylidene group from **3** yielded the *cis*-diol **4** (85% based on **2**). Various means are available to convert this to the desired 1-alcohol **7** [21] [27] [28]. We decided to adopt the route: stannylidene-activated allylation [29] (**4**→**5**), benzylation (**5**→**6**), and deallylation (**6**→**7**). By using the intermediates **5** and **6** in their crude state and, thus, avoiding losses often incurred during purification, the overall yield of **7** was 74% (based on **4**). The advantage of this Sn-mediated procedure can be appreciated when it is compared to the allylation of **4** by a conventional method which yielded only 33% of **5** [30]. Oxidation of **7** to ketone **8** proceeded satisfactorily (72% yield) by the use of pyridinium chlorochromate. Ketone **8** has been reported in a patent [31], but its spectral properties have not been published before.

The next objective was to add a C_1-fragment to ketone **8** by means of a *Wittig* reaction. In the first instance, methyl(triphenyl)phosphonium bromide was used *(Scheme 2)* and afforded the methylidene compound **9** almost quantitatively.

Scheme 2



a) $CH_3(Ph)_3PBr$, BuLi, THF, 1–25°, 1 h. *b*) 1) $BH_3 \cdot Me_2S$, toluene, 60°, 1 h; 2) 5M NaOH, 30% H_2O_2, 50°, 1 h. *c*) $CH_3(CH_2)_{14}COCl$, pyridine, 4-(dimethylamino)pyridine, CH_2Cl_2, 25°, 20 min. *d*) Pd/C, 1 atm H_2, EtOH, 25°, 2–3 h.

Hydroboration of **9** yielded 37% of the epimeric mixture **10a**/**10b**. In addition, we isolated 26% of the unexpected by-product **11** which has only 4 benzyl groups.

The formation of **11** can be rationalised in the manner shown in *Scheme 3* which is in accordance with the known facility for the loss of benzyloxy groups from inositol compounds [20] [27] [32] [33]. Such a tendency is further illustrated later in this report *(cf. Scheme 4)*.

The mixture **10a**/**10b** was readily esterified with palmitoyl chloride, and the resulting esters **12** and **13** could be separated cleanly by MPLC. The ratio of *chiro*-ester **12** to

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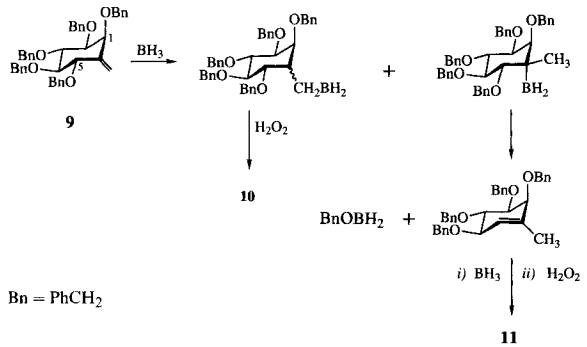
[3]) The method is very similar to that originally described by *Angyal* and coworkers [23] [26] who used benzene as the solvent and removed unreacted *myo*-inositol by filtration before ethanolysis. That method was elaborated by *Lee et al.* [24] who used cyclohexane instead of benzene. However, these methods are apparently not always satisfactory [22], and this has led to the development of procedures based on derivatives of cyclohexanone [21] [22]. But the simple method used in the present work has consistently given 85–95% yields without difficulty.

Scheme 3



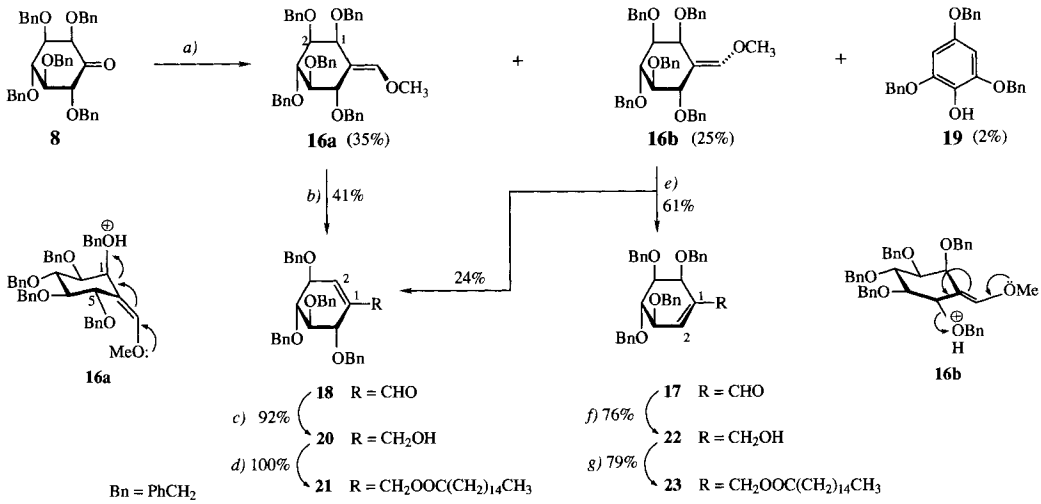
myo-ester **13** was *ca.* 2.5:1. The structures of **12** and **13** were tentatively assigned on the basis of their ^{1}H-NMR spectra. The assignment here is not fully convincing, however, because the high degree of substitution apparently causes some distortion to the regular chair conformation. The structures assigned are, however, fully confirmed by the NMR spectra of the corresponding deprotected compounds **14** and **15** which were obtained as pure, crystalline compounds.

Thus, the key coupling constant $J(1,6) = 9.5$ Hz in the case of **13** is consistent with the expected *trans*-diaxial coupling, but in the case of **12**, the signal of H–C(2) gives a clear coupling constant $J(1,2) = 8$ Hz which is rather high for a *cis*-axial/equatorial coupling. Approximately the same constant is found in the complex signal of H–C(1) of **12** which incorporates $J(1,2) = 7$ Hz. In the case of **14**, H–C(2) shows $J(1,2) = 5.6$ Hz consistent with an axial/equatorial relationship, and in the case of **15**, H–C(1) displays $J(1,6) = 11$ Hz, *i.e.* axial/axial coupling, confirmed at the H–C(6) signal.

With the aim of preparing homologous aldehydes (and thence carboxylic acids), ketone **8** was reacted with (methoxymethyl)triphenylphosphonium chloride to yield enol ethers **16a** (35%) and **16b** (25%) *(Scheme 4)*. The geometry at the double bond of these compounds was established by NOE experiments. A small amount of the tris(benzyloxy)phenol **19** was isolated as a by-product. Conversion of these enol ethers to the corresponding aldehydes proved to be impossible without losing a benzyloxy group and introducing ring unsaturation. In the case of **16a**, this transformation occurred spontaneously on allowing a solution in CH_2Cl_2 to stand at r.t. for a few days and gave the unsaturated aldehyde **18** in 41% yield. The reaction appeared to be catalysed by traces of HCl present in the solvent since no appreciable decomposition was observed in EtOH. Enol ether **16b** did not decompose in CH_2Cl_2 solution, but on refluxing it in Et_2O with BF_3, the unsaturated aldehyde **17** was obtained in 61% yield. In this case, a different benzyloxy group was lost, as compared with **18**. However, the reaction also gave rise to a minor amount of **18** (24%). On the other hand, no **17** could be detected in the products of decomposition of **16a**. The structures of **17** and **18** were readily ascertained from their NMR spectra. *E.g.*, the proton at the double bond was distinct in each case (*d* at 6.44 and 6.68 ppm, respectively), loss of benzyl was evident, and the presence or absence of an equatorial ring proton, inferred from coupling constants, located the position of the double bond.

The more facile elimination of benzyloxy from **16a** as compared with **16b** deserves some comment. We think that a 1-step elimination is likely in both cases (see *Scheme 4*), rather than a 2-step elimination proceeding *via* saturated aldehydes. With **16a**, the axial

Scheme 4

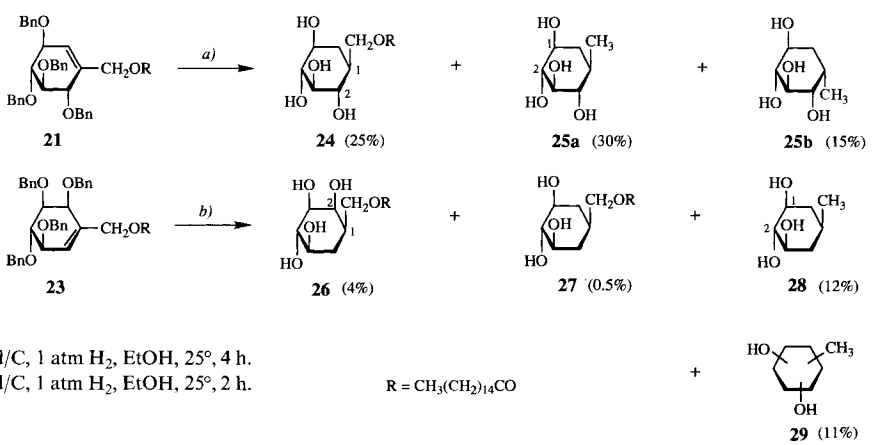


a) $(CH_3OCH_2)(Ph)_3PCl$, BuLi, THF, 0–21°, ¾ h. *b*) CH_2Cl_2 (trace of adventitious HCl), 25°, 4 d. *c*) $NaBH_4$, EtOH, 25°, 25 min. *d*) $CH_3(CH_2)_{14}COCl$, pyridine, 4-(dimethylamino)pyridine, CH_2Cl_2, 25°, 2 h. *e*) $BF_3 \cdot Et_2O$, Et_2O, reflux, 1½ h. *f*) $NaBH_4$, EtOH, 25°, 10 min. *g*) $CH_3(CH_2)_{14}COCl$, Et_3N, 4-(dimethylamino)pyridine, CH_2Cl_2, 25°, 10 min.

benzyloxy group at C(1) is ideally placed for elimination, being almost at right angles to the developing double bond. This is not the case for the benzyloxy group at C(5). With **16b**, similar elimination of the benzyloxy group at C(1) may be restricted by the closeness of the charges in the transition state, whereas elimination at C(5) can be envisaged with a slight conformational change.

Having a reasonable route to aldehydes **17** and **18**, it was decided to investigate their conversion to target compounds of the deoxy type, *i.e.* **1** where $n = 1$, $R^1 = R^3 = H$, $R^2 = OH$ (from **17**) and $n = 1$, $R^1 = R^2 = H$, $R^3 = OH$ (from **18**). Thus, reduction of aldehydes **17** and **18** using $NaBH_4$ gave alcohols **20** and **22** which were then converted to esters **21** and **23**, respectively, in good yields *(Scheme 4)*. However, conversion of these

Scheme 5

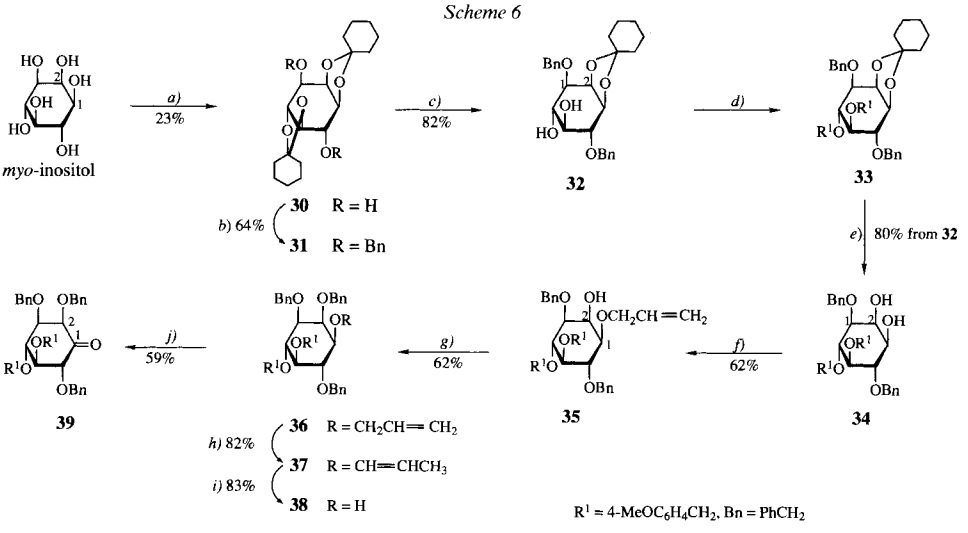


a) Pd/C, 1 atm H_2, EtOH, 25°, 4 h.
b) Pd/C, 1 atm H_2, EtOH, 25°, 2 h.

esters to the target compounds by concomitant hydrogenolysis of the benzyl groups and reduction of the double bonds was not straightforward *(Scheme 5)*. The method employed was that which is normally used to remove benzyl-ether groups, *i.e.* treatment with Pd/C and H_2 at atmospheric pressure. In the case of **21**, only a 25% yield of the desired product **24** was obtained, but 45% of an epimeric mixture **25a**/**25b** was also isolated. The formation of **25a**/**25b** appears to be the result of hydrogenolysis of ester **21** which is allylic [34]. To avoid loss of **21**, it would be necessary first to reduce the double bond selectively. For this purpose, Rh or Ru are stated to be much better than Pd [34]. Benzyl ether **23** was treated in the same way as **21**, *i.e.* with H_2 catalysed by Pd, and in this case, the yield of the anticipated product **26** was only 4%. As unwanted by-products, the *meso*-triol **28** and the diol mixture **29** were separated and identified in minor yields, together with a major amount (73%) of palmitic acid. While attempting to separate and identify the numerous reaction products, a very small amount (*ca.* 0.5%) of pure *meso*-ester **27** could be isolated and characterised by ^{1}H-NMR and MS. This compound, obtained more or less fortuitously, proved to be a 2,6-dideoxy product, nicely complementing the deoxy compounds already obtained (**24** and **26**).

Homologation at C(1) with Ionic Groups at C(4) and C(5). The route followed is shown in *Scheme 6*. The synthetic pathway requires temporary protection of the C(4) and C(5) OH groups of *myo*-inositol at two stages. In the first of these, protection was accomplished by forming the 1,2:4,5-di-*O*-cyclohexylidene compound **30**. The method adopted was based on that used for the preparation of **2** described above, *i.e.* reaction of *myo*-inositol with cyclohexanone in DMF/toluene at 143°, catalysed by TsOH. After neutralisation and removal of volatiles, **30** could be easily obtained by crystallisation

Scheme 6



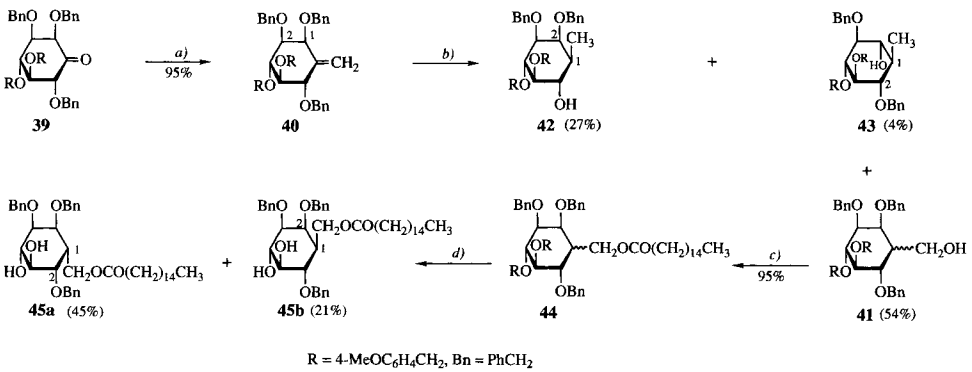
a) Cyclohexanone, TsOH, DMF, toluene, 143°, 12 h. *b*) $PhCH_2Cl$, KOH, 100–125°, 3½ h. *c*) Ethane-1,2-diol, CH_2Cl_2, TsOH, 22°, 30 min. *d*) 4-$MeOC_6H_4CH_2Cl$, NaH, DMF, 25–60°, 1 h. *e*) Toluene/EtOH/1M HCl (aq.) 3:6:1, 60°, 2½ h. *f*) 1) Bu_2SnO, toluene, 100°, ¾ h; 2) CH_2=$CHCH_2Br$, DMF, 95°, 1½ h. *g*) $PhCH_2Br$, NaH, DMF, 25–40°, 2 h. *h*) *t*-BuOK, DMSO, 50°, 19 h. *i*) Toluene/EtOH/1M HCl (aq.) 3:6:1, 23°, 8½ h. *j*) Pyridinium chlorochromate, CH_2Cl_2, 25°, 19 h.

from the mixture of acetals in 23% yield. This procedure [35] represents an advance over existing methods which either require separation of **30** by chromatography [26] or utilise a more expensive starting material [22] [36]. The diacetal **30** was then dibenzylated after which the OH groups at C(4) and C(5) were reexposed by selective removal of one cyclohexylidene group using an exchange reaction with ethane-1,2-diol. The preparation of **32** by this route has been described previously [37] [38].

For the second temporary protection of the OH groups at C(5) and C(6) in **32**, there are rather stringent requirements. The protective groups should be stable during removal of the 2,3-di-*O*-cyclohexylidene group and during the addition, isomerisation, and removal of the allyl group at C(3) (numbering of **34**) and finally be themselves removable without effects on the benzyl groups at C(1), C(2), and C(4) (numbering of **37**). These requirements proved to be fulfilled by the 4-methoxybenzyl group. Thus, diol **32** was reacted with 4-methoxybenzyl chloride to give **33**, the acetal group of which was then carefully hydrolysed in toluene/EtOH 1M HCl (aq.) 3:6:1 (*v*/*v*) at 60°. The yield of **34** was 80% based on **32**. The procedure up to this point has already been reported briefly by *Watanabe et al.* [39]. Selective benzylation of the axial OH–C(2) of **34** was accomplished *via* **35** by the allyl-ether technique described above *(Scheme 1)*, except that here it was necessary to perform the isomerisation of the benzylated allyl ether **36** to the 1-propenyl ether **37** and hydrolytic removal of the propenyl-ether group in separate stages in order to maintain reaction conditions which would preserve the 4-methoxybenzyl groups. The conversion of **36** to **37** was carried out using *t*-BuOK in DMSO [40]. Oxidation of **38** to ketone **39** could be accomplished in reasonable yield (59%) by treatment with pyridinium chlorochromate.

Treatment of ketone **39** with methyl(triphenyl)phosphonium bromide and BuLi yielded the methylidene compound **40** almost quantitatively *(Scheme 7)*. Hydroboration with $BH_3 \cdot SMe_2$ followed by treatment with an alkaline H_2O_2 solution gave the epimeric mixture **41a**/**41b** in 54% yield, together with 27% of by-product **42** (*cf.* **11**, *Scheme 2*) and 4% of alcohol **43**, a 1-methyl-*scyllo*-inositol derivative. The presence of this last compound is not at variance with the principal features of the mechanism outlined in *Scheme*

Scheme 7

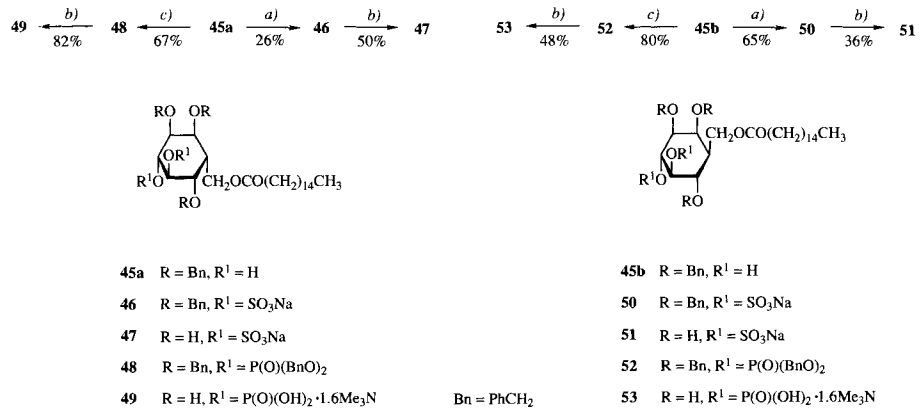


a) $CH_3(Ph)_3PBr$, BuLi, THF, 0–22°, 40 min. *b*) 1) $BH_3 \cdot Me_2S$, toluene, 25–68°, 1½ h; 2) 5M NaOH, EtOH, 30% H_2O_2, 10 min, 60°. *c*) $CH_3(CH_2)_{14}COCl$, pyridine, 4-(dimethylamino)pyridine, CH_2Cl_2, 25°, 1 h. *d*) DDQ, CH_2Cl_2, H_2O, 25°, 1½ h.

3, requiring only that the elimination should be at C(1) instead of at C(5). Then, the second hydroboration gives rise to an equatorial OH group at C(6) in **43** in the same way as at C(6) in compounds **11** and **42**. The alcohol mixture **41a**/**41b** was separated after esterification (→**44**) and removal of the 4-methoxybenzyl groups by oxidation with DDQ yielding **45a** and **45b**, the *chiro*- and *myo*-type compounds, in a *ca.* 2:1 ratio. A sample of the pure fully protected ester **44b** (*myo*-type) was separated from the epimeric mixture **44a**/**44b** and characterised.

The diols **45a** and **45b** were converted to the corresponding sulfates **46** and **50** using SO_3/pyridine complex in dry DMF at 25°. Removal of the benzyl groups by hydrogenolysis yielded the target compounds **47** and **51** *(Scheme 8)*.

Scheme 8

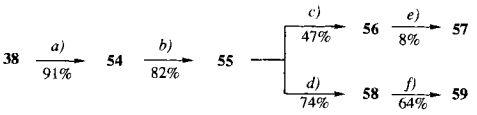


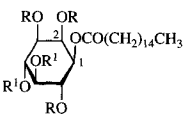
a) SO_3/pyridine complex, DMF, 25°, 18–20 h. *b*) Pd/C, 1 atm H_2, EtOH, 25°, 2–6 h. *c*) 1) 1*H*-Tetrazole, $P(BnO)_2[(i\text{-}Pr)_2N]$, CH_2Cl_2, 25°, 2–2½ h; 2) 3-$ClC_6H_4CO_3H$, CH_2Cl_2, −40° to +25°, 1–1½ h.

Until recently, the poly-phosphorylation of *myo*-inositol derivatives has been beset with difficulties [38] [41], but now a number of promising methods have been reported [42–48]. Of these, it was decided to try the use of bis(benzyloxy)(diisopropylamino)phosphine in the presence of 1*H*-tetrazole, followed by oxidation of the phosphite ester to phosphate using 3-chloroperbenzoic acid [43] [44]. The phosphorus reagent was easily prepared from PCl_3 in two steps by published methods [49] [50] and purified by column chromatography [43] (hexane/Et_3N 10:1) in an overall yield of 54%. The heptabenzyl compound **48**, thus, prepared from **45a** was then fully deprotected by hydrogenolysis (Pd/C, H_2) and converted to the trimethylammonium phosphate **49** *(Scheme 8)*. Me_3N was chosen as the base because it is convenient both for elemental analysis as well as for analysis by ^{1}H-NMR. The product was very hygroscopic, but this was not a particular consequence of the use of Me_3N, since a cyclohexylamine salt behaved similarly. These products did not crystallise, and the trimethylammonium salt had to be isolated by precipitation in Et_2O. Similarly, diol **45b** with the *myo*-configuration, was converted to phosphate **53** *via* **52** *(Scheme 8)*.

Compounds with Ionic Groups at C(4) and C(5), but without Homologation. Alcohol **38** *(Scheme 6)* which can be selectively deprotected at the 5,6 positions is a potentially useful new intermediate for the synthesis of 1,4,5-substituted *myo*-inositols; it could readily be employed in a resolution step by esterification with a chiral acid derivative such as (−)-(*S*)-camphanoyl chloride [46]. However, to complete our series of racemic compounds as potential PLC inhibitors, we decided to esterify **38** with a fatty acid, to deprotect the 5,6 positions, and to sulfate or phosphorylate the exposed OH groups. In this way, using palmitoyl chloride in the first step (**38**→**54**), products **57** and **59**, analogous to **51** and **53** *without* homologation at C(1), were prepared *via* **55**→**56** and **55**→**58**, respectively *(Scheme 9)*.

Scheme 9





Bn = $PhCH_2$

54 R = Bn, R^1 = 4-$MeOC_6H_4CH_2$

55 R = Bn, R^1 = OH

56 R = Bn, R^1 = $SO_3(^1/_2Ba)$

57 R = H, R^1 = SO_3Na

58 R = Bn, R^1 = $P(O)(BnO)_2$

59 R = H, R^1 = $P(O)(OH)_2 \cdot 2.5Me_3N$

a) $CH_3(CH_2)_{14}COCl$, pyridine, 4-(dimethylamino)pyridine, CH_2Cl_2, 25°, 21 h. *b*) DDQ, CH_2Cl_2/H_2O, 25°, 1 h. *c*) SO_3/pyridine complex, DMF, 25°, 14 h, $BaCO_3$. *d*) 1) 1*H*-Tetrazole, $P(BnO)_2[(i\text{-}Pr)_2N]$, CH_2Cl_2, 25°, 2 h; 2) 3-$ClC_6H_4CO_3H$, CH_2Cl_2, *ca.* 35°, 30 min. *e*) 1) Pd/C, 1 atm H_2, EtOH, 25°, 2 h; 2) *Dowex 50 W* (H^+); 3) NaOH. *f*) 1) Pd/C, 1 atm H_2, EtOH, 25°, 2 h; 2) Me_3N.

We should like to thank our colleagues from the Central Research Units for elemental analyses (Dr. *A. Dirscherl* †), NMR (Dr. *W. Arnold*), IR (Dr. *M. Grosjean*), and MS (Mr. *W. Meister*), and Ms. *Perrin* for typing the manuscript. One of us (*D.J.R.M.*) thanks *F. Hoffmann-La Roche Ltd.* for the award of a Postdoctoral Fellowship.

Experimental Part

General. DMSO was dried by distillation from CaH_2; other solvents were dried over molecular sieves (4 Å); 1*H*-tetrazole was purified by sublimation at 100°/0.02 mbar. Bis(benzyloxy)(diisopropylamino)phosphine was prepared from PCl_3 in 2 steps [43] [49] [50]. M.p.: open capillary (not corrected) or hot-stage microscope. TLC: 0.25-mm precoated silica gel plates (silica gel *60* F_{254}, *Merck*); solvent systems (*v/v*): *A* = CH_2Cl_2/AcOEt *B* = toluene/AcOEt, *C* = AcOEt/MeOH, *D* = CH_2Cl_2/MeOH, *E* = hexane/Et_2O, *F* = hexane/AcOEt, *G* = $CHCl_3$/MeOH/H_2O, *H* = AcOEt/acetone/AcOH/H_2O 6:2:1:1, *I* = BuOH/AcOEt/AcOH/H_2O 1:1:1:1; detection: *a* = spraying with 0.1M aq. $KMnO_4$ and warming; *b* = dipping in 4% phosphomolybdic acid in EtOH followed by heating at *ca.* 200°; *c* = UV (254 nm); *d* = *Zinzadze* spray [51] [52] and warming. Flash chromatography (FC): silica gel *H (Fluka)*. Medium-pressure liquid chromatography (MPLC): *LiChroprep Si 60*, 25–40 μm (*Merck*). IR: *Nicolet-FT-IR spectrometer*. NMR: δ in ppm rel. to internal TMS (^1H and ^{13}C) or to external H_3PO_4 (^{31}P); coupling constants *J* in Hz; multiplicities in ^{13}C spectra refer to gated signals; assignments were assisted by correlation spectroscopy (COSY) where indicated. MS: *MS9/ZAB* (*A.E.I.*), direct, 250°, 70 eV. FAB-MS: *MS902/DS2050* (*A.E.I.*, *V.G.*); FAB gun: *Kratos*, Xe, 7 KeV. CI-MS: *7070* (*V.G.*), direct, 250°, NH_3, 1 mbar. TS-MS: *Finnigan-MAT*, MeOH/H_2O 8:2 as solvent, 0.1M NH_4OAc as electrolyte.

DL-*1,2-O-Cyclohexylidene*-myo-*inositol* (**2**). The cloudy mixture of *myo*-inositol (47.0 g, 260 mmol), cyclohexanone (410 ml, 4.0 mol), TsOH (10% in DMF, 12 ml), DMF (460 ml), and toluene (100 ml) was heated to reflux under stirring and under a *Dean-Stark* separator filled with toluene. Four additional 12-ml portions of 10% TsOH soln. were added at 2-h intervals. After 9 h, H_2O separation had ceased (23.5 ml) and the temp. reached 144°. The clear, pale yellow mixture obtained was evaporated at 100°/13 mbar and the viscous residue diluted with 1 l of abs. EtOH and allowed to stand. Crystalline **2** was removed by filtration, washed with EtOH containing 0.1% Et_3N, and dried at 70°/15 mbar to constant weight (35.5 g). After reacidification (1 g TsOH), the filtrate yielded similarly further two crops (20.8 and 6.7 g). Total yield of **2**, 63 g (93%). As a qualitative test for purity, **2** (100 mg) was dissolved in boiling abs. EtOH (2.0 g). Turbidity indicated the presence of free *myo*-inositol. The first crop obtained was completely pure by this test; the second and third crops contained traces of *myo*-inositol.

DL-*1,4,5,6-Tetra-O-benzyl-2,3-O-cyclohexylidene*-myo-*inositol* (**3**). A mixture of **2** (63.0 g, 242 mmol), powdered KOH (82.2 g, 1.56 mol), and benzyl chloride (315 ml, 2.74 mol) was heated under stirring to 100°. The temp. rose exothermically to 140° (cooling in ice/water bath). A further quantity of powdered KOH (96.9 g, 1.73 mol) was then added and the temp. kept at 120° for ½ h. H_2O (500 ml) was added and the mixture well stirred. The lower aq. phase was removed, washed with CH_2Cl_2 (400 ml), diluted with H_2O (400 ml), and washed finally with CH_2Cl_2 (100 ml). The CH_2Cl_2 solns. were combined and returned to the product mixture which was then dried (Na_2SO_4), cooled to 5°, filtered (*Dicalite*, No.*4* glass sinter) and freed of volatiles at 100°/0.1 mbar: 183 g of clear yellow oil which was used in the next step without purification.

DL-*1,4,5,6-Tetra-O-benzyl*-myo-*inositol* (**4**). A mixture of crude **3** (183 g), AcOH (1 l), and H_2O (250 ml) was heated at 80–100° for 1½ h and then evaporated (17 mbar): 168 g. Toluene (175 ml) and hexane (500 ml) were added, and the slurry of crystals obtained was kept overnight at 4°, filtered under suction, washed with toluene/hexane 1:3 (100 ml), and dried under vacuum: 112.2 g (85% on **2**). M.p. 127.5–128° [(27]:127°). R_f (*A* 10:1, *a*) 0.21 (1 spot).

DL-*1,2,4,5,6-Penta-O-benzyl*-myo-*inositol* (**7**). At 100°, **4** (27.0 g, 50 mmol), dibutyltin oxide (98%, 13.2 g, 53 mmol) and toluene (200 ml) were refluxed with H_2O separation for 1 h. After evaporation, DMF (100 ml) and allyl bromide (7.05 ml, 81.5 mmol) were added and reacted at 80° for 4 h. Then, the soln. was evaporated (86°/17 mbar) and the residue dissolved in Et_2O (100 ml) and treated with sat. $NaHCO_3$ soln. (100 ml) and brine (100 ml). To the resulting dispersion, *Dicalite* was added, and the mixture was filtered and the filtrate evaporated. The residue (27.3 g) was subjected to FC (petroleum ether (b.p. 40–60°)/CH_2Cl_2 4:10): 22.1 g of a mixture of allyl ethers (principally **5**). To the crude **5** in dry DMF (100 ml), NaH (55% in oil; 3.33 g, 76.2 mmol) was added, followed, after the frothing had subsided, by benzyl bromide (9.06 ml, 76.2 mmol). The mixture was held at 40° for 4 h, then excess NaH was decomposed by adding MeOH (10 ml) and H_2O (25 ml). The mixture was evaporated, diluted with Et_2O (100 ml), filtered (*Dicalite*), and reevaporated: crude **6** (26.7 g) as a clear, viscous, yellow liquid. To the crude **6** was added EtOH (500 ml), 5% Pd/C (3.35 g), and TsOH (2.68 g) in H_2O (25 ml). The mixture was refluxed for 22 h, $NaHCO_3$ (1.68 g) was added, the mixture cooled and filtered, and the solvent evaporated. The residue (25.3 g) was crystallised from hexane: **7** (23.5 g, 74%). The product was recrystallised from hexane. M.p. 86–88° ([28]: 92–94°). R_f (*B* 15:1, *a*) 0.50. IR (KBr): 3458*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.21 (*d*, *J* = 6.3, OH–C(3)); 3.44–3.52 (*m*, H–C(1), H–C(3), H–C(5)); 3.81 (*dd* app. as *t*, *J* = 9.5, H–C(4) or H–C(6)); 4.03 (*dd*, app. as *t*, *J* = 2.5, H–C(2)); 4.06 (*dd* app. as *t*, *J* = 10, H–C(6) or H–C(4)); 5.02–4.69 (*m*, 10 H); 7.24–7.34 (*m*, 25 H). ^{13}C-NMR ((D$_6$)DMSO, 62.9 MHz): 71.29, 71.51, 74.02, 74.13, 74.52, 74.62, 78.27, 80.09, 81.37, 81.95, 82.73 (gated multiplicities are not clear cut, but 11 signals represent 6 ring *C*H and 5 benzyl *C*H$_2$ groups); 127.08–128.15 (overlapping *d*, Ar); 138.69 (*s*); 138.87 (*s*, 2 C); 139.22 (*s*); 139.41 (*s*). MS: 539 ([*M* – Bn]$^+$).

DL-*2,3,4,5,6-Penta-O-benzyl-2,3,5/4,6-pentahydroxycyclohexanone* (**8**). Pyridinium chlorochromate (63.7 g, 296 mmol) was added to a soln. of **7** (93.2 g, 148 mmol) in CH_2Cl_2 (1 l) and stirred at 25° for 24 h. After concentration to *ca.* 300 ml, the dark liquid together with black, granular solid was added to the top of a column of SiO_2 (500 g) and eluted with Et_2O: the oily product fractions (83 g) crystallised. Treatment with MeOH (200 ml), filtration, and drying (40°/26 mbar) yielded **8** (66.9 g, 72%) containing a trace of **7** (TLC). Recrystallisation from MeOH gave colourless needles. M.p. 92–92.5° ([31]: 87–89°). R_f (*B* 5:1, *a*) 0.56. IR (KBr): 1730*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 3.45 (*dd*, *J* = 9.6, 3, H–C(3)); 3.51 (*dd* app. as *t*, *J* = 9.2, H–C(5)); 3.97 (*d*, *J* = 2.9, H–C(2)); 4.28 (*dd* app. as *t*, *J* = 9.1, H–C(4)); 4.42–4.63 (*m*, 6 H); 4.69 (*d*, *J* = 9.5, H–C(6)); 4.76–4.93 (*m*, 4 H); 7.24–7.36 (*m*, 25 H). ^{13}C-NMR ((D$_6$)DMSO, 125.8 MHz): 71.31 (*t*); 71.99 (*t*); 72.23 (*t*); 74.39 (*t*); 74.48 (*t*); 78.37 (*d*); 80.34 (*d*); 80.82 (*d*); 80.86 (*d*); 82.43 (*d*); 127.11–128.30 (overlapping *d*, Ar); 137.13 (*s*); 137.72 (*s*); 138.05 (*s*); 138.36 (*s*); 138.48 (*s*); 205.22 (*s*, C=O). MS: 429 ([*M* – Bn – BnOH]$^+$). Anal. calc. for $C_{41}H_{40}O_6$ (628.77): C 78.32, H 6.41; found: C 78.23, H 6.68.

DL-*1,2,3,4,5-Penta*-O-*benzyl-6-methylidenecyclohexane-1,2,4/3,5-pentol* (**9**). $Me(Ph)_3PBr$ (14.3 g, 40 mmol) was dried by stirring at 70° in a stream of dry Ar. Dry THF (50 ml) was added and the soln. cooled to −5°. BuLi (1.6M in hexane; 25 ml, 40 mmol) was added by syringe and the turbid orange mixture allowed to warm to 0° under a vigorous flow of Ar. A soln. of **8** (12.6 g, 20 mmol) in THF (20 ml) was added dropwise over 9 min at < 12°. The mixture was allowed to warm to 24° over 1 h, poured on ice (100 g), and extracted with AcOEt (100 ml). The aq. phase was washed with AcOEt and the combined org. phase dried (Na_2SO_4), evaporated, and submitted to FC (toluene, *B* 5:1): **9** (12.3 g, 98%). Colourless oil which crystallised after 24 h. M.p. 39–42° ([31]: oil). R_f (*B* 5:1, *a*) 0.64. IR: 1660*w*, 925*m*, (=CH_2). ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.39 (*dd* app. as *t*, *J* = 9.3, H–C(4)); 3.39 (*dd*, *J* = 9.5, 3, H–C(2)); 4.08 (*d*, *J* = 2.6, H–C(1)); 4.11 (*dd* app. as *t*, *J* = 9.5, H–C(3)); 4.25 (*ddd* app. as *dt*, *J* = 10 (*d*); 1.5 (*t*); H–C(5)); 4.3–5.0 (*m*, 10 H); 5.03 (*dd* app. as *t*, *J* = 1.5, 1 H, CH_2=C(6)); 5.43 (*dd* app. as *t*, *J*=1.5, 1 H, CH_2=C(6)); 7.25–7.35 (*m*, 25 H). ^{13}C-NMR ((D_6)DMSO, 100.6 MHz; H, C COSY): 69.27 (*t*); 70.76 (*t*); 72.50 (*t*); 74.64 (*t*); 74.64 (*t*); 74.72 (*t*); 77.45 (*d*, C(1)); 78.85 (*d*, C(5)); 81.27 (*d*, C(3)); 81.50 (*d*, C(2)); 84.47 (*d*, C(4)); 113.57 (*t*, CH_2=C(6)); 127.16–128.13 (overlapping *d*, Ar); 138.04 (*s*); 138.14 (*s*); 138.45 (*s*); 138.72 (*s*); 138.84 (*s*); 141.50 (*s*). MS: 535 ([*M* − Bn]$^+$). Anal. calc. for $C_{42}H_{42}O_5$ (626.79): C 80.48, H 6.75; found: C 80.50, H 6.80.

DL-*(1,2,3,5/4,6)-* and DL-*(1,2,4/3,5,6)-2,3,4,5,6-Penta*-O-*benzyl-2,3,4,5,6-pentahydroxycyclohexane-1-methanol* (**10a** and **10b**, resp.) *and* DL-*2,3,4,5-Tetra*-O-*benzyl-1-deoxy-1-methyl*-myo-*inositol* (**11**). A soln. of **9** (1.48 g, 2.36 mmol) in dry toluene (100 ml) was heated to reflux under Ar bubbling, and 50 ml of toluene were removed by distillation at 1 atm over 1½ h. After cooling to 1°, *ca.* 10M $BH_3 \cdot SMe_2$ in THF (0.5 ml, 5 mmol) was added by syringe. After 30 min, the mixture was warmed to 24° for 2 h and finally to 60° for 1 h. H_2O (1 ml), 5M NaOH (5 ml), and 30% H_2O_2 soln. (1 ml) were added successively and dropwise under vigorous stirring and the mixture held at 50° for 1 h. The org. phase was separated, washed with 2M HCl (10 ml), aq. sat. $NaHCO_3$ soln. (10 ml), and brine (10 ml), dried (Na_2SO_4), and evaporated: turbid, colourless oil (1.54 g). MPLC (CH_2Cl_2, *A* 30:1) yielded **10a**/**10b** (0.57 g, 37%) as an oil. R_f (*A* 10:1, *a*) 0.74, 0.69. They were used without separation in the next step. The crystalline by-product **11** (0.34 g, 26%) was recrystallised from hexane.

Data of **11**: M.p. 96–97.5°. R_f (*B*, 1:1, *a*) 0.65. IR (KBR): 3361*s* (br.). ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.11 (*d*, *J* = 6.7, Me–C(1)); 1.51 (*m*, H–C(1)); 2.22 (*d*, *J* = 2.3, OHC–C(6)); 3.30 (*dd* app. as *t*, *J* = 9.5, H–C(5)); 3.51 (*dd*, *J* = 9.7, 2.6, H–C(3)); 3.62 (*ddd*, *J* = 10, 9.5, 2.0, H–C(6)); 3.75 (*dd* app. as *t*, *J* = 2.0, H–C(2)); 4.05 (*dd* app. as *t*, *J* = 9.7, H–C(4)); 4.55–5.05 (*m*, 8 H); 7.28–7.36 (*m*, 20 H). ^{13}C-NMR ((D_6)DMSO, 62.9 MHz): 13.98 (*q*, Me); 38.03 (*d*, C(1)); 71.49 (*t*); 72.88 (*d*); 74.13 (*t*); 74.48 (*t*); 78.20 (*d*); 81.33 (*d*); 83.46 (*d*); 86.10 (*d*); 126.95–128.15 (overlapping *d*, Ar); 138.75 (*s*); 139.03 (*s*); 139.20 (*s*); 139.38 (*s*). CI-MS: 556 ([*M* + NH_4]$^+$). Anal. calc. for $C_{35}H_{38}O_5$ (538.68): C 78.04, H 7.11; found: C 78.11, H 7.13.

*[*DL-*(1,2,4/3,5,6)-2,3,4,5,6-Penta*-O-*benzyl-2,3,4,5,6-pentahydroxycyclohexyl]methyl Hexadecanoate* (**12**) *and [*DL-*(1,2,3,5/4,6)-2,3,4,5,6-Penta*-O-*benzyl-2,3,4,5,6-pentahydroxycyclohexyl]methyl Hexadecanoate* (**13**). The mixture **10a**/**10b** (0.518 g, 0.80 mmol) was dissolved in a soln. of palmitoyl chloride (0.33 g, 1.20 mmol), pyridine (0.319 g, 4.0 mmol), 4-(dimethylamino)pyridine (DMAP; 0.005 g, 0.04 mmol), and CH_2Cl_2 (10 ml). After 20 min at 25° (reaction complete), the mixture was agitated with 1N HCl (10 ml). The org. phase was separated, washed with sat. $NaHCO_3$ soln., dried (Na_2SO_4), and evaporated. MPLC (hexane, *E* 10:1, *E* 3:1) yielded **12** (0.40 g, 56%), mixed epimers (0.06 g, 8%), and **13** (0.15 g, 21%).

Data of **12**: colourless oil. IR: 1736 (C=O, ester), ^{1}H-NMR ($CDCl_3$, 400 MHz, COSY): 0.879 (*t*, *J* = 6, 3 H); 1.25 (*m*, 24 H); 1.55 (*m*, 2 H); 2.16 (*t*, 2 H); 2.57 (*dddd* app. as *sext.*, *J* = 10, 7, 4.5, 3, H–C(1)); 3.59 (*dd* app. as *t*, *J* = 9.4, H–C(3)); 3.68 (*dd*, *J* = 10, 3, H–C(5)); 3.78 (*dd* app. as *t*, *J* = 3, H–C(6)); 3.95 (*dd* app. as *t*, *J* = 11, 1 H, CH_2–C(1)); 3.96 (*dd* app. as *t*, *J* = 10, H–C(4)); 3.98 (*dd* app. as *t*, *J* = 8, H–C(2)); 4.33 (*dd*, *J* = 11, 4.5, 1 H, CH_2–C(1)); 4.49–4.92 (*m*, 10 H); 7.26–7.36 (*m*, 25 H). FAB-MS: 883 ([*M* + H]$^+$). Anal. calc. for $C_{58}H_{74}O_7$ (883.22): C 78.87, H 8.45; found: C 78.65, H 8.33.

Data of **13**: colourless crystalline solid. M.p. 47–49°. IR (KBr): 1737 (C=O, ester). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.880 (*t*, *J* = 6, 3 H); 1.24 (*m*, 24 H); 1.56 (*m*, 2 H); 1.86 (*m*, H–C(1)); 2.20 (*t*, *J* = 7, CH_2CO); 3.49 (*dd*, *J* = 10, 2, H–C(3)); 3.58 (*dd* app. as *t*, *J* = 9, H–C(4)); 3.70 (*dd*, *J* = 10, 9, H–C(5)); 3.98 (*m*, H–C(2)); 4.07 (*dd* app. as *t*, *J* = 9.5, H–C(6)); 4.10 (*dd* app. as *t*, *J* = 10.5, 1 H, CH_2–C(1)); 4.36 (*dd*, *J* = 11, 4, 1 H, CH_2–C(1)); 4.51–5.0 (*m*, 10 H); 7.36–7.25 (*m*, 25 H). FAB-MS: 881 ± 1?, 627 ([*M* + H − palmitic acid]$^+$). Anal. calc. for $C_{58}H_{74}O_7$ (883.22): C 78.87, H 8.45; found: C 78.90, H 8.69.

*[*DL-*(1,2,4/3,5,6)-2,3,4,5,6-Pentahydroxycyclohexyl]methyl Hexadecanoate* (**14**). A soln. of **12** (0.38 g, 0.44 mmol) in EtOH (15 ml) was agitated with H_2 at 1 atm in the presence of 5% Pd/C (0.15 g) for 1½ h. The catalyst was removed by filtration and washed with hot EtOH. The combined solns. were evaporated and the residue recrystallised form EtOH/hexane: pure **14** (0.136 g, 71%). Lustrous plates. M.p. 108–110°. R_f (*C* 3:1, *a*) 0.48. IR (KBr): 3371*s* (br.), 1724*s* (C=O, ester), 1162*s* (COC, ester), 1103*m*, 1033*m* (alc. II), 722*m* ($(CH_2)_n$). ^{1}H-NMR (D_2O, 400 MHz; COSY): 0.854 (*t*, *J* = 7.0, 3 H); 1.23 (*m*, 24 H); 1.51 (*m*, 2 H); 2.20 (*m*, H–C(1)); 2.28 (*t*, *J* = 7.4,

CH_2CO); 3.15 (*dd* app. as *t*, J = 8.4, H–C(3)); 3.37 (*dd* app. as *t*, J = 8.6, H–C(4)); 3.41 (*dd*, J = 8, 2.5, H–C(5)); 3.73 (*dd*, J = 9.2, 5.6, H–C(2)); 3.78 (*dd* app. as *t*, J = 3.1, H–C(6)); 3.95 (*dd* app. as *t*, J = 10.5, 1 H, CH_2–C(1)); 4.23 (*dd*, J = 11.2, 4.7, 1 H, CH_2–C(1)). ^{13}C-NMR ($(D)_6$DMSO, 100.6 MHz; H, C COSY): 13.99 (*q*); 22.17 (*t*); 24.56 (*t*); 29.13–28.58 (10 CH_2, overlapping); 31.38 (*t*); 33.64 (*t*); 43.86 (*d*, C(1)); 61.05 (*t*, CH_2–C(1)); 68.62 (*d*, C(6)); 68.83 (*d*, C(2)); 71.44 (*d*, C(4)); 73.14 (*d*, C(5)); 73.86 (*d*, C(3)); 172.95 (*s*, C=O). CI-MS: 450 ($[M + NH_4]^+$), 433 ($[M + H]^+$), 415 ($[M + H - H_2O]^+$). Anal. calc. for $C_{23}H_{44}O_7$ (432.60): C 63.86, H 10.25; found: C 63.71, H 10.17.

*[*DL*-(1,2,3,5/4,6)-2,3,4,5,6-Pentahydroxycyclohexyl]methyl Hexadecanoate* (**15**). For 3 h, **13** (0.117 g, 0.132 mmol) in EtOH (5 ml) was agitated with H_2 at 1 atm in the presence of 5% Pd/C (0.050 g). The catalyst was removed by filtration and washed with hot aq. EtOH (10 ml) and then hot MeOH (2 × 10 ml). The combined solns. were evaporated, and the residue (0.055 g) was recrystallised from MeOH (2.3 g): pure **15** (0.047 g, 82%). Colourless, microscopic plates. M.p. 120–121°. IR (KBr): 3400*m* (br., OH), 1731*s* (C=O), 1175*s* (COC, ester), 1048*m* (alc. II), 720*m* ($(CH_2)_n$). ^{1}H-NMR ((D_6)DMSO/D_2O, 400 MHz; COSY): 0.840 (*t*, J = 6.6, 3 H); 1.22 (*m*, 24 H); 1.49 (*m*, 2 H); 1.57 (*dddd* app. as *tt*, J = 11, 3, H–C(1)); 2.25 (*t*, J = 7.3, CH_2CO); 2.98 (*dd* app. as *t*, J = 9, H–C(5)); 3.12 (*dd*, J = 9.5, 3); 3.24 (*dd* app. as *t*, J = 11, 9, H–C(6)); 3.34 (*dd* app. as *t*, J = 9.5, H–C(4)); 3.74 (*m* app. as *s*, H–C(2)); 3.99 (*dd* app. as *t*, J = 11, 1 H, CH_2–C(1)); 4.33 (*dd*, J = 10.5, 3, 1 H, CH_2–C(1)); in the absence of D_2O: 4.52 (*d*, J = 5.2, OH); 4.53 (*d*, J = 4.6, OH); 4.55 (*d*, J = 4.4, OH); 4.67 (*d*, J = 5.6, OH); 4.69 (*d*, J = 4.3, OH). MS: 432 (M^+). Anal. calc. for $C_{23}H_{44}O_7$ (432.60): C 63.86, H 10.25; found: C 63.70, H 10.51.

DL*-(6E)- and* DL*-(6Z)-1,2,3,4,5-Penta-*O*-benzyl-6-(methoxymethylidene)cyclohexane-1,2,4/3,5-pentol* (**16a** and **16b**, resp.). (Methoxymethyl)triphenylphosphonium chloride (4.11 g, 12 mmol) in dry THF (6 ml) was cooled to –12° and BuLi (1.6M in hexane; 7.5 ml, 12 mmol) added dropwise with stirring. A soln. of **8** (1.89 g, 3 mmol) in THF (5 ml) was added to the red ylide soln. at 10° and the mixture allowed to warm to 21° over 45 min. It was then filtered to remove some of the Ph_3PO. The filtrate was poured on ice (40 g), extracted with Et_2O (2 × 25 ml), dried (Na_2SO_4), and evaporated: brownish-red oil (*ca.* 5 g). MPLC (hexane, *E* 5:1 to 1:1) yielded **16a** (0.685 g, 35%) as a yellow oil and **16b** (0.505 g, 25%) as a pale yellow oil which crystallised slowly and was recrystallised from EtOH.

Data of **16a**: R_f (*B* 5:1, *a*) 0.49. IR: 1678*s* (C=C). ^{1}H-NMR ($CDCl_3$, 270 MHz): 3.41 (*dd*, J = 10, 3.5, H–C(2)); 3.58 (*dd* app. as *t*, J = 9, H–C(4)); 3.65 (*s*, MeO); 3.76 (*d*, J = 3.5, H–C(1)); 4.03 (*dd* app. as *t*, J = 9, H–C(3)); 4.30 (*dd*, J = 9.5, 1.5, H–C(5)); 4.33–5.02 (*m*, 10 H); 5.91 (*d*, J = 1.5, CH=C(6)); 7.27–7.38 (*m*, 25 H); NOE experiments established the (6*E*)-configuration. ^{13}C-NMR ((D_6)DMSO, 62.9 MHz): 60.38 (*q*, MeO); 68.76 (*t*); 70.72 (*t*); 71.92 (*t*); 74.36 (*t*); 74.51 (*t*); 75.98 (*d*); 81.26 (*d*); 82.14 (*d*); 83.22 (*d*); 107.22 (*s*, C(6)); 127.2–128.2 (overlapping *d*, Ar); 138.53 (*s*); 138.74 (*s*); 138.80 (*s*); 138.98 (*s*); 139.03 (*s*); 146.93 (*d*, *C*H=C(6)). CI-MS: 674 ($[M + NH_4]^+$), 566 ($[M + NH_4 - BnOH]^+$).

Data of **16b**: M.p. 63–65°. R_f (*B* 5:1, *a*) 0.63. IR (KBr): 1677*s* (C=O, conj.). ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.36 (*dd*, J = 9.5, 3.5, H–C(2)); 3.37 (*dd* app. as *t*, J = 9, H–C(4)); 3.56 (*s*, MeO); 4.04 (*dd* app. as *t*, J = 9.5, H–C(3)); 4.21 (*dd*, J = 9.2, 1.8, H–C(5)); 4.75 (*d*, J = 3.5, H–C(1)); 4.45–4.94 (*m*, 10 H); 6.24 (*d*, J = 18, CH=C(6)); 7.25–7.32 (*m*, 25 H). ^{13}C-NMR ((D_6)DMSO, 62.9 MHz): 59.91 (*q*, MeO); 68.49 (*d*); 68.93 (*t*); 70.62 (*t*); 72.89 (*t*); 74.59 (*t*); 74.71 (*t*); 77.22 (*d*); 81.19 (*d*); 81.26 (*d*); 85.55 (*d*); 108.26 (*s*, C(6)); 127.13–128.12 (overlapping *d*, Ar); 138.18 (*s*); 138.27 (*s*); 138.43 (*s*); 138.77 (*s*); 138.88 (*s*); 146.08 (*d*, *C*H=C(6)). Anal. calc. for $C_{43}H_{44}O_6$ (656.82): C 78.63, H 6.75; found: C 78.56, H 6.79.

DL*-3,4,5,6-Tetra-*O*-benzyl-3,5,6/4-tetrahydroxycyclohex-1-ene-1-carboxaldehyde* (**17**) *and* DL*-3,4,5,6-Tetra-*O*-benzyl-3,5/4,6-tetrahydroxycyclohex-1-ene-1-carboxaldehyde* (**18**). To a soln. of **16b** (1.00 g, 1.52 mmol) in Et_2O (10 ml) at 1° was added $BF_3 \cdot Et_2O$ (0.108 g) in Et_2O (10 ml). The mixture was allowed to warm to r.t. and, after 6 h, was refluxed for 1½ h. After evaporation, the products were separated by MPLC (*E* 5:1 to 3:1): **17** (0.50 g, 61%) as an oil and **18** (0.20 g, 24%) as an oil which crystallised on standing.

Data of **17**: R_f (*E* 1:1, *a*) 0.44. IR: 2719*w*, 1691*s* (C=O, conj.). ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.48 (*dd*, J = 10.1, 3.3, H–C(5)); 4.26 (*dd*, J = 8.5, 2.5, H–C(3)); 4.36 (*dd*, J = 10.6, 7.9, H–C(4)); 4.65 (*d*, J = 3.3, H–C(6)); 4.70–5.06 (*m*, 8 H); 6.44 (*d*, J = 2.5, H–C(2)); 7.27–7.34 (*m*, 20 H); 9.51 (*s*, CH=O). FAB-MS: 573 ($[M + K]^+$), 557 ($[M + Na]^+$).

Data of **18**: Recrystallised from 92% EtOH (*v*/*v*). M.p. 68–69°. R_f (*E* 1:1, *a*) 0.51. IR (KBr): 2770*w*, 1701*s* (C=O, conj.). ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.72 (*dd* app. as *t*, J = 8.3, H–C(5)); 3.90 (*dd*, J = 9, 6.4, H–C(4)); 4.42 (*ddd* app. as *dt*, J = 7.2, 2, H–C(6)); 4.56 (*dd*, J = 6.3, 2, H–C(3)); 4.73–4.93 (*m*, 8 H); 6.68 (*d*, J = 2, H–C(2)); 7.29–7.34 (*m*, 20 H); 9.53 (*s*, CH=O). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 73.31 (*t*); 74.89 (*t*); 74.96 (*t*); 75.09 (*t*); 76.28 (*d*); 78.68 (*d*); 83.24 (*d*); 83.49 (*d*); 127.8–128.6 (overlapping *d*, Ar); 137.54–138.19 (overlapping *s*, 4Ar); 140.01 (*s*, C(1)); 147.17 (*d*, C(2)); 191.63 (*d*, CH=O). CI-MS: 552 ($[M + NH_4]^+$). Anal. calc. for $C_{35}H_{34}O_5$ (534.65): C 78.63, H 6.41; found: C 78.60, H 6.67.

18 *from* **16a**. A soln. of **16a** (0.65 g, 1.0 mmol) in CH_2Cl_2 (*puriss.*, > 99% GC, stab. with 0.002% amylene; 10 ml) was allowed to stand exposed at r.t. for 4 days, with periodic replenishment of solvent. TLC then showed that no **16a** remained. MPLC (hexane, *E* 5:1 to 1:1) yielded **18** (0.22 g, 41%) as an oil.

A similar experiment in which 92% EtOH (*v*/*v*) was used instead of CH_2Cl_2 showed that a major amount of **16a** remained after 24 days at r.t. A sample of **16b** dissolved in CH_2Cl_2 and allowed to stand exposed at r.t. for 14 days, with periodic replenishment of solvent, remained essentially unchanged (TLC).

2,4,6(or *3,4,5)-Tris(benzyloxy)phenol* (**19**). On working up a 20-mmol-scale preparation of **16a**/**16b** in the manner described above, 0.225 g (2%) of **19** were isolated as colourless needles. M.p. 106–107° ([20]: 108–109°). R_f (*E* 1:1, *a*) 0.49. IR (KBr): 3480*s* (OH); 1614, 1511 (Ar). ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.88 (*s*, 1 $PhCH_2$); 5.07 (*s*, 2 $PhCH_2$); 5.22 (*s*, exchange with D_2O, 1 OH); 6.29 (*s*, 2 arom. H); 7.31–7.42 (*m*, 15 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 70.77 (*t*); 71.44 (*t*); 95.42 (*d*); 127.55–128.61 (6 *d*); 130.45 (*s*); 136.69 (*s*); 136.98 (*s*); 146.50 (*s*); 151.86 (*s*). MS: 412 (M^+), 321 ($[M - Bn]^+$). Anal. calc. for $C_{27}H_{24}O_4$ (412.49): C 78.62, H 5.86; found: C 78.45, H 6.10.

DL-*3,4,5,6-Tetra*-O-*benzyl-3,5/4,6-tetrahydroxycyclohex-1-ene-1-methanol* (**20**). To a soln. of **18** (0.043 g, 0.08 mmol) in EtOH (0.86 g) was added sat. $NaBH_4$ soln. (0.043 g, 1.14 mmol). The reaction appeared complete after 5 min but was left at r.t. for 25 min. Then, brine and Et_2O were added and the mixture agitated. The org. phase was dried (Na_2SO_4) and evaporated and the crystalline residue recrystallised from Et_2O/hexane: **20** (0.040 g, 92%). Colourless needles. M.p. 87.5–88°. R_f (*E* 1:1, *a*) 0.20. IR (KBr): 3422*s* (br.). ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.99 (*m*, CH_2OH); 3.75 (*dd*, *J* = 10.6, 7.5, H–C(4) or H–C(5)); 3.83 (*dd*, *J* = 10.6, 7.5, H–C(4) or H–C(5)); 4.06 (*m*, 1 H, CH_2OH); 4.24 (*m*, H–C(3) or H–(6)); 4.33 (*m*, H–C(3) or H–C(6)); 4.70–5.04 (*m*, 8 H); 5.73 (*m*, H–C(1)); 7.30–7.32 (*m*, 20 H). CI-MS: 554 ($[M + NH_4]^+$). Anal. calc. for $C_{35}H_{36}O_5$ (536.67): C 78.33, H 6.76; found: C 78.14, H 6.99.

*[*DL-*3,4,5,6-Tetra*-O-*benzyl-3,5/4,6-tetrahydroxycyclohex-1-en-1-yl]methyl Hexadecanoate* (**21**). To a soln. of **20** (0.84 g, 1.56 mmol), DMAP (0.010 g, 0.08 mmol), and pyridine (0.622 g, 7.86 mmol) in CH_2Cl_2 (15 ml) at r.t. was added palmitoyl chloride (0.640 g, 2.33 mmol). After 2 h, no **20** could be detected (TLC). The mixture was then washed with 1N HCl (30 ml) and sat. $NaHCO_3$ soln. (30 ml), the aq. phases were extracted with CH_2Cl_2, and the combined organic phase was dried (Na_2SO_4) and evaporated: **21** as a crystalline, waxy solid (1.43 g, > 100%) with a slight smell of pyridine. A sample for analysis was recrystallised from EtOH. M.p. 44–45°. R_f (*E* 2:1, *a*) 0.55. IR (KBr): 1737*s* (C=O, ester), 1675*w* (C=C). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.879 (*t*, *J* = 7, 3 H); 1.25 (*m*, 24 H); 1.56 (*m*, 2 H); 2.27 (*t*, *J* = 7, CH_2CO); 3.76 (*dd*, *J* = 10.5, 7.5, H–C(4) or H–C(5)); 3.83 (*dd*, *J* = 10.5, 7.5, H–C(4) or H–C(5)); 4.22 (*m*, H–C(3) or H–C(6)); 4.29 (*m*, H–C(3) or H–C(6)); 4.57 (*d*, *J* = 13, 1 H, CH_2–C(1)); 4.69 (*d*, *J* = 13, 1 H, CH_2–C(1)); 4.62–5.03 (*m*, 8 H); 5.74 (*m*, H–C(2)); 7.27–7.33 (*m*, 20 H). FAB-MS: 813 ($[M + K]^+$), 797 ($[M + Na]^+$). Anal. calc. for $C_{51}H_{66}O_6$ (775.08): C 79.03, H 8.58; found: C 78.79, H 8.58.

DL-*3,4,5,6-Tetra*-O-*benzyl-3,5,6/4-tetrahydroxycyclohex-1-ene-1-methanol* (**22**). To a soln. of **17** (1.36 g, 2.54 mmol) in EtOH (30 ml) was added sat. $NaHCO_3$ soln. (1 ml) and $NaBH_4$ (1.36 g, 36 mmol). After 13 min 100 ml of brine was added, the mixture extracted with Et_2O (3 × 50 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue subjected to MPLC (*E* 3:1 to 2:1): **22** as a colourless oil (1.04 g, 76%). R_f (*D* 20:1, *a*) 0.49. IR: 3433*s* (br.). ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.40 (*t*, *J* = 11, CH_2OH); 3.59 (*dd*, *J* = 10.5, 3.5, H–C(5)); 4.02 (*m*, CH_2OH); 4.08 (*m*, H–C(3)); 4.18 (*d*, *J* = 4, H–C(6)); 4.21 (*dd*, *J* = 10.5, 7.5, H–C(4)); 4.64–5.06 (*m*, 8 H); 5.73 (*d*, *J* = 3, H–C(2)); 7.32–7.38 (*m*, 20 H). Anal. calc. for $C_{35}H_{36}O_5$ (536.67): C 78.33, H 6.76; found: C 78.26, H 6.78.

*[*DL-*3,4,5,6-Tetra*-O-*benzyl-3,5,6/4-tetrahydroxycyclohex-1-en-1-yl]methyl Hexadecanoate* (**23**). To a soln. of **22** (0.99 g, 1.84 mmol) in CH_2Cl_2 (10 ml) was added DMAP (0.0112 g, 0.092 mmol) and Et_3N (0.279 g, 2.76 mmol) in CH_2Cl_2 (5 ml) followed by a soln. of palmitoyl chloride (0.759 g, 2.76 mmol) in CH_2Cl_2 (5 ml). After 7 min (reaction complete), the mixture was washed with 1N HCl (50 ml), brine (50 ml), and sat. $NaHCO_3$ soln. (50 ml). The aq. phases were washed with CH_2Cl_2 and the combined org. solns. dried (Na_2SO_4) and evaporated. FC (*F* 20:1) yielded **23** as a colourless oil (1.13 g, 79%). R_f (*B* 15:1, *a*) 0.42. IR: 1738*s* (C=O, ester). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.878 (*t*, *J* = 6.5, 3 H); 1.25 (*m*, 24 H); 1.56 (*m*, 2 H); 2.22 (*t*, *J* = 7.5, CH_2CO); 3.57 (*dd*, *J* = 10.5, 3.5, H–C(5)); 4.09 (*m*, H–C(3)); 4.09 (*d*, *J* = 3, H–C(6)); 4.21 (*dd*, *J* = 10.5, 7.5, H–C(4)); 4.42 (*d*, J_{gem} = 13, 1 H, CH_2–C(1)); 4.53 (*d*, J_{gem} = 13, 1 H, CH_2–C(1)); 4.7–5.1 (*m*, 8 H); 5.75 (*d*, *J* = 2.5, H–C(2)); 7.28–7.33 (*m*, 20 H). CI-MS: 792 ($[M + NH_4]^+$). Anal. calc. for $C_{51}H_{66}O_6$ (775.08): C 79.03, H 8.58; found: C 78.96, H 8.85.

*[*DL-*(1,3,5/2,4)-2,3,4,5-Tetrahydroxycyclohexyl]methyl Hexadecanoate* (**24**) *and* DL-*(1,3,5/2,4)- and* DL-*(1,3/2,4,5)-5-Methylcyclohexane-1,2,3,4-tetrol* (**25a** and **25b**, resp.). To a soln. of **21** (1.146 g, 1.48 mmol) in EtOH (30 ml) was added 5% Pd/C (0.309 g), and the mixture was agitated with H_2 at 1 atm. for 4 h. After removal of the catalyst by filtration, further extracting the catalyst on the filter with hot EtOH, and evaporating the combined filtrates, 0.73 g of a crystalline residue were obtained. Column chromatography (*G* 80:20:2) yielded **24** (0.154 g, 25%) as a crystalline solid which was recrystallised from $CHCl_3$ for analysis and **25a**/**25b** (0.108 g, 45%) as a mixture.

Data of **24**: M.p. 121–122°. R_f (*G* 80:20:2, *a*) 0.35. IR (KBr): 3403*s* (br.), 1740 (C=O, ester). ^{1}H-NMR ((D$_6$)DMSO, 250 MHz): 0.854 (*t*, *J* = 6.7, 3 H); 1.04 (*ddd*, *J* = 12, 12, 12, H–C(6)); 1.24 (*m*, 24 H); 1.51 (*m*, 3 H, may include H–C(1)); 1.73 (*ddd*, *J* = 12, 4, 4, H′–C(6)); 2.28 (*t*, *J* = 7, CH_2CO); 2.84–3.03 (*m*, H–C(2), H–C(3), H–C(4)); 3.22 (*m*, H–C(5)); 3.89 (*dd*, *J* = 11, 7, 1 H, CH_2–C(1)); 4.20 (*dd*, *J* = 11, 3, 1 H, CH_2–C(1)); 4.59 (*d*, *J* = 4, OH); 4.69 (*d*, *J* = 4, OH); 4.71 (*d*, *J* = 4, OH); 4.75 (*d*, *J* = 3, OH). CI-MS: 434 ($[M + NH_4]^+$), 196 ($[M + NH_4 - C_{16}H_{30}O]^+$). Anal. calc. for $C_{23}H_{44}O_6$ (416.60): C 66.31, H 10.65; found: C 66.24, H 10.82.

Data of **25a**/**25b**: M.p. 117–120°. R_f (*G* 80:20:2, *a*) 0.16. IR (KBr): 3422*s* (br.); 1700–1800 *no signal*, C=O of ester absent. ^{1}H-NMR ((D$_6$)DMSO, 250 MHz): 0.861 (*d*, *J* = 7.3, Me–C(5) (**25b**)); 0.904 (*d*, *J* = 6.5, Me–C(5) (**25a**)); 0.930 (*ddd*, *J* = 12, 12, 12, H_{ax}–C(6) (**25a**)); 3.6 H total integration for these 3 signals (integrations based on 14 H for the whole spectrum); 1.2–1.4 (*m*, 1.1 H); 1.55–1.70 (*m*, 1.0 H); 1.90 (*m*, 0.3 H (**25b**)); 2.70 (*m* [with D_2O: *dd*, app. as *t*], 0.7 H (**25a**)); 2.91 (*m*, 1.7 H); 3.1–3.5 (*m*, 1.7 H); 4.60–4.62 (*m*, exchanges with D_2O, 3.9 H, OH (**25a**/**25b**)); from the ratio of the peak heights of the Me signals in the ^{1}H-NMR of this mixture, it was estimated that the constituents were present in a ratio of 2:1; the magnitude of the *ddd* at 0.93 (0.6 H–C(6)) showed **25a** to be the major component; the 3 *J*'s of this *ddd*, each *ca.* 12 Hz, are taken to be $J_{gem} = J(5,6) = J(6,1)$, *i.e.* H–C(5) must be axial, an interpretation supported by the rest of the spectrum. CI-MS: 180 ($[M + NH_4]^+$).

*[*DL*-(1,2,3,5/4)-2,3,4,5-Tetrahydroxycyclohexyl]methyl Hexadecanoate* (**26**), *[*meso*-(1,3,5/4)-3,4,5-Trihydroxycylohexyl]methyl Hexadecanoate* (**27**), *(1,3,5/2)-5-Methylcyclohexane-1,2,3-triol* (**28**), *and Methylcyclohexanediols* (**29**). To a soln. of **23** (1.07 g, 1.38 mmol) in EtOH (30 ml) was added 5% Pd/C (0.30 g), and the mixture was agitated with H_2 at 1 atm for 2 h. After removal of catalyst by filtration and further extracting the catalyst on the filter with hot EtOH (2 × 30 ml) and boiling aq. EtOH (50%), the combined filtrates were evaporated: 0.544 g of colourless solid. TLC (*G* 80:20:2, *a*) showed the presence of several components. FC (same eluent) yielded in turn: 0.258 g (73%) of palmitic acid, 0.063 g of a crystalline solid purified by recrystallisation (hexane/(*t*-Bu)OMe) and FC (*G* 90:10:1) to give 0.020 g (11%) of **29**, 0.021 g of a crystalline solid which was crystallised from $CHCl_3$ to give 0.003 g (0.5%) of **27**, 0.045 g of a crystalline solid which on further FC (*G* 90:10:1 to 115:10:1) gave 0.024 g (4%) of **26**, and 0.061 g of a crystalline solid which was crystallised from $CHCl_3$/hexane to give 0.025 g (12%) of **28** containing traces of an impurity (TLC).

Data of **26**: M.p. 118–121°. R_f (*G* 24:7:1, *a*) 0.51. IR (KBr): 3391*s* (br.), 1796*s* (C=O, ester). ^{1}H-NMR ((D$_6$)DMSO/D_2O, 400 MHz): 0.864 (*t*, *J* = 6.8, 3 H); 1.23 (*m*, 24 H); 1.315 (*ddd*, *J* = 12, 12, 12, H_{ax}–C(6)); 1.51 (*m*, H–C(1), CH_2CH_2CO); 1.70 (*m*, H_{eq}–C(6)); 2.27 (*t*, *J* = 7.2, CH_2CO); 3.09 (*dd*, *J* = 9, 3, H–C(3)); 3.21 (*ddd*, *J* = 11, 9, 5, H–C(5)); 3.30 (*dd* app. as *t*, *J* = 9, H–C(4)); 3.70 (*m*, H–C(2)); 390 (*dd*, *J* = 11, 7.8, 1 H, CH_2–C(1)); 3.96 (*dd*, *J* = 11, 7.8, 1 H, CH_2–C(1)). CI-MS: 434 ($[M_1 + NH_4]^+$), 400 (impurity, $[M_2 + NH_4]^+$). Anal. calc. for $C_{23}H_{44}O_6$ (416.60): C 66.31, H 10.65; found: C 65.82, H 10.83.

Data of **27**: M.p. 96–98°. R_f (*G* 24:7:1, *a*) 0.62. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.880 (*t*, *J* = 6.5, 3 H); 1.19 (*ddd*, *J* = 12.5, 12, 12, H–C(2), H–C(6)); 1.25 (*m*, 24 H); 1.59 (*m*, 2 H); 1.85 (*m*, $\Sigma J = 41$, H_{ax}–C(1)); 2.0 (*m*, app. as *dm*, J_{gem} = 12.5, H′–C(2), H′–C(6)); 2.30 (*m*, app. as *t*, *J* = 7.5, CH_2CO, OH–C(3), OH–C(5)); 2.84 (br. *s*, OH–C(4)); 3.24 (*t*, *J* = 9, H–C(4)); 3.53 (*m*, H–C(3), H–C(5)); 3.96 (*d*, *J* = 6.3, CH_2–C(1)). CI-MS: 418 ($[M + NH_4]^+$), 401 ($[M + H]^+$).

Data of **28**: M.p. 119–121°. R_f (*G* 24:7:1, *a*) 0.47, trace impurity at 0.54 (possibly **26**). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.986 (*d*, Me–C(5)); 1.10 (*m*, H_{ax}–C(6), H_{ax}–C(4)); 1.26 (*s*, 2 H, probably fatty acid $(CH_2)_{12}$ impurity); 1.65 (*m*, H–C(5)); 1.93 (*ddd* app. as *dt*, H_{eq}–C(6), H_{eq}–C(4)); 2.71 (*s*, OH–C(1), OH–C(3)); 3.21 (*t*, *J* = 9, H–C(2)); 3.35 (br. *s*, OH–C(2)); 3.49 (*m*, H–C(1), H–C(3)). CI-MS (NH_3): 164 ($[M + NH_4]^+$), minor signal 434 (impurity, $[M + NH_4]^+$ of **26**).

Data of **29**: M.p. 52–55°. R_f (*G* 24:7:1, *a*) 0.60. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.936 (*d*, *J* = 6.5, Me); 0.991 (*d*, *J* = 7.2, Me, similar intensity to previous signal); 0.8–2.2 (*m*); 2.30 (br. *d*); 3.37 (*m*); 3.66 (*m*). MS: 130 (M^+), 112 ($[M - H_2O]^+$), 97 ($[112 - Me]^+$), 84 ($[M - C_2H_4 - H_2O]^+$).

DL*-1,2:4,5-Di-*O*-cyclohexylidene-*myo*-inositol* (**30**). A 1-step method yielding a crystalline product without chromatography was used [35]. Thus, the procedure described above for the preparation of **2** was followed, based on 390 mmol of *myo*-inositol instead of 260 mmol, to the point at which reaction at 144° was complete. After cooling, Et_3N (5.0 g, 49 mmol) was added and the soln. evaporated at 75°/15 mbar. The viscous, clear brown residue (183 g) was diluted with CH_2Cl_2 (250 ml) and washed with H_2O (4 × 400 ml). The separated org. phase was then evaporated (65°/20 mbar) to leave a residue (127 g) which was dissolved with warming in a mixture of hexane (200 ml) and acetone (30 ml). After scratching and seeding with authentic **30**, the soln. crystallised copiously. It was refrigerated overnight, filtered, and washed on the filter with hexane/acetone 3:1 (50 ml × 2) and the solid dried to constant weight: 30.42 g (22.9%) of colourless, crystalline **30**. M.p. 170–171.5° ([26]: 174°). R_f (*B* 1:1, *b*) 0.30.

DL-*1,4-Di*-O-*benzyl-2,3:5,6-di*-O-*cyclohexylidene*-myo-*inositol* (**31**). The method described in [37] was followed starting from **30** (61.3 g, 180 mmol): **31** as colourless crystals (60.47 g, 64.5%). M.p. 115–116° ([37]: 116–117.5°).

DL-*1,4-Di*-O-*benzyl-2,3*-O-*cyclohexylidene*-myo-*inositol* (**32**). The method described in [37] was followed in principle, using 26.03 g (50.0 mmol) of **31**, CH_2Cl_2 (520 ml), 1,2-dihydroxyethane (2.82 ml, 50.6 mmol), and TsOH (0.202 g, 1.06 mmol). After 47 min at 24°, Et_3N (4.05 ml, 29.1 mmol) was added and the soln. evaporated. The residue was taken up in CH_2Cl_2 (204 ml) and filtered (*Speedex*). The filtrate was evaporated to ½ volume and hexane (100 ml) added. After allowing the mixture to crystallise for 5 d, **32** (17.7 g, 80.4%) was collected by filtration. M.p. 143–144° ([37]: 147.5–148.8°).

DL-*1,4-Di*-O-*benzyl-5,6-bis*-O-*(4-methoxybenzyl)*-myo-*inositol* (**34**). To a soln. of **32** (4.41 g, 10.0 mmol) in dry DMF (10 ml) was added NaH (57% in oil; 1.09 g, 25 mmol) in portions, followed by 4-methoxybenzyl chloride (3.64 ml, 25.0 mmol; dropwise). The modest temp. rise was controlled by cooling. After 1 h, MeOH (2 ml) and H_2O (2 ml) were added to quench the reaction, and the mixture was evaporated, extracted with toluene (20 ml), filtered, and the filtrate evaporated (80°/25 mbar): crude **33** (7.36 g) as a viscous liquid. It was dissolved in toluene (30 ml) and EtOH (60 ml), and 1M aq. HCl (10 ml) was added. The mixture was held at 60° for 2½ h, cooled, extracted with sat. aq. $NaHCO_3$ soln. (20 ml), dried (Na_2SO_4), and filtered. The aq. phase was treated with brine and reextracted with toluene and twice with AcOEt. The combined evaporated extracts were taken up in toluene (20 ml), and hexane (10 ml) was added. After crystallisation was complete, **34** (4.80 g, 80%) was collected by filtration. A sample for analysis was recrystallised from $CHCl_3$/hexane 1:2. M.p. 130.4–130.6°. R_f (*B* 1:1, *a*) 0.43. IR (KBr): 3388*s*, 3321*m*, 1619*s*, 1514*s*, 1250*s*, 1132*s*, 1099*s*, 1067*s*, 1033*s*, 822*m*, 794*s*, 697*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.43 (*d*, J = 4, OH); 2.50 (*s*, OH); 3.45 (*m*, 2 H); 3.45 (*dd* app. as *t*, J = 9, H–C(5)); 3.79 (*s*, MeO); 3.80 (*s*, MeO); 3.81 (*dd* app. as *t*, J = 9.5, 1 H); 3.94 (*dd* app. as *t*, J = 9.5, 1 H); 4.19 (*dd* app. as *t*, J = 3.5, H–C(2)); 4.71–4.98 (*m*, 8 H); 6.84 (*d*, J = 7.5, 4 H, H–C(3′), H–C(5′) (4′-MeOC_6H_4)); 7.22–7.33 (*m*, 14 H). FAB-MS: 639 ([M + K]$^+$), 623 ([M + Na]$^+$). Anal. calc. for $C_{36}H_{40}O_8$ (600.71): C 71.98, H 6.71; found: C 71.81, H 6.76.

DL-*1*-O-*Allyl-3,6-di*-O-*benzyl-4,5-bis*-O-*(4-methoxybenzyl)*-myo-*inositol* (**35**). Diol **34** (1.20 g, 2.00 mmol) and dibutyltin oxide (0.53 g, 2.12 mmol) were dispersed in toluene (20 ml) and refluxed for ¾ h with removal of H_2O under a *Dean-Stark* separator (the originally insoluble Sn compound gradually dissolved). Toluene was then removed by distillation at 140° in a stream of Ar, and to the remaining clear syrup, a soln. of allyl bromide (0.28 ml, 3.33 mmol) in DMF (10 ml) was added. The mixture was held at 95° for 1½ h and then cooled. After addition of H_2O (25 ml) and extraction with Et_2O (25 ml × 2), the combined extracts were dried (Na_2SO_4) and evaporated. FC (*B* 15:1) yielded **35** as an oil which crystallised (0.74 g, 62%). A sample from selected fractions was recrystallised from EtOH. M.p. 90–92°. R_f (*B* 5:1, *a*) 0.22. IR (KBr): 3408*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.45 (*s*, OH); 3.28 (*dd*, J = 10, 2.5, H–C(3)); 3.39 (*dd*, J = 10, 2.5, H–C(1)); 3.41 (*dd* app. as *t*, J = 9.5, H–C(5)); 3.80 (*s*, 2 MeO); 3.92 (*dd*, J = 9.5, 7.5, 1 H); 3.96 (*dd*, J = 9.5, 7.5, 1 H); 4.17 (*dt*, J = 6, 2, CH_2CH=CH_2); 4.22 (*dd* app. as *t*, J = 2.7, H–C(2)); 4.70–4.85 (*m*, 8 H); 5.18 (*ddd*, J = 10.5, 2.5, 1.5, 1 H, CH_2CH=CH_2); 5.28 (*ddd*, J = 17, 2.5, 1.5, 1 H, CH_2CH=CH_2); 5.94 (*m*, CH_2CH=CH_2); 6.84 (*d*, J = 8, 4 H, H–C(3′), H–C(5′) (4′-MeOC_6H_4)); 7.21–7.36 (*m*, 14 H). FAB-MS: 679 ([M + K]$^+$), 663 ([M + Na]$^+$). Anal. calc. for $C_{39}H_{44}O_8$ (640.77): C 73.10, H 6.92; found: C 72.93, H 6.97.

DL-*1*-O-*Allyl-2,3,6-tri*-O-*benzyl-4,5-bis*-O-*(4-methoxybenzyl)*-myo-*inositol* (**36**). NaH (57% in oil, 0.078 g, 1.76 mmol) was added in portions to a soln. of **35** (0.74 g, 1.15 mmol) in DMF (2 ml). After frothing had subsided, benzyl bromide (0.208 ml, 1.75 mmol) was added dropwise and the mixture stirred at 40°, cooling to 25° over 2 h. MeOH (0.2 ml), H_2O (0.2 ml), and 1M HCl (0.15 ml) were added, and the mixture was evaporated, taken up in Et_2O (20 ml), filtered (*Dicalite*), and evaporated again affording 0.813 g of a yellow oil which crystallised on standing. Slurrying in hexane yielded 0.486 g of crystals, and further 0.032 g were obtained from the mother liquor. Total yield of **36**: 0.518 g (61.6%). A sample for analysis was obtained by recrystallisation from Et_2O/hexane. M.p. 69.5–71°. R_f (*B* 5:1, *a*) 0.58. IR (KBr): 3085*w* (CH_2=C); 1645*w* (C=C). ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.24 (*dd*, J = 10, 2.5, 1 H); 3.34 (*dd*, J = 10, 2.5, 1 H); 3.43 (*dd* app. as *t*, J = 9.5, H–C(5)); 3.786 (*s*, MeO); 3.793 (*s*, MeO); 4.01 (*dd* app. as *t*, J = 9.5, 1 H); 4.05 (*dd* app. as *t*, J = 9.5, 1 H); 4.09 (*m*, CH_2CH=CH_2); 4.59–4.93 (*m*, 10 H); 5.16 (*ddd*, J = 11, 2.5, 1.5, 1 H, CH_2CH=CH_2); 5.30 (*ddd*, J = 17, 2.5, 1.5, 1 H, CH_2CH=CH_2); 5.91 (*m*, CH_2CH=CH_2); 6.83–6.85 (*m*, 4 H, H–C(3′), H–C(5′) (4′-MeOC_6H_4)); 7.25–7.33 (*m*, 19 H). FAB-MS: 729 ± 1 (M^+), 609 ([M – MeOBn]$^+$). Anal. calc. for $C_{46}H_{50}O_8$ (730.90): C 75.59, H 6.90; found: C 75.19, H 7.08.

DL-*1,2,4-Tri*-O-*benzyl-5,6-bis*-O-*(4-methoxybenzyl)-3*-O-*(prop-1-enyl)*-myo-*inositol* (**37**). Following the procedure described in [53], a soln. of **36** (0.427 g, 0.584 mmol) in dry DMSO (5 ml) was treated with *t*-BuOK (0.43 g) and stirred at 50° for 19 h. H_2O (30 ml) was then added and the mixture extracted with Et_2O (25 ml × 2). The aq. layer was saturated with NaCl and reextracted with Et_2O (25 ml × 2). The combined extracts were dried (Na_2SO_4) and evaporated yielding a yellow oil (0.47 g) which crystallised on adding Et_2O. After slurrying the crystalline

material with pentane/Et_2O 3:1, pale yellow crystals were collected by filtration. Recrystallisation from Et_2O/pentane afforded **37** (0.35 g, 82%). M.p. 90–93°. R_f (*B* 5:1, *a*) 0.52. IR (KBr): 1668*s* (C=C). ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.66 (*dd*, *J* = 6.8, 2, *Me*CH=CH); 3.38 (*dd*, *J* = 10, 2, 1 H); 3.44 (*dd* app. as *t*, *J* = 9.5, H–C(5)); 3.54 (*dd*, *J* = 10, 2, 1 H); 3.78 (*s*, MeO); 3.80 (*s*, MeO); 4.05 (*m*, H–C(2), H–C(4), H–C(6)); 4.44 (*dq* app. as *quint.*, *J* = 6.5, 6.5, MeC*H*=CH); 4.58–4.88 (*m*, 10 H); 6.10 (*m* app. as *dd*, *J* = 6, 1, MeCH=C*H*); 6.80–6.86 (*m*, 4 H, H–C(3′), H–C(5′) (4′-$MeOC_6H_4$)); 7.19–7.32 (*m*, 19 H). FAB-MS: 769 ($[M + K]^+$), 753 ($[M + Na]^+$). Anal. calc. for $C_{46}H_{50}O_8$ (730.90): C 75.59, H 6.90; found: C 75.47, H 7.03.

DL-*1,2,4-Tri*-O-*benzyl-5,6-bis*-O-*(4-methoxybenzyl)*-myo-*inositol* (**38**). To a soln. of **37** (0.29 g, 0.40 mmol) in toluene/EtOH 1:2 (4.5 ml), 1M aq. HCl (0.5 ml) was added (→cloudy soln.). The mixture was stirred at 23° and became homogeneous after 2 h. After a further 6½ h, only a trace of **37** appeared to be present (TLC). The mixture was neutralised with $NaHCO_3$ (0.2 g) and stirred for a further 16 h, filtered, and evaporated. The residue was taken up in Et_2O, the filter was washed with Et_2O, and the combined soln. dried (Na_2SO_4), filtered, and evaporated: 0.281 g of a yellow oil. Crystallisation was induced by adding EtOH and cooling: impure (TLC) crystals. The whole product was, therefore, purified by FC (*B* 15:1 to 5:1): **38** as colourless crystals (0.23 g, 83%). An anal. pure sample was obtained from selected fractions. M.p. 60.5–62.5°. R_f (*B* 5:1, *a*) 0.32. IR (KBr): 3568*m*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.20 (*d*, *J* = 6, OH–C(3)); 3.45 (*m*, H–C(1), H–C(3), H–C(5)); 3.79 (*s*, 2 MeO); 3.79 (*dd* app. as *t*, *J* = 9.5, 1 H); 4.02 (*m*, H–C(2)); 4.03 (*dd* app. as *t*, *J* = 10, 1 H); 4.65–5.01 (*m*, 10 H); 6.82 (*d*, *J* = 8, 2 H, H–C(3′), H–C(5′) (4′-$MeOC_6H_4$)); 6.84 (*d*, *J* = 8, 2 H, H–C(3′), H–C(5′) (4′-$MeOC_6H_4$)); 7.22–7.33 (*m*, 19 H). FAB-MS: 729 ($[M + K]^+$), 713 ($[M + Na]^+$). Anal. calc. for $C_{43}H_{46}O_8$ (690.83): C 74.76, H 6.71; found: C 74.63, H 6.90.

DL-*2,3,6-Tri*-O-*benzyl-2,3,5/4,6-pentahydroxy-4,5-bis*-O-*(4-methoxybenzyl)cyclohexanone* (**39**). To a soln. of **38** (0.15 g, 0.22 mmol) in CH_2Cl_2 (4 ml) was added pyridinium chlorochromate (0.10 g, 0.46 mmol) in CH_2Cl_2 (2 ml). The mixture was stirred for 19 h at 25° and then evaporated at < 25° and the sticky black residue extracted with Et_2O and AcOEt. The soln. was evaporated and chromatographed (*B* 15:1) affording a colourless oil (0.104 g) which could be crystallised from Et_2O: **39** (0.089 g, 59%). Colourless crystals. M.p. 105–106°.

When the synthesis of **39** was repeated, starting from **35** but without purifying the intermediates **36**–**38**, 8.03 g (49% on **35**) of **39** were obtained. M.p. 105–106°. R_f (*B* 5:1, *a*) 0.47. ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.42 (*dd*, *J* = 9.5, 2.5); 3.47 (*dd* app. as *t*, *J* = 9.5, H–C(5)); 3.80 (*s*, 2 MeO); 3.96 (*d*, *J* = 2.5, H–C(2)); 4.25 (*dd* app. as *t*, *J* = 9, H–C(4)); 4.66 (*d*, *J* = 9.5, H–C(6)); 4.41–4.83 (*m*, 10 H); 6.84 (*d*, *J* = 8.6, H–C(3′), H–C(5′) (4′-$MeOC_6H_4$)); 7.21–7.34 (*m*, 19 H). ^{13}C-NMR ((D_6)DMSO, 62.9 MHz): 55.28 (*q*, MeO); 72.74 (*t*); 72.91 (*t*); 73.49 (*t*); 75.62 (*t*); 75.74 (*t*); 79.34 (*d*); 80.70 (*d*); 81.35 (*d*); 81.79 (*d*); 83.28 (*d*); 113.77 (*d*); 113.79 (*d*); 127.81–129.78 (overlapping *d*, Ar); 130.48 (*s*); 130.76 (*s*); 137.50 (*s*); 137.48 (*s*); 137.66 (*s*); 159.22 (*s*); 159.29 (*s*); 205.99 (*s*, C=O). FAB-MS: 711 ($[M + Na]^+$). Anal. calc. for $C_{43}H_{44}O_8$ (688.82): C 74.98, H 6.44; found: C 74.82, H 6.79.

DL-*1,2,5-Tri*-O-*benzyl-3,4-bis*-O-*(4-methoxybenzyl)-6-methylidenecyclohexane-1,2,4/3,5-pentol* (**40**). $Me(Ph_3)PBr$ (3.55 g, 10.0 mmol) was suspended in dry THF (10 ml), stirred under Ar, and cooled to 0°. BuLi (1.6M in hexane; 6.25 ml, 10.0 mmol) was added, followed by a soln. of **39** (3.45 g, 5.0 mmol) in THF (5 ml). The temp. of the mixture was kept at 0–6° during these additions. The cloudy orange suspension obtained was allowed to warm to 22° over the next 22 min and was then poured on to 30 g of ice. The mixture was extracted with toluene (50 ml × 2), and the extracts were dried (Na_2SO_4) and evaporated: yellow oil (5.3 g). Chromatography (toluene, *B* 1:15 to 1:10) afforded 3.27 g (95%) of **40** as a clear, colourless oil which slowly crystallised. R_f (*B* 5:1, *a*) 0.60. IR (film): 3095*w* (C=CH_2), 1655*w* (C=C). ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.36 (*dd* app. as *t*, *J* = 9, H–C(4)); 3.37 (*dd*, *J* = 9.5, 3.5, H–C(2)); 3.79 (*s*, MeO); 3.80 (*s*, MeO); 4.07 (*d*, *J* = 3.5, H–C(1)); 4.08 (*dd* app. as *t*, *J* = 10, H–C(3)); 4.23 (*dt*, *J* = 9.5, 1.5, H–C(5)); 4.25–4.90 (*m*, 10 H); 5.02 (*t*, *J* = 1.5, 1 H, CH_2=C(6)); 5.42 (*t*, *J* = 1.5, 1 H, CH_2=C(6)); 6.82–6.86 (*m*, 4 H, H–C(3′), H–C(5′) (4′-$MeOC_6H_4$)); 7.23–7.36 (*m*, 19 H). TS-MS: 704 ($[M + NH_4]^+$). Anal. calc. for $C_{44}H_{46}O_7$ (686.85): C 76.94, H 6.75; found: C 77.09, H 6.95.

DL-*(1,2,4/3,5,6)-2,5,6-Tri*-O-*benzyl-2,3,4,5,6-pentahydroxy-3,4-bis*-O-*(4-methoxybenzyl)cyclohexane-1-methanol* (**41a**), DL-*(1,2,3,5/4,6)-2,3,6-Tri*-O-*benzyl-2,3,4,5,6-pentahydroxy-4,5-bis*-O-*(4-methoxybenzyl)cyclohexane-1-methanol* (**41b**), DL-*2,3-Di*-O-*benzyl-1-deoxy-4,5-bis*-O-*(4-methoxybenzyl)-1-methyl*-myo-*inositol* (**42**), *and* DL-*2,5-Di*-O-*benzyl-1-deoxy-3,4-bis*-O-*(4-methoxybenzyl)-1-methyl*-scyllo-*inositol* (**43**). A soln. of **40** (3.67 g, 5.34 mmol) in toluene (100 ml) was distilled at atmospheric pressure until 63 ml of toluene and traces of moisture had been removed. After cooling to 25° under a stream of Ar, $BH_3 \cdot SMe_2$ (10M; 1.20 ml, 120 mmol) was added dropwise by syringe. The mixture warmed up slightly to 29° and was allowed to react without external heating for 1 h. A sample of the mixture (5 drops) to which were added succesively 3 drops each of 92% EtOH, 5M NaOH, and 30% H_2O_2, showed (TLC) that unreacted **40** remained and two major products had been formed. The bulk of the mixture was then heated to 68° and held for 30 min when a sample showed (by the same method) that only a trace of **40** remained. After cooling to r.t., 92% EtOH (20 ml) was added, with further cooling to < 10°, followed by 5M NaOH (10 ml, 50 mmol) and 30% H_2O_2 (5 ml, 44 mmol) at 0–10°. The mixture was finally heated to 75° for 5 min

and cooled, and the phases were separated. The aq. phase was extracted with toluene (25 ml), and the combined org. solns. were washed with 2N HCl (25 ml) and sat. $NaHCO_3$ soln. (25 ml) and then dried and evaporated to give a slightly turbid oil (3.89 g). MPLC (*F* 5:1 to 1:1) yielded 2.04 g (54%) of **41a**/**41b** as an oil, 0.88 g (27%) of **42**, and 0.12 g (3.8%) of **43**, the latter two as colourless crystalline substances. **41a**/**41b** was used in the next reaction without further purification.

Data of **41a**/**41b**: R_f (*B* 5:1, *a*) 0.22. IR (film): 3452*m*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.6–2.7 (*m*); 3.792, 3.797, 3.804 (3*s*, showing product to be a mixture, 6 H, 2 MeO); 3.3–4.2 (*m*); 4.4–5.1 (*m*, 5 ArCH_2); 6.8–6.9 (*m*, 4 arom. H); 7.24–7.35 (*m*, 19 H). TS-MS: 722 ($[M + NH_4]^+$). Anal. calc. for $C_{44}H_{48}O_8$ (704.86): C 74.98, H 6.86; found: C 74.67, H 6.93.

Data of **42**: M.p. 93.5–94°. R_f (*B* 5:1, *a*) 0.30. IR (KBr): 3427*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.09 (*d*, *J* = 6.8, Me–C(1)); 1.49 (*m*, $\Sigma J \approx 20$, H–C(1)); 2.17 (*d*, *J* = 3, OH–C(6)); 3.26 (*dd* app. as *t*, *J* = 9.5, H–C((5)); 3.50 (*dd*, *J* = 9.5, 2, H–C((3)); 3.58 (*ddd*, *J* = 10, 9.5, 3, H–C((6)); 3.74 (*dd* app. as *t*, *J* = 2, H–C(2)); 3.788 (*s*, MeO); 3.793 (*s*, MeO); 4.02 (*dd*, app. as *t*, *J* = 9.5, H–C(4)); 4.54–5.05 (*m*, 8 H); 6.80–6.89 (*m*, 4 H, H–C(3′), H–C(5′) (4′-$MeOC_6H_4$)); 7.23–7.37 (*m*, 14 H). TS-MS: 616 ($[M + NH_4]^+$). Anal. calc. for $C_{37}H_{42}O_7$ (598.74): C 74.22, H 7.07; found: C 74.03, H 7.05.

Data of **43**: M.p. 149–151°. R_f (*B* 5:1, *a*) 0.35. IR (KBr): 3334*m*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.15 (*d*, *J* = 6.4, Me–C(1)); 1.63 (*m*, H–C(1)); 2.32 (*s*, exchange with D_2O, OH–C(6)); 3.06 (*dd* app. as *t*, *J* = 9, H–C(6)); 3.12 (*m*, H–C(2)); 3.33 (*dd* app. as *t*, *J* = 9, H–C(4)); 3.51 (*dd* app. as *t*, *J* = 9.5, 1 H); 3.59 (*dd* app. as *t*, *J* = 9.5, 1 H); 3.79 (*s*, 2 MeO); 4.59–5.03 (*m*, 8 H); 6.84 (*d*, *J* = 8.6, 4 H, H–C(3′), H–C(5′) (4′-$MeOC_6H_4$)); 7.22–7.36 (*m*, 14 H). TS-MS: 616 ($[M + NH_4]^+$). Anal. calc. for $C_{37}H_{42}O_7$ (598.74): C 74.22, H 7.07; found: C 74.20, H 7.09.

*[*DL*-(1,2,4/3,5,6)-2,5,6-Tri-*O*-benzyl-2,3,4,5,6-pentahydroxy-3,4-bis*O*-(4-methoxybenzyl)cyclohexyl]methyl Hexadecanoate* (**44a**) *and [*DL*-(1,2,3,5/4,6)-2,3,6-Tri-*O*-benzyl-2,3,4,5,6-pentahydroxy-4,5-bis-*O*-(4-methoxybenzyl)cyclohexyl]methyl Hexadecanoate* (**44b**). To a soln. of **41a**/**41b** (0.352 g, 0.50 mmol) in CH_2Cl_2 (5 ml) was added successively, DMAP (0.003 g, 0.02 mmol), pyridine (0.20 g, 2.5 mmol), and palmitoyl chloride (0.20 g, 0.75 mmol). The mixture was stirred at r.t. for 1 h, evaporated, taken up in toluene and chromatographed (*B* 15:1) to give 0.45 g (95%) of **44a**/**44b** as a colourless oil. Anal. calc. for $C_{60}H_{78}O_9$ (943.28): C 76.40, H 8.34; found: C 76.38, H 8.62.

A similar preparation on a larger scale (2 mmol) afforded 1.93 g (99%) of **44a**/**44b**. In this case, a sample of **44b** could be isolated from the last fractions eluted during FC (*F* 20:1 to 5:1). It was crystallised from EtOH.

Data of **44b**: M.p. 69–70°. R_f (*E* 2:1, *a*) 0.20 (R_f (**44a**) 0.25). IR (nujol): 4000–3000 no absorptions (OH absent); 1738*s* (ester C=O). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.878 (*t*, *J* = 6.5, 3 H); 1.24 (*m*, 24 H); 1.56 (*m*, 2 H); 1.85 (*m* app. as br. *t*, *J* = 10, H–C(1)); 2.19 (*t*, 2 H); 3.47 (*dd*, *J* = 10, 2, H–C(3)); 3.55 (*dd* app. as *t*, *J* = 9.5, H–C(5)); 3.68 (*dd*, *J* = 10, 9.5, H–C(6)); 3.79 (*s*, 2 MeO); 3.97 (*dd* app. as *t*, *J* = 1.5–2, H–C(2)); 4.05 (*dd* app. as *t*, *J* = 9.5, H–C(4)); 4.09 (*dd* app. as *t*, *J* = 10.5, 1 H, CH_2–C(1)); 4.35 (*dd*, *J* = 10.5, 4, 1 H, CH_2–C(1)); 4.48–5.03 (*m*, 10 H); 6.59–6.65 (*m*, 4 H, H–C(3′), H–C(5′) (4′-$MeOC_6H_4$)); 7.20–7.37 (*m*, 19 H). Anal. calc. for $C_{60}H_{78}O_9$ (943.28): C 76.40, H 8.34; found: C 76.15, H 8.51.

*[*DL*-(1,2,4/3,5,6)-2,5,6-Tri-*O*-benzyl-2,3,4,5,6-pentahydroxycyclohexyl]methyl Hexadecanoate* (**45a**) *and [*DL*-(1,2,3,5/4,6)-2,3,6-Tri-*O*-benzyl-2,3,4,5,6-pentahydroxycyclohexyl]methyl Hexadecanoate* (**45b**). To a soln. of **44a**/**44b** (1.89 g, 2.00 mmol) in CH_2Cl_2 (20 ml) 1.1 ml of H_2O were added [54] followed by DDQ (1.09 g, 4.8 mmol). The stirred mixture immediately became dark green, changing to brown after 2–3 min. After 1½ h, the mixture (now reddish) was chromatographed on Al_2O_3 (neutral, act. I) eluting successively with CH_2Cl_2, AcOEt, *C* 1:1, and MeOH. In this way, *p*-anisaldehyde and some of the excess DDQ was removed. Final traces of DDQ were removed with activated charcoal. From the resulting mixture, MPLC (*E* 1:1 to 1:2) yielded **45a** (0.628 g, 45%) as a colourless oil and **45b** (0.298 g, 21%) as a colourless oil which later crystallised.

Data of **45a**: R_f (*B* 1:1, *a*) 0.53. IR: 3428*s*, 1736*s*. ^{1}H-NMR ((D_6)DMSO, 250 MHz): 0.848 (*t*, *J* = 6.5, 3 H); 1.20 (*m*, 24 H); 1.45 (*m*, 2 H); 2.19 (*t*, *J* = 7.5, 2 H); 2.60 (*m*, H–C(1)); 3.36 (*ddd*, *dd* app. as *t* with D_2O, *J* = 9, 4.5, H–C(3)); 3.45 (*dd*, *J* = 10, 2.5, H–C(5)); 3.57 (*dd*, *J* = 10, 2.5, H–C(2)); 3.57 (*ddd*, overlapping previous signal, altered with D_2O, but obscured by HOD signal, *J* = 9, 5.5, H–C(4)); 3.83 (*dd* app. as *t*, *J* = 2.7, H–C(6)); 3.93 (*dd* app. as *t*, *J* = 10.5, 1 H, CH_2–C(1)); 4.24 (*dd*, *J* = 12, 4.5, 1 H, CH_2–C(1)); 4.45–4.65 (*m*, 6 H); 4.92 (*d*, *J* = 5.3, exchange with D_2O, OH–C(4)); 4.96 (*d*, *J* = 4.8, exchange with D_2O, OH–C(3)); 7.29–7.34 (*m*, 15 H). TS-MS: 720 ($[M + NH_4]^+$). Anal. calc. for $C_{44}H_{62}O_7$ (702.97): C 75.18, H 8.89; found: C 74.89, H 8.94.

Data of **45b**: M.p. 47.5–48.2°. R_f (*B* 1:1, *a*) 0.62. IR: 3409*s*, 1738*s*. ^{1}H-NMR ((D_6)DMSO, 250 MHz): 0.844 (*t*, *J* = 6.6, 3 H); 1.11–1.30 (*m*, 24 H); 1.47 (*m*, 2 H); 1.88 (*dddd* app. as *tt*, $\Sigma J \approx 30$, H–C(1)); 2.22 (*t*, *J* = 7, 2 H); 3.28–3.36 (*m*, H–C(3), H–C(5), H–C(6)); 3.65 (*m*, with D_2O becomes *dd* app. as *t*, *J* = 9, H–C(4)); 3.95 (*dd* app. as *t*, *J* = 2, H–C(2)); 3.98 (*dd* app. as *t*, *J* = 11, 1 H, CH_2–C(1)); 4.25 (*dd*, *J* = 11, 4, 1 H, CH_2–C(1)); 4.43–4.92 (*m*, 6 H); 5.03 (*d*, *J* = 5, exchange with D_2O, OH–C(?)); 5.10 (*d*, *J* = 4.5, exchange with D_2O, OH–C(?)); 7.27–7.41 (*m*,

15 H). TS-MS: 720 ($[M + NH_4]^+$). Anal. calc. for $C_{44}H_{62}O_7$ (702.97): C 75.18, H 8.89; found: C 75.09, H 9.04.

[DL-(1,2,4/3,5,6)-2,5,6-Tri-O-benzyl-2,3,4,5,6-pentahydroxycyclohexyl]methyl Hexadecanoate 3,4-Bis(sodium sulfate) (**46**). To a soln. of **45a** (0.268 g, 0.381 mmol) in dry DMF (4 ml) was added SO_3-pyridine complex (*ca.* 45% SO_3; 0.54 g, 3.0 mmol). The clear, brown soln. was allowed to stand for 18 h at 25°. $BaCO_3$ (2.0 g) slurried in H_2O (25 ml) was then added to neutralise the excess sulfating reagent, and the mixture was heated at 50° with stirring for 1 h. The mixture was filtered (*Speedex*) and the filter cake extracted with warm AcOEt (25 ml × 4). After evaporation (45°/35 mbar), the residue (0.15 g) was taken up in EtOH/H_2O and Na_2SO_4 (0.025 g in H_2O) added (pH *ca.* 5) and then 5% NaOH soln. which raised the pH to *ca.* 9. The soln. was filtered to remove the precipitated $BaSO_4$ and the filtrate concentrated and then subjected to FC (*G* 24:7:1) which yielded **46** (0.090 g, 26%) as a resinous solid used directly in the next step without characterisation. R_f (*C* 3:1, *a*) 0.52 (1 spot).

[DL-(1,2,4/3,5,6)-2,3,4,5,6-Pentahydroxycyclohexyl]methyl Hexadecanoate 3,4-Bis(sodium sulfate) (**47**). To a soln. of **46** (0.090 g, 0.10 mmol) in EtOH/H_2O 1:1 (10 ml) was added 5% Pd/C (0.10 g), and the mixture was agitated with H_2 for 5 h at 1 atm. The catalyst was removed by filtration, extracted with further EtOH (2 ml × 5), and the combined filtrates were evaporated to yield a resinous solid. This was dispersed in EtOH (2.5 g), and H_2O was added to the boiling mixture until a clear soln. was just obtained (0.1 g H_2O needed). On cooling overnight, **47** separated as glistening plate-like crystals (0.018 g). Further 0.014 g were obtained from the mother liquor. Total yield 0.032 g (50%). M.p. 210° (dec.). R_f (*I*, *a*) 0.48 (1 spot). IR (KBr): 3566*s*, 3473*s*, 3319*s*, 1753*s*, 1218*s*. ^{1}H-NMR ((D$_6$)DMSO, 400 MHz; H,H COSY): 0.854 (*t*, *J* = 6.8, 3 H); 1.24 (*m*, 24 H); 1.51 (*m*, 2 H); 2.26 (*dddd*, *J* = 9, 5.5, 5.5, 5.5, H–C(1)); 2.29 (*t*, 2 H); 3.72 (*ddd*, *J* = 8, 3.5, 2, H–C(5)); 3.77 (*ddd* app. as *dt*, *J* = 4, 4, H–C(6)); 3.99 (*ddd*, *J* = 9, 5, 2.2, H–C(2)); 4.02 (*dd*, *J* = 11, 9, 1 H, CH_2–C(1)); 4.12 (*dd* app. as *t*, *J* = 7.8, H–C(3)); 4.21 (*dd*, *J* = 11.2, 5.6, 1 H, CH_2–C(1)); 4.29 (*dd* app. as *t*, *J* = 7.7, H–C(4)); 4.74 (*d*, *J* = 4, OH–C(6)); 5.20 (*s*, OH–C(2), OH–C(5)). ^{13}C-NMR ((D$_6$)DMSO, 100.62 MHz; C,H COSY): 13.87 (Me_3); 22.00–28.96 (12 overlapping signals, palmitate CH_2); 31.20 (palmitate CH_2); 33.42 (palmitate CH_2); 60.99 (CH_2–C(1)); 68.35 (C(2)); 70.67 (C(5)); 77.10 (C(4)); 173 (C=O); other signals (C(1), C(3), C(6)) were not discernible. Anal. calc. for $C_{23}H_{42}Na_2O_{13}S_2$ (636.68): C 43.39, H 6.65, S 10.07; found: C 42.51, H 7.00, S 7.39.

[DL-(1,2,4/3,5,6)-2,5,6-Tri-O-benzyl-2,3,4,5,6-pentahydroxycyclohexyl]methyl Hexadecanoate 3,4-Bis(dibenzyl phosphate) (**48**). To a soln. of **45a** (0.176 g, 0.25 mmol) in dry CH_2Cl_2 (5 ml), 1*H*-tetrazole (0.105 g, 1.50 mmol) was added, followed by a soln. of bis(benzyloxy)(diisopropylamino)phosphine (0.259 g, 0.750 mmol) in CH_2Cl_2 (2 ml) [43]. After stirring at 25° for 35 min, all tetrazole had dissolved and TLC showed that **45a** was absent. Reaction was continued at 25° for further 2 h, the soln. cooled to −40°, and then 3-chloroperbenzoic acid (70%; 0.247 g, 1.0 mmol) in CH_2Cl_2 (4 ml) added slowly. The mixture was allowed to warm and remain at r.t. over 1½ h. After evaporation, the mixture was chromatographed on a column slurry-loaded consecutively with 50 g each of Al_2O_3 (neutral, act. I) and SiO_2 (60–200 μm) in *A* 10:1. Elution with *A* 10:1 to 1:1 yielded 0.205 g (67%) of **48** as a colourless oil. Pure by TLC. R_f (*A* 5:1, *b*) 0.64. IR: 1736*s*, 1281*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.878 (*t*, *J* = 6.5, 3 H); 1.23–1.25 (*m*, 24 H); 1.50 (*m*, 2 H); 2.09 (*t*, *J* = 7, 2 H); 2.63 (*m*, H–C(1)); 3.77 (*dd*, *J* = 7, 4, 1 H); 3.87 (*m*, 1 H); 3.98 (*dd*, *J* = 6.5, 4.5, 1 H); 4.21 (*dm*, CH_2–C(1)); 4.24–4.62 (*m*, 6 H); 4.75 (*m*, 1 H); 4.86 (*dd* app. as *t*, *J* = 2, H–C(6)); 4.88–5.05 (*m*, 8 H); 7.24–7.26 (*m*, 35 H). Anal. calc. for $C_{72}H_{88}O_{13}P_2$ (1223.43): C 70.69, H 7.25, P 5.06; found: C 69.90, H 7.47, P 4.87.

[DL-(1,2,4/3,5,6)-2,3,4,5,6-Pentahydroxycyclohexyl]methyl Hexadecanoate 3,4-Bis(dihydrogen phosphate) Trimethylammonium Salt (1:1.6; **49**). A soln. of **48** (0.177 g, 0.144 mmol) in EtOH (10 ml) was agitated with H_2 at 1 atm in the presence of 5% Pd/C (0.15 g) for 2 h at 25°. After removing the catalyst by filtration, Me_3N (33% in EtOH; 0.20 g, 1.15 mmol) was added, and volatile materials were removed by evaporation (35°/0.5 mbar), leaving a residue of 0.90 g. This was extracted with boiling Et_2O (4 ml × 3) to remove some impurities and the residue dissolved in hot EtOH (1.5 ml). Et_2O (7 ml) was added, and the precipitated, very hygroscopic product was removed by filtration. The filtrate was evaporated and the precipitation procedure repeated: total 0.081 g of **49** as a colourless solid, containing *ca.* 1.6 mol of Me_3N (by ^{1}H-NMR) and, thus, corresponding to 82% yield. R_f (*I*, *d*) 0.00. IR (KBr): 3428*s*, 1734*s*. ^{1}H-NMR ((D$_6$)DMSO, 400 MHz; COSY): 0.854 (*t*, *J* = 6.8, 3 H); 1.24 (*m*, 24 H); 1.51 (*m*, 2 H); 2.23 (*m*, H–C(1)); 2.29 (*t*, *J* = 7.4, 2 H); 2.65 (*s*, *ca.* 14 H, Me_3N); 3.60 (*dd*, *J* = 9.5, 3, H–C(5)); 3.79 (*dd* app. as *t*, *J* = 3, H–C(6)); 3.88–3.95 (*m*, H–C(2), H–C(3), 1 H of CH_2–C(1)); 4.09 (*m*, H–C(4)); 4.27 (*dd*, 1 H, CH_2–C(1)). ^{31}P-NMR ((D$_6$)DMSO, 202.5 MHz): 2.35 (*d*, *J* (P, H) = 7.5, 1 P); 2.89 (*d*, *J* (P, H) = 10.3, 1 P). Anal. calc. for $C_{23}H_{46}O_{13}P_2 \cdot 1.55\ C_3H_9N$ (682.979): C 48.45, H 8.84, N 3.18, P 9.07; found: C 48.14, H 8.95, N 3.30, P 8.83.

[DL-(1,2,3,5/4,6)-2,3,6-Tri-O-benzyl-2,3,4,5,6-pentahydroxycyclohexyl]methyl Hexadecanoate 4,5-Bis(sodium sulfate) (**50**). Sulfation of **45b** (0.176 g, 0.25 mmol) was carried out in the manner described above (prep. of **46**). After 20 h, the clear, brown mixture was added to a soln. of Na_2CO_3 (3.6 g in 20 ml H_2O) and mixed thoroughly. Extraction with Et_2O (25 ml × 6), evaporation of the extracts and FC (*C* 10:1) yielded a resinous solid

(0.231 g) which still contained a faster-running impurity by TLC (*G* 24:7:1, *b*). It was, therefore, rechromatographed (*C* 19:1 to 10:1) affording 0.220 g of a resinous product which crystallised upon adding AcOEt. The crystalline product was collected by filtration, and a second amount was obtained from the mother liquor. Total yield of **50**: 0.148 g (65%). M.p. 185° (dec.). R_f (*H*, *b*) 0.48. IR (KBr): 1739*s*, 1211*s*. ^{1}H-NMR ((D$_6$)DMSO, 400 MHz; COSY): 0.849 (*t*, *J* = 6.8, 3 H); 1.22 (*m*, 24 H); 1.44 (*m*, 2 H); 2.15 (*t*, *J* = 7.4, 2 H); 2.28 (*dddd*, $\Sigma J \approx 23$, H–C(1)); 3.96 (*dd* app. as *t*, *J* = 4, H–C(6)); 4.00 (*dd*, *J* = 4, 3, H–C(2)); 4.08 (*dd* app. as *t*, *J* = 4, H–C(3)); 4.27 (*dd*, *J* = 11, 9, 1 H, CH$_2$–C(1)); 4.38 (*dd*, *J* = 11, 5, 1 H, CH$_2$–C(1)); 4.38 (*d*, J_{gem} = 12, 1 H, PhC*H*$_2$); 4.45 (*d*, J_{gem} = 12, 1 H, PhC*H*$_2$); 4.48 (*d*, J_{gem} = 11, 1 H, PhC*H*$_2$); 4.53 (*d*, J_{gem} = 12, 1 H, PhC*H*$_2$); 4.57 (*dd* app. as *t*, *J* = 4, H–C(5)); 4.75 (*d*, J_{gem} = 12, 1 H, PhC*H*$_2$); 4.79 (*d*, J_{gem} = 12, 1 H, PhC*H*$_2$); 4.82 (*dd* app. as *t*, *J* = 4, H–C(4)); 7.20–7.43 (*m*, 15 H). Anal. calc. for $C_{44}H_{60}Na_2O_{13}S_2$ (907.05): C 58.26, H 6.67, S 7.07; found: C 58.02, H 7.32, S 7.08.

*[*DL*-(1,2,3,5/4,6)-2,3,4,5,6-Pentahydroxycyclohexyl]methyl Hexadecanoate 4,5-Bis(sodium sulfate)* (**51**). Hydrogenolysis and workup of **50** (0.082 g, 0.090 mmol) as described for **47** yielded **51** as microscopic crystals (0.021 g, 36%). M.p. 270–300° (dec. without melting). IR (nujol): 3614*w*, 3554*w*, 3468*w*, 3282*s*, 1719*s*, 1223*s*. ^{1}H-NMR ((D$_6$)DMSO, 400 MHz; COSY): 0.854 (*t*, *J* = 6.7, 3 H); 1.24 (*m*, 24 H); 1.51 (*m*, 2 H); 1.67 (*m*, ΣJ = 27, H–C(1)); 2.27 (*t*, *J* = 7.4, 2 H); 3.40 (*dd*, *J* = 10, 2.5, H–C(3)); 3.52 (*dd*, *J* = 11, 9, H–C(6)); 3.72 (*m*, *J*(2, OH) ≈ 3, H–C(2)); 3.92 (*dd* app. as *t*, *J* = 9, H–C(5)); 3.99 (*dd* app. as *t*, *J* = 10, 1 H, CH$_2$–C(1)); 4.22 (*dd* app. as *t*, *J* = 10, H–C(4)); 4.30 (*dd*, *J* = 10, 4, 1 H, CH$_2$–C(1)); 4.76 (*d*, *J* = 3.6, OH–C(2)); 5.85 (*s*, OH–C(6)); 5.90 (OH–C(3)).

*[*DL*-(1,2,3,5/4,6)-2,3,6-Tri-*O*-benzyl-2,3,4,5,6-pentahydroxcyclohexyl]methyl Hexadecanoate 4,5-Bis(dibenzyl phosphate)* (**52**). Phosphorylation of **45b** (0.101 g, 0.144 mmol) was carried out as described above for **48**, but with different workup. Thus, after treatment with 3-chloroperbenzoic acid, the mixture in CH_2Cl_2 was washed consecutively with 10% Na_2SO_3 (10 ml × 2), 8% $NaHCO_3$ (10 ml × 2), and sat. NaCl soln. (20 ml) and H_2O (20 ml), the aq. phases being washed each time with CH_2Cl_2 (2–3 ml). The combined org. phase was evaporated and the residue chromatographed (Al_2O_3 (neutral, act. 1, 10 g)/SiO_2 (40–63 μm, 10 g), CH_2Cl_2, *A* 20:1 to 3:1) affording **52** (0.141 g, 80%) as a colourless oil. R_f (*A* 5:1, *b*) 0.44. IR: 1737*s*, 1271*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz; COSY): 0.878 (*t*, *J* = 6.8, 3 H); 1.24 (*m*, 24 H); 1.52 (*m*, 2 H); 1.92 (*m*, ΣJ = 27.5, H–C(1)); 2.13 (*t*, *J* = 7.5, 2 H); 3.51 (*dd*, *J* = 9.5, 2.5, H–C(3)); 3.76 (*dd*, *J* = 11, 10, H–C(6)); 3.89 (*dd* app. as *t*, *J* = 2.5, H–C(2)); 3.95 (*dd* app. as *t*, *J* = 10, 1 H, CH$_2$–C(1)); 4.26 (*dd*, *J* = 11, 4, 1 H, CH$_2$–C(1)); 4.42–4.76 (*m*, 5 H, PhC*H*$_2$); 4.64 (*ddd* app. as *dd*, *J* = 10.5, 8, H–C(5)); 4.8–5.1 (*m*, 9 H, PhC*H*$_2$); 5.00 (*ddd*, *J* = 11, 9.5, 8, H–C(4)); 7.4–7.4 (*m*, 35 H).

*[*DL*-(1,2,3,5/4,6)-2,3,4,5,6-Phentahydroxycyclohexyl]methyl Hexadecanoate 4,5-Bis(dihydrogen phosphate) Trimethylammonium Salt* (1:1.6; **53**). Hydrogenolysis and workup of **52** (0.188 g, 0.097 mmol) as described for **49** yielded **53** as a hygroscopic, colourless solid (0.032 g, 48%). R_f (*I*, *d*) 0.00. IR (nujol): 1737*s*. ^{1}H-NMR ((D$_6$)DMSO, 400 MHz; COSY): 0.854 (*t*, *J* = 6.7, 3 H); 1.24 (*m*, 24 H); 1.51 (*m*, 2 H); 1.64 (*m*, ΣJ = 27, H–C(1)); 2.27 (*t*, *J* = 7.4, 2 H); 2.68 (*s*, 14.4 H, Me$_3$N); 3.35 (*dd*, *J* = 9.5, 2.5, H–C(3)); 3.47 (*dd* app. as *t*, *J* = 9.8, H–C(6)); 3.74 (*dd* app. as *s*, H–C(2)); 3.82 (*ddd* app. as *q*, *J* = 9.3, H–C(5)); 3.99 (*dd* app. as *t*, *J* = 10.5, 1 H, CH$_2$–C(1)); 4.13 (*ddd* app. as *q*, *J* = 9.5, H–C(4)); 4.29 (*dd*, *J* = 10.5, 3.5, 1 H, CH$_2$–C(1)). ^{31}P-NMR ((D$_6$)DMSO, 202.5 MHz): 2.5 (*d*, *J* (P, H) = 10, 1 P); 3.2 (*d*, *J* (P, H) = 10, 1 P). Anal. calc. for $C_{23}H_{46}O_{13}P_2 \cdot 1.6\ C_3H_9N$ (687.14): C 48.59, H 8.86, N 3.26, P 9.02; found: C 47.76, H 9.26, N 3.29, P 8.80.

DL*-2,3,6-Tri-*O*-benzyl-4,5-bis-*O*-(4-methoxybenzyl)*-myo*-*inositol* 1-Hexadecanoate* (**54**). Alcohol **38** (1.38 g, 2.0 mmol) in CH_2Cl_2 (15 ml) and pyridine (1.0 ml) was esterified with palmitoyl chloride (0.73 ml, 2.4 mmol), catalysed by DMAP (0.015 g), at r.t. for 17 h. Neutralisation with 1N HCl (40 ml), washing with sat. $NaHCO_3$ soln., then H_2O and drying the org. phase (Na_2SO_4) yielded, after evaporation, crude **54** (2.05 g) as an oil which crystallised. Recrystallisation from EtOH afforded pure product (1.69 g, 91%). M.p. 69–70°. R_f (*B* 5:1, *a*) 0.64. IR (KBr): 1733*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.889 (*t*, *J* = 6.8, 3 H); 1.24 (*m*, 24 H); 1.53 (*m*, 2 H); 2.17 (*t*, *J* = 7.5, 2 H); 3.52 (*dd*, *J* = 9, 2, H–C(3)); 3.786 (*s*, MeO); 3.788 (*s*, MeO); 4.05 (*dd* app. as *t*, *J* = 10, 1 H); 4.06 (*dd* app. as *t*, *J* = 10, 1 H); 4.10 (*dd* app. as *t*, *J* = 2, H–C(2)); 4.76 (*dd*, *J* = 10, 2, H–C(1)); 4.61–4.87 (*m*, 10 H); 6.82 (*d*, *J* = 7.8, 4 H, H–C(3′), H–C(5′) (4′-MeOC$_6$H$_4$)); 7.19–7.33 (*m*, 19 H). TS-MS: 951 ([*M* + Na]$^+$), 946 ([*M* + NH$_4$]$^+$). Anal. calc. for $C_{59}H_{76}O_9$ (929.25): C 76.26, H 8.24; found: C 75.95, H 8.40.

DL*-2,3,6-Tri-*O*-benzyl-*myo*-inositol* 1-Hexadecanoate* (**55**). As described for **45a**/**45b**, **54** (1.574 g, 1.69 mmol) was oxidised to the corresponding diol with DDQ, but using a 10% excess of this reagent and reacting for 1 h. With the smaller excess of DDQ, traces remaining after the reaction could be removed on a glass sinter filter (No. 4) containing a mixture of Al_2O_3 (neutral, act. I, 10 g) and Na_2SO_4 (10 g), being washed through with *A* 1:1 (25 ml × 3). Evaporation yielded an oil which was crystallised from pentane: 0.96 g (82%) of **55**. A sample for analysis was further purified by recrystallisation from MeOH. M.p. 80–85°. R_f (*B* 1:1, *a*) 0.50. IR (KBr): 3551*m*, 3399*m* (br.), 1734*s*. ^{1}H-NMR ((D$_6$)DMSO, 250 MHz): 0.847 (*t*, *J* = 6.5, 3 H); 1.20 (*m*, 24 H); 1.44 (*m*, 2 H); 2.20 (*t*, *J* = 7, 2 H); 3.30 (*ddd* app. as *dt*, *J* = 9.5, 5.5, H–C(5)); 3.39 (*dd*, *J* = 10, 2, H–C(3)); 3.66 (*ddd* app. as *dt*, *J* = 9.5, 5,

H–C(4)); 3.67 (*dd*, $J = 9.5$, H–C(6)); 4.04 (*dd* app. as *t*, $J = 2$, H–C(2)); 4.78 (*dd*, $J = 10, 2.5$, H–C(1)); 4.55–4.84 (*m*, 6 H); 5.08 (*d*, $J = 5.0$, OH–C(4)); 5.20 (*d*, $J = 5.5$, OH–C(5)); 7.28–7.39 (*m*, 15 H). TS-MS: 706 ($[M + NH_4]^+$), 689 ($[M + H]^+$). Anal. calc. for $C_{43}H_{60}O_7$ (688.95): C 74.97, H 8.78; found: C 74.74, H 8.83.

DL-*2,3,6-Tri*-O-*benzyl*-myo-*inositol 1-Hexadecanoate 4,5-Bis(½ barium sulfate)* (**56**). Diol **55** (0.345 g, 0.50 mmol) was sulfated for 14 h at 25° by the procedure described for **46**. After workup, FC (*C* 3:1) afforded **56** (0.16 g, 47%) as a resinous solid. R_f (*C* 3:1, *a*) 0.59 ('1 spot'). It was used directly in the next step of the synthesis.

DL-myo-*Inositol 1-Hexadecanoate 4,5-Bis(sodium sulfate)* (**57**). Hydrogenolysis of **56** (0.15 g, 0.21 mmol) for 2 h as described for **47** yielded, on evaporation of the filtered mixture, 0.07 g of a solid residue. It was dissolved in H_2O (2 ml) forming a turbid, frothy soln. to which was added *Dowex 50W* (H^+ form, 6.7 g). After stirring for 2 min, the ion-exchange resin was removed by filtration, washed with H_2O, and the combined filtrates were treated with 0.1N NaOH (1.57 ml) until pH *ca.* 8 (thymol blue). Upon evaporation, a residue of 0.07 g was obtained which was crystallised and recrystallised from H_2O/EtOH/BuOH 1:3:1 affording **57**, pure by TLC, as colourless, microscopic crystals (0.010 g, 8%). M.p. 223–227° (softens). R_f (*H*, *b*) 0.17. ^{1}H-NMR ((D_6)DMSO, 400 MHz): 0.854 (*t*, $J = 6.6$, 3 H); 1.24 (*m*, 24 H); 1.51 (*m*, 2 H); 2.28 (*t*, $J = 7.3$, 2 H); 3.49 (*dd*, $J = 9.8, 2.2$, H–C(3)); 3.73 (*m*, simplified to *dd* app. as *t* with D_2O at 3.75, $J = 2.4$, H–C(2)); 3.85 (*dd* app. as *t*, $J = 9.4$, 1 H); 3.93 (*dd* app. as *t*, $J = 9$, 1 H); 4.26 (*dd* app. as *t*, $J = 9.4$, H–C(4)); 4.54 (*dd*, $J = 10, 2.2$, H–C(1)); 5.04 (*d*, $J = 4$, exchange with D_2O, OH–C(2)); 5.83 (*s*, exchange with D_2O, OH); 5.88 (*s*, exchange with D_2O, OH). Anal. calc. for $C_{22}H_{40}Na_2O_{13}S_2 \cdot 1.5\ H_2O$ (649.67): C 40.67, H 6.67, S 9.87; found: C 40.76, H 6.52, S 9.50.

DL-*2,3,6-Tri*-O-*benzyl*-myo-*inositol 1-Hexadecanoate 4,5-Bis(dibenzyl phosphate)* (**58**). Diol **55** (0.209 g, 0.30 mmol) was phosphorylated by means of bis(benzyloxy)(diisopropylamino)phosphine followed by oxidation (3-chloroperbenzoic acid) as described for **52**. After chromatography on Al_2O_3 (neutral, act. I; *B* 1:1), an oil was obtained which was crystallised from Et_2O/pentane: 0.269 g (74%) of **58** as colourless crystals. M.p. 83–84.5°. R_f (*B* 1:1, *a*) 0.68. IR (KBr): 1731*s*, 1259*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.880 (*t*, $J = 6$, 3 H); 1.16–1.26 (*m*, 24 H); 1.43 (*m*, 2 H); 2.03 (*dt*, $^3J = 8$, $^4J = 2$, 2 H); 3.58 (*dd*, $J = 10$, 2, H–C(3)); 4.08 (*dd* app. as *t*, $J = 2$, H–C(2)); 4.16 (*dd* app. as *t*, $J = 10$, H–C(6), not P-coupled); 4.5–5.1 (*m*, 17 H, 7 ArCH_2, H–C(1), H–C(4), H–C(5)); 7.00–7.33 (*m*, 35 H). Anal. calc. for $C_{71}H_{86}O_{13}P_2$ (1209.40): C 70.51, H 7.17, P 5.12; found: C 70.63, H 7.35, P 4.99.

DL-myo-*Inositol 1-Hexadecanoate 4,5-Bis(dihydrogen phosphate) Trimethylammonium Salt* (1:2.5; **59**). For 2 h, **58** (0.302 g, 0.25 mmol) was hydrogenated as described above (prep. of **49**), filtered, evaporated (30°/1 mbar), extracted with Et_2O, dissolved in CH_2Cl_2/EtOH and precipitated with Et_2O affording 0.116 g (64%) of **59** as colourless, hygroscopic solid. A sample dried at 100° underwent partial decomposition (^{1}H-NMR). A sample dried at 50°/0.03 mbar for 30 min had the following characteristics: M.p. > 250° (dec.). R_f (*I*, *d*) 0.00. ^{1}H-NMR ((D_6)DMSO, 250 MHz): 0.854 (*t*, $J \approx 7$, 3 H); 1.25 (*m*, 24 H); 1.52 (*m*, 2 H); 2.29 (*t*, $J \approx 7$, 2 H); 2.71 (*s*, 23 H, Me_3N); 3.45 (*dd*, $J = 10$, 2, H–C(3)); 3.77 (*m*, H–C(2)); 3.80 (*dd* app. as *t*, $J = 9.5$, H–C(6)); 3.89 (*ddd* app. as *q*, $J = 9$, H–C(4)); 4.19 (*ddd* app. as *q*, $J = 9.3$ H–C(5)); 4.50 (*dd*, $J = 9.5$, 2, H–C(1)). Anal. calc. for $C_{22}H_{44}O_{13}P_2 \cdot 2.5\ C_3H_9N$ (726.31): C 48.78, H 9.23, N 4.82; found: C 45.01, H 9.17, N 5.05.

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