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News on Inositol Liquid Crystals[1]

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A greater number of selected, partially *O*-alkylated derivatives of three (**myo**-, **scyllo**-, and **chiro**-) inositols, stereoisomers of 1,2,3,4,5,6-hexahydroxycyclohexane, as well as of hexahydroxybenzene and tetrahydroxy-1,4-benzoquinone were synthesized and characterized by usual methods. From the study of the various liquid crystalline target compounds (long-chained alkyl ethers) by polarizing microscopy and differential scanning calorimetry it emerges that the occurrence, type, and stability of their mesophases are clearly determined by the number, the position, and the stereochemical arrangement of both the hydroxyl groups and the alkoxy chains on the cyclohexane ring which is discussed in detail. Here, unsaturated six-membered ring units—for example quinoic or aromatic in character—as carriers of the numerous hydroxyl functions have been proved damaging to the exhibition of mesophases; our multihydroxy model compounds of this type have not been found liquid crystalline. In general, it was found that axial hydroxy and alkoxy groups destabilize the smectic A or hexagonal columnar phase exhibited here. Moreover two types of mesophase transformation from hexagonal columnar to smectic A have been found, i) by changing the stereochemistry of two vicinal hydroxyl functions in a peg-shaped **chiro**-inositol diether (derived from quebrachitol) or ii) by blocking of a (special) equatorial hydroxyl function in a peg-shaped **myo**-inositol diether through etherification. A complete homologous stereoisomeric series (five members) of **myo**- and **scyllo**-inositol monoalkyl ethers with each a dodecyl chain at their respective oxygen functions is also presented; the three thermomesogenic ones of them exhibit the smectic A phase. In this connection and with regard to a homologous series of *D*-glucopyranose monoethers, molecular symmetry effects originating from the different localization of the one ether group in both homologous series on their ability/inability of mesophase formation are discussed in detail.

*Keywords: carbohydrates, cyclitols/**chiro**-, **myo**-, **scyllo**-inositol ethers, liquid crystals, chiral, thermotropic, mesogens, hexahydroxybenzene, quebrachitol, tetrahydroxy-1,4-benzoquinone ethers, stereochemistry, symmetry effects*

1. INTRODUCTION

For several years it has been known that carbohydrate/inositol chemistry can provide a vast source of mesogens. Thus, the work of nearly two dozen groups of researchers, located mainly in Europe, has given impetus to the rapid development in this very important field of studies on biomolecule liquid crystals. This family of mesomorphic materials is possibly best suited to serve as models for discussions on the effects of related biological structures based on such a "delicate phase of matter"[2] in nature. Already two reviews[3,4] have appeared summarizing most of

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the elaborated results on the synthesis and physics of far more than one thousand liquid crystalline derivatives of this type known today. Moreover, in the course of the last few months further progress on this complex topic is documented in numerous original papers of which a few are selected here.[1,5-9]

Three geometrical forms of mesophases of carbohydrate thermomesogens have been found so far: predominantly (mono- and bi-) layers,[3-6,8c,f,g,10] but in some cases also columns,[4,7,8a-e,g,9-14a] or even cubes.[4,9b,11,12] The process of such spontaneous molecular aggregations of species containing at least[15] two vicinal hydroxyl (or related, e.g., NH—[13]) functions[8d,e,13] is strongly directed by the formation of intermolecular hydrogen-bonding networks as the driving force. Similar observations have also been made with comparable diols of purely synthetic, unnatural parent compounds.[16] The type of thermotropic mesophase formed in this way is determined by a) the number, b) the position, and c) the stereochemical arrangement of both the hydrogen-bridges forming groups and the alkylhetero chains of a molecule cyclic or acyclic in structure. After initial findings[10,14,17-19] on the stereochemical impact of substituents on the occurrence and stability of carbohydrate mesophases in the mid-eighties this important topic has rapidly moved to a focus of growing scientific interest.[8,9a,20-26] Due to their preferred, stable three-dimensional shapes appropriate derivatives of inositols[1,8a-e,g,14,23] and of cyclic sugars[1,6,7,9a,14a,18,19,26,27] possess the best conditions for this kind of studies. Naturally, remarkable results on effects of such changes in configuration—in part also in constitution—on the thermotropic properties have also been reported extensively about various series of open chain carbohydrate systems[5,8f,9b,c,10,18,20-22,24,25,27] of which the so-called aldose dialkyl dithioacetals[20-22] are the most complete studied representatives of this acyclic group of compounds.

As a further contribution to this field of inquiry we here describe the syntheses and their thermomorphic behaviour of various types of novel ethers derived from three members (**1–3**) of the inositol family shown encircled in Figure 1. These derivatives are different in constitution and configuration, i.e., in the degree of substitution and in stereochemistry.

For purposes of comparison some unsaturated analogues of inositiol ethers with six-membered cyclic cores, but quinoic or aromatic in character, are also included in this paper.

2. SYNTHESES OF THE VARIOUS MULTIHYDROXY MODEL COMPOUNDS

The syntheses of the numerous novel inositol ethers along with selected unsaturated/aromatic analogues outlined in the six reaction schemes of this chapter and fully described in the experimental section of this paper aimed the goal to obtain the sixteen new target molecules **17–21**, **25a,b**, **27a**, **30**, **32**, **36**, **39**, **40a,b**, and **41a,b** as model compounds for studies of the relationship between substitution pattern, stereochemistry, and the degree of saturation of the six-membered cyclic molecular core versus liquid crystalline property.

Starting material for most of the compounds synthesized here was the commer-

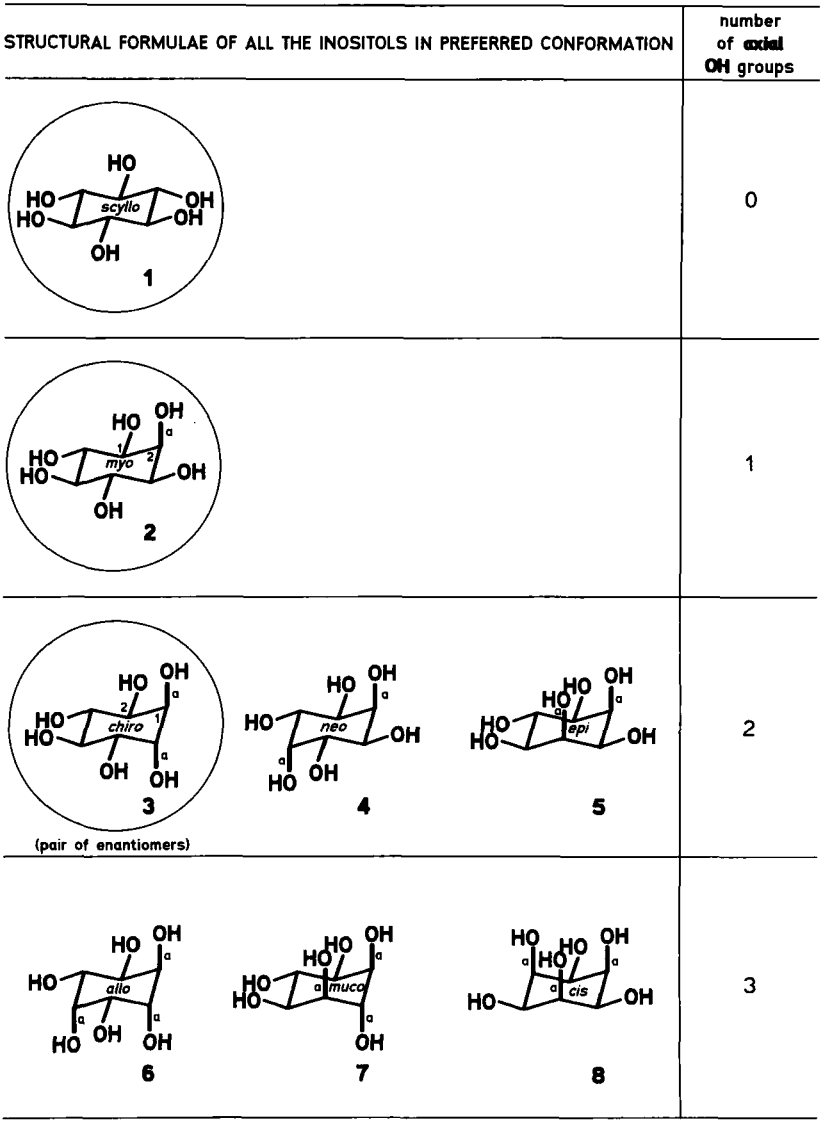
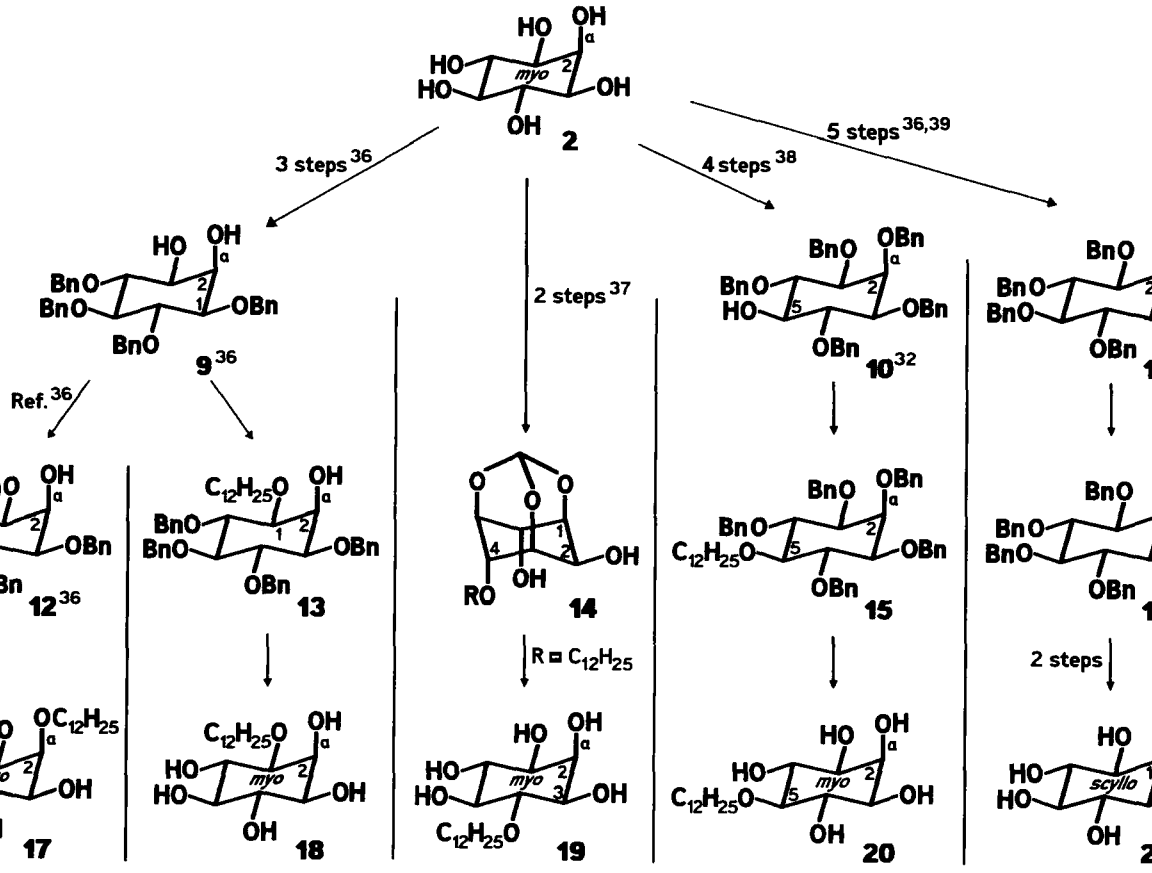


FIGURE 1 Survey of the inositol stereoisomers (**1–8**, naturally occurring) compiled here accordingly to the growing number of their axial (a) hydroxyl functions. Their nomenclature is based on the prefixes shown inside of the eight cyclohexane rings.[28] The syntheses and physical studies of various ethers of the three encircled members **1–3** of the inositol family are the subject of this paper.

cially available **myo**-inositol (**2**, see Figure 1). However, in special cases (**36**, Scheme 5, **39**, **40a,b**, and **41a,b**, Scheme 6), **chiro**-(−)-inositol (**3**, see Figure 1) accessible from naturally occurring quebrachitol[28,29] (**33**), 2-methyl-(−)-inositol, by hydrolysis[30] or tetramethoxy-1,4-benzoquinone[31] (**37**), respectively, were the sources of choice.

In this context we also want to emphasize a new synthesis of the 1,2,3,4,6-penta-*O*-benzyl-**myo**-inositol[32] (**10**), key intermediate in the pathway to the target mol-



he synthetic routes to the five novel stereoisomeric inositol monododecyl ethers **17**–**21** starting from **myo**-inositol (**2**). Note
ot yet published, are described in the Experimental. Whereas **17**–**19** are liquid crystalline (smectic, S_A) **20** and **21** are not

ecule **20** (Scheme 1). The easily, in three steps[33,34] from **myo**-inositol (**2**) accessible 2,4,6-tris-*O*-benzyl-**myo**-inositol[34] (**28**) could be benzylated selectively (30% yield, see Experimental) at the two equatorial hydroxyl functions each vicinal to the axial, **cis**-standing 2-benzyloxy group out of their plane. Most probably, this interesting result was possible due to the relatively less crowded molecular vicinity of these two hydroxyls compared with the situation of the third hydroxyl group located at the 5-position between two benzyloxy groups in the same plane.

On the other hand, however, we had some trouble with the selective alkylation reactions of the **myo**-inositol orthoformate (**14**, R = H). In comparison to its three-fold benzylation reported four years ago[34] and giving the corresponding tris-*O*-benzyl ether as a crystalline solid in 79% yield, our mono- and bis-alkylations ran less good. In the first case, the 4-monoether **14** ($R-C_{12}H_{25}$, Scheme 1, 20% yield) was the only defined, oily, but later crystallizing, product; in the other one, the 4,6-diether **31** (Scheme 4) obtained as an oil in 17% yield was one out of four reaction products which all could be separated and characterized. Anyhow, the two target molecules **19** (Scheme 1) and **32** (Scheme 4), respectively, could also be realized in these ways, followed by acidic hydrolyses, see Experimental. Eventually, the three step sequence **37**→**38** (Scheme 6) was possible due to the surprising fact that tribenzylphosphite did not react with tetrabenzyloxy-1,4-benzoquinone in a usual way, i.e., under the formation of the 4-benzyl ether of the corresponding [4-hydroxy-tetra(benzyloxy)phenyl]-dibenzyl phosphate as one should expect in comparison to analogous reactions.[35] Instead, the 4-hydroxy function remained free and, hence, could be alkylated with bromododecane to obtain the desired intermediate **38** on the route to the aromatic target molecule **39**.

However, it shouldn't be withheld to stress that the three multihydroxybenzene derivatives **39** as well as **41a** and **b** are extremely sensitive to air whereas, on the other hand, the two dihydroxyquinone diethers **40a** and **b** are stable compounds.

All inositol derivatives of this paper are racemates unless otherwise stated. Solutions of the various pairs of enantiomers have not been carried out; the respective structural formulae show only one enantiomer. However, the four derivatives **33**–**36** of **chiro**-(−)-inositol (**3**), see Scheme 5, are enantiomerically pure; their optical rotations are either known or for **35** and **36** given in the Experimental.

The molecular structures of all thirty seven intermediate and target compounds are verified by I.R., ^1H, ^{13}C N.M.R. and mass spectroscopy, as well as by combustion analyses, or high resolution of their molar peaks.

In the following chapter, the properties of the various multihydroxy model compounds will be discussed in order of the increasing number of their ether functions as well as in view of the degree of saturation of the six-membered cyclic core common for all the molecular structures subject of this report.

3. RESULTS AND DISCUSSION

3.1. Cyclic Pentols/Monododecyl Ethers

In continuation of our synthetic and physico-chemical work on inositol derivatives in the frame of our liquid crystal interests we now completed the series consisting

TABLE I

Phase transition data* of six cyclic pentols, i.e., of the six possible monododecyl ethers **17**–**21** of **myo**- and **scyllo**-inositol (cf. Scheme 1), respectively, as well as **39** of hexahydroxybenzene (cf. Scheme 6)

Pentol/ dodecyl ether	Cr		M		Iso
17	●	220.5 / 223.5 (48.8)	{ M_1	215.2 / 216.7 (6.6) }+	●
18	●	124.4 / 127.6 (32.0)	S_A	221.1 / 221.7 (1.8)	●
19	●	147.6 / 150.2 (29.1)	S_A	216.0 / 216.3 (1.8)	●
20	●	≈ 250## / ————	—		●
21$	●	241.9 / 240.0 (35.4)§	—		●
39	●	170.9 / 172.5 (32.3)	—		●

Cr: crystalline; M: the type of mesophase; Iso: isotropic liquid; M_1: a mesophase most probably of a smectic type; S_A: smectic A. { }: A monotropic mesophase.

*Temperatures in °C; polarizing microscopy/differential scanning calorimetry: P.M./D.S.C.; enthalpies (kJ/mol) in brackets; heating rate 5 K/min. Most of these data are also presented in Reference 8g.

+The clearing temperature was determined on cooling from the isotropic liquid.

##Decomposition.

$Heating rate 10 K/min.

§However, the thioanalogous dodecyl ether of thioscyllitol is an S_A phase exhibiting liquid crystal:[8c,g] Cr 216.9 / 217.6 (39.6) S_A 231.0 / 229.6 (2.1) Iso.

of monoethers (one dodecyl chain each) of **myo**- and **scyllo**-inositol as well as of hexahydroxybenzene, see **17**–**21** and **39** (Scheme 1 and 6, respectively, and Table I). Meanwhile, three liquid crystalline thioanalogues of the scyllitol ether **21** with each an *S*-alkyl chain instead are already known[8c]; the phase transition data[8c,g] of the dodecyl thioether are quoted as an example in a footnote of Table I.

The structural formulae of the five members **17**–**21** of this homologous series depict the differences in position and stereochemical situation of the hydroxyl functions and the one dodecyloxy group relatively to each other. The scyllitol monoether **21** differs from the hexahydroxybenzene analogue **39** in the degree of saturation of their flat cyclic hydrophilic parts. In particular, our inositol ethers **17**–**21** having only one long alkoxy chain are of special interest for comparisons of their thermo-mesomorphic properties with those of i) a thio-analogous derivative mentioned in a footnote to Table I and ii) analogous monoethers recently[6] derived from D-glucopyranose.

At first glance on Table I it becomes clear that the temperatures for the transitions of the monoethers into their isotropic liquids are very high and, interestingly, almost identical for the three **myo**-inositol monoethers **17**–**19**; the other two inositol analogues melt even still higher (**20** around 250°C!), but not so the aromatic one. Whereas the (planar and fully saturated) scyllitol monoether **21** is stable and reproducibly melting around 240°C, its (also planar) about 70 K lower melting aromatic counterpart **39** is extremely sensitive to air and, therefore, very difficult to work with.

Table I also tells that only the first half (**17**–**19**) of its six monoethers is thermotropic liquid crystalline; the second half of them doesn't exhibit any mesophase

TABLE II

Phase transition data* of sixteen multiol di- and trialkyl ethers of **chiro**-, **myo**-, and **scyllo**-inositol (**A**–**D** and **25**, **27**, **30**, **32**, **36**, cf. Schemes 2–5, respectively) as well as of tetrahydroxy-1,4-benzoquinone and hexahydroxybenzene (**40** and **41**; cf. Scheme 6)

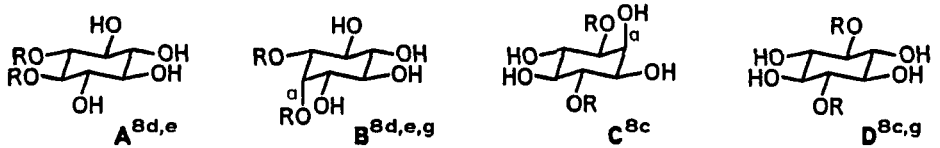
Multiol/ di- or trialkyl ether*		Cr		M		Iso
A	(6)	●	—— / 111.5 (16.0)	H_X	—— / 167.1 (1.8)	●
B1	(6)	●	110.0 / 110.2 (21.9)	–		●
B2	(8)	●	102.0 / 101.8 (20.8)	H_X	131.5 / 131.7 (1.2)	●
25a	(6)	●	112.7 / 112.9	H_X	125.1 / 125.2 (1.2)	●
25b	(8)	●	111.2 / 112.7 (18.6)	H_X	148.1 / 147.2 (1.6)	●
36	(6)	●	69.0 / 70.1 (10.7)	S_A	82.3 / 80.9 (1.1)	●
27a	(6)	●	111.7 / 113.1 (38.1)	(S_A	97.1 / ————)	●
30	(8)	●	47.2 / 49.2 (13.6)	–		●
32	(8)	●	48.4 / 49.2 (10.6)	–		●
C1	(6)	●	144.4 / 144.8 (27.9)	S_A	176.1 / 176.9 (9.3)	●
C2	(8)	●	139.5 / 141.2 (28.8)	S_A	168.1 / 170.1 (10.5)	●
D	(6)	●	258.3 / 265.2 (40.5)	–		●
40a	(6)	●	124.3 / ————	–		●
40b	(8)	●	113.0 / ————	–		●
41a	(6)	●	112.2 / ————	–		●
41b	(8)	●	112.1 / ————	–		●

TABLE II (*Continued*)

Cr: crystalline; M: the type of mesophase; Iso: isotropic liquid; H_X: hexagonal columnar mesophase, cf. Reference 22b; S_A: smectic A; { }: a monotropic mesophase.

*Temperatures in °C; polarizing microscopy/differential scanning calorimetry: P.M./D.S.C.; enthalpies (kJ/mol) in brackets; heating rate 5 K/min. Most of these data are also presented in Reference 8g.

†The number of carbon atoms of the alkyl chains in these multiol/di- or trialkyl ethers are given in brackets.



at all. The axial member **17** is monotropic; its unstable mesophase—most probably of a smectic type—could not be studied in detail due to rapid crystallization. Unlike **17**, each of the two equatorial and lowest melting **myo**-inositol monoethers **18** and **19** form an enantiotropic (smectic A) phase, identified by their typical texture and by miscibility studies (contact method) with the known S_A phase of the tetrol diether C^{8c} (cf. Table II; see also Reference 8g for surface effects of these amphiphilic smectogens between glass plates).

As clearly can be seen and already pointed out in part,[8g] the phase transition data for the six pentols in Table I reveal a strong dependence of their melting temperatures on i) the position of each of the one (lipophilic) dodecyl ether function, ii) the fixed stereochemistry in the inositol units of **17–21**, and iii) the degree of saturation of the hydrophilic head group, i.e., cyclohexyl in **21** compared to phenyl in **39**. On the other hand, however, the clearing temperatures of the three **myo**-inositol liquid crystals **17**, **18**, and **19** are very similar—close to 220°C! We are convinced, that our observations on these differently structured inositol monoethers **17–21** strongly support the revised model[45,46] for the molecular arrangement in the smectic A phase of carbohydrate-derived amphiphiles with one alkyl chain. It is incredible, but relatively small structural/sterical changes at the inositol ring, for instance the formal migration of an axial hydroxyl function away from the dodecyl group into its opposite ring position (cf. **18** or **19**→**20**, Scheme 1 and Table I), has a dramatic effect on the liquid crystallinity of these compounds. Their melting points get steeply pushed up (over 100 K!) making the thermomesogenic property vanish. A similar, though slightly smaller effect becomes visible by comparing **18** and **19** on the one side with **21** on the other, having now all hydroxyl functions equatorial. These observations seem to demonstrate that the sterical arrangement (a or e) of the hydroxyl function opposite to or farest away from an equatorial alkyl ether group is insignificant for these pentol derivatives to be or not to be liquid crystals. Neither has an aromatization of the inositol ethers (cf. **17–21**→**39**) a positive effect on a mesophase formation; as already emphasized above, it rather lowers the chemical stability of the material.

Apparently, due to their comparatively most disturbed molecular symmetry—

18 more than **19**—these two members of that group of natural product liquid crystals exhibit wide, enantiotropic smectic A phases, starting from below 150°C and ranging over 97 or 68 K, respectively. Even in the sub-group of the inositol monoethers **17, 20**, and **21**, each possessing a plane of symmetry, a tiny little effect of disturbance can be seen, allowing **17** (in difference to **21**) with its alkoxy chain axial or above the plane of the inositol ring to exhibit a very narrow, monotropic mesophase at a very high temperature, about 23 K below the melting point of **21** (cf. Table I and Scheme 1).

We mean that such a discussion on effects of molecular symmetry vs. liquid crystalline behaviour could be extended on, for example, the dodecyl ether series of D-glucopyranose published recently[6] in which the 1-β-, 2- and 6-ethers—in our opinion the most symmetry disturbed ones—have the widest smectic A phase ranges with the relatively lowest melting and highest clearing temperatures, whereas the 3-ether as the most symmetric one gives the narrowest range with the highest melting and a relatively low clearing temperature. Figure 2 illustrates our statement concerning the influence of molecular symmetry effects (arising from the fact of the differently located ether group) on the appearance of the mesophase on heating of the compounds in both series discussed here.

Finally, at present due to insufficient data, we can't yet comment on the conspicuous difference in the thermotropic behaviour of the **scyllo**-inositol ether **21** and its thioanalogue (see Table I), identical in the stereochemistry at the cyclohexane ring apart from the fact that the sulfur atom implies another bonding and electronic situation, probably decisive for the occurrence of mesogenity.

3.2. Cyclic Multiols/Di- and Trialkyl Ethers

The substitution patterns of the sixteen mainly saturated, but in four cases unsaturated (quinoic or aromatic) multiol di- and trialkyl ethers collected in Table II (cf. also the Schemes 2–6) show three different types of molecule geometries: i) peg-shaped or tripodal in the first six cases, ii) angled in **30** and **32**, and iii) rod-shaped and linear in **27a** and in the last seven members of Table II.

Our investigations on mesogenic representatives showing the first type of geometry, e.g., the compounds **A** and **B**, started already some time ago during which we found it characteristic that their molecules aggregate into columns which are arranged in a hexagonal lattice; details about this so-called H_X type thermotropic mesophase are discussed elsewhere.[8b,d] It became also clear that their two vicinal alkoxy groups should advantageously be in equatorial positions, otherwise the thermomesogenic properties get weakened or even lost totally[8d,e,g] (cf. the top part of Table II).

Moreover, also in this family of multiol liquid crystals the stereochemical arrangement of the hydroxyl functions affects the occurrence of a mesophase. In comparison to the scyllitol diether[8d,e] **A**, the two **myo**-inositol analogues **25a** and **b** (cf. Scheme 2) having each one axial hydroxyl opposite to an alkoxy group exhibit a less stable H_X phase, here, as a result of lower clearing points. The melting points of these three compounds are almost equal.

Important is the fact that the reported stereochemical modifications at only **one** ring position do not change the type of mesophase found. In these cases, they are

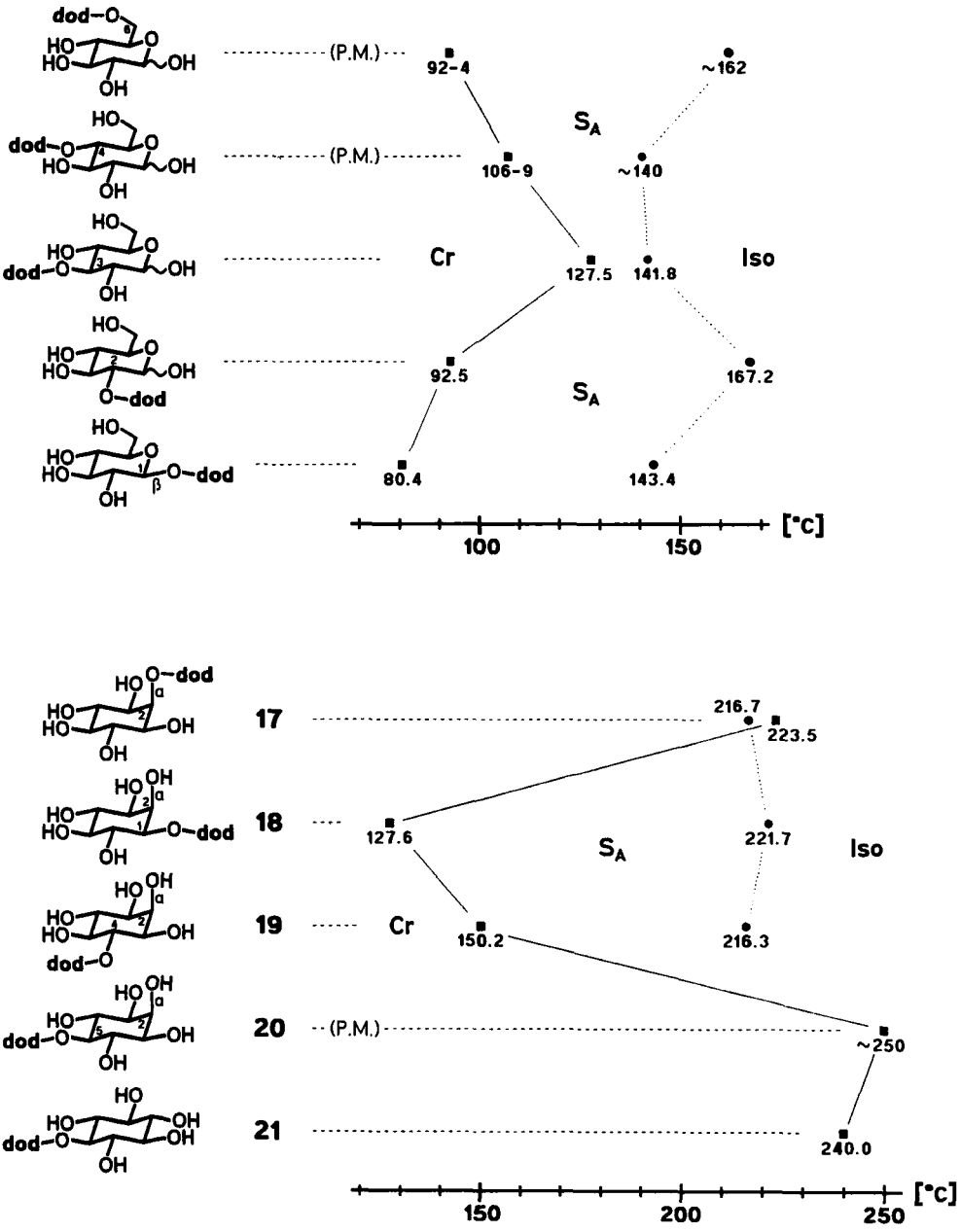
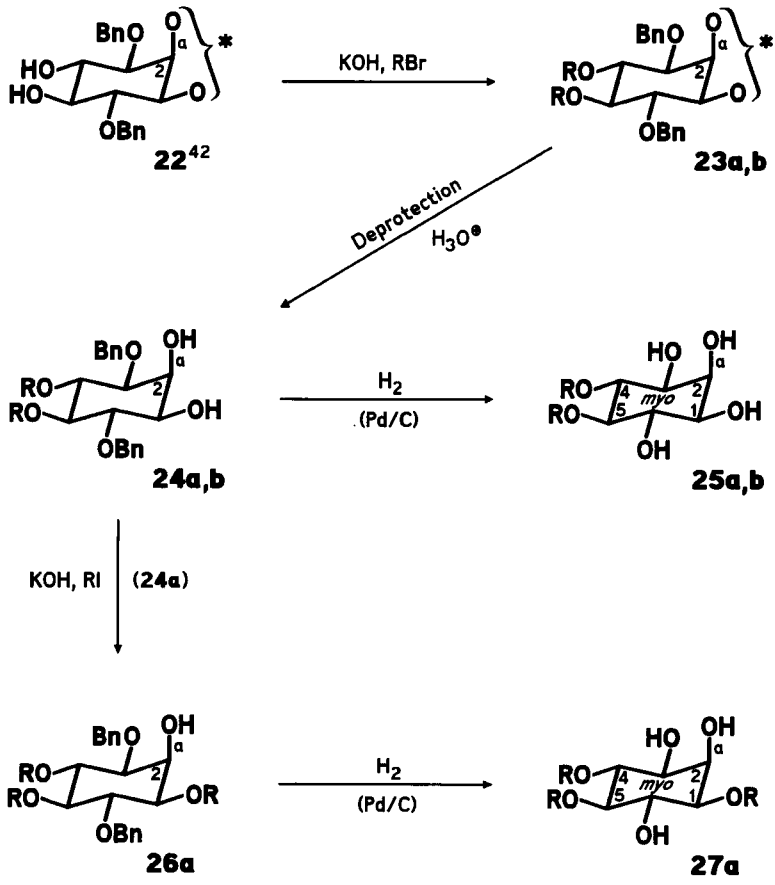


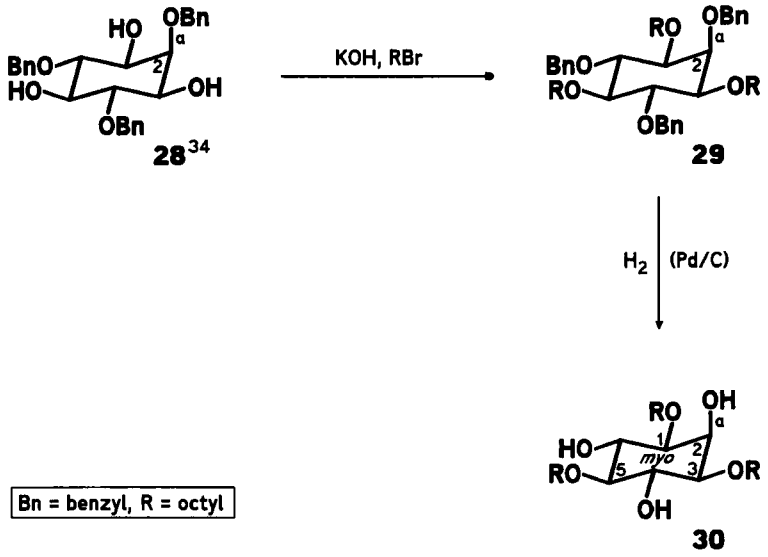
FIGURE 2 Plots of the phase transition temperatures against the structures of each the five possible monododecyl ethers of the now known two series of D-glucopyranose[6] (top) or **myo-/scyllo**-inositol (*bottom*; cf. Scheme 1 and Experimental). Obviously, the appearance of the mesophase on heating of each of these ten compounds seems to be determined by their relative molecular symmetry originating from the different localization of the one ether group in both homologous series. Iso: isotropic liquid, S_A: smectic A, Cr: crystalline phase; dod = dodecyl; ■: m.p., ●: cl.p.; ~: α- and β-stereoisomer of the pyranose ether; a: axial. The temperatures (cf. Reference 6 or Table I) were obtained by D.S.C., except otherwise marked (P.M.) in three cases.



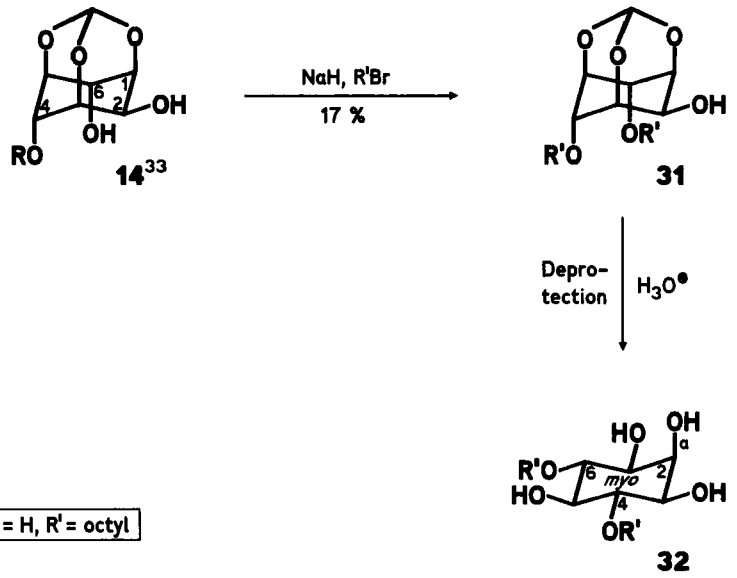
SCHEME 2 The novel and liquid crystalline (hexagonal columnar or smectic A phase forming) **myo**-inositol di- or triethers **25a,b** and **27a**, respectively, accessible via the two homologous key intermediates **24a,b**; see Experimental.

or remain hexagonal columnar (H_X)! This statement is proved by texture and miscibility studies (contact method) using glucosedioctyldithioacetal[22] as compound of reference.

Very much to our surprise, a change in the configuration of **two** hydroxyl functions, those ones opposite the alkoxy groups in the scyllitol diether **A** under the creation of the **chiro**-analogue **36** (see these two formulae in Table II and Scheme 5), has a **twofold** effect on the mesophase i) it gets lowered and narrowed much stronger than in the previous case and ii) even the type of mesophase is changed from hexagonal columnar to a layered array of the molecules, i.e., a unique transformation from $H_X \rightarrow S_A$ takes place! See more remarks on this matter in Reference



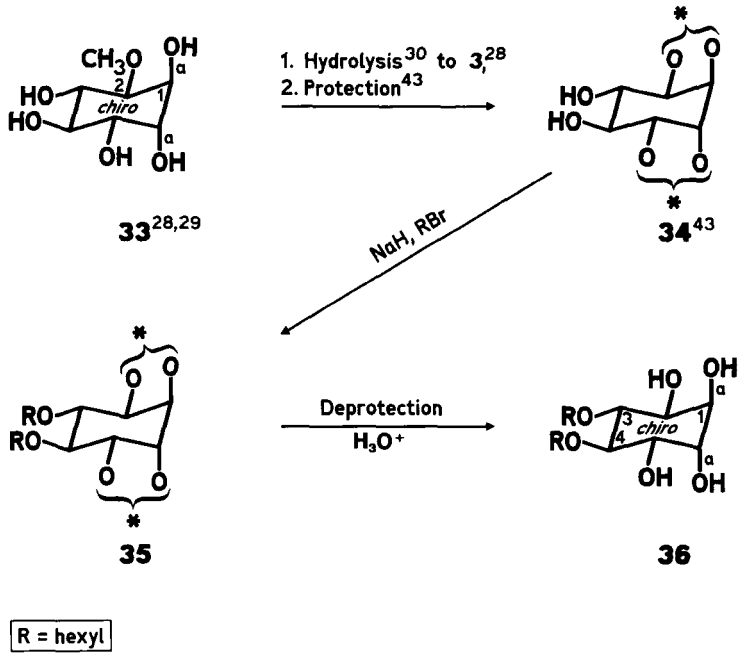
SCHEME 3 The novel, but non-liquid crystalline 1,3,5-**myo**-inositol trioctyl ether **30** obtained in two steps from the 2,4,6-tribenzyl protected **myo**-inositol derivative[34] **28**; see Experimental.



SCHEME 4 The synthetic access to the novel, but non-liquid crystalline model diether **32** of **myo**-inositol (**2**, see Figure 1) via its (partially protected) orthoformate[33] **14** (R = H); see Experimental.

8g. The mesophase of **36** was securely identified as smectic A by microscopy studies of its texture and by miscibility investigations (contact method) using **C**[8c] and 1,2(S),3(S),4(R)-('D-xylo')icosanetetrol[8f] as the materials of reference.

The next two model compounds **30** and **32**, here, of an angled shape, i.e., neither peg- nor rod-like structured, having their alkoxy groups not in vicinal positions,

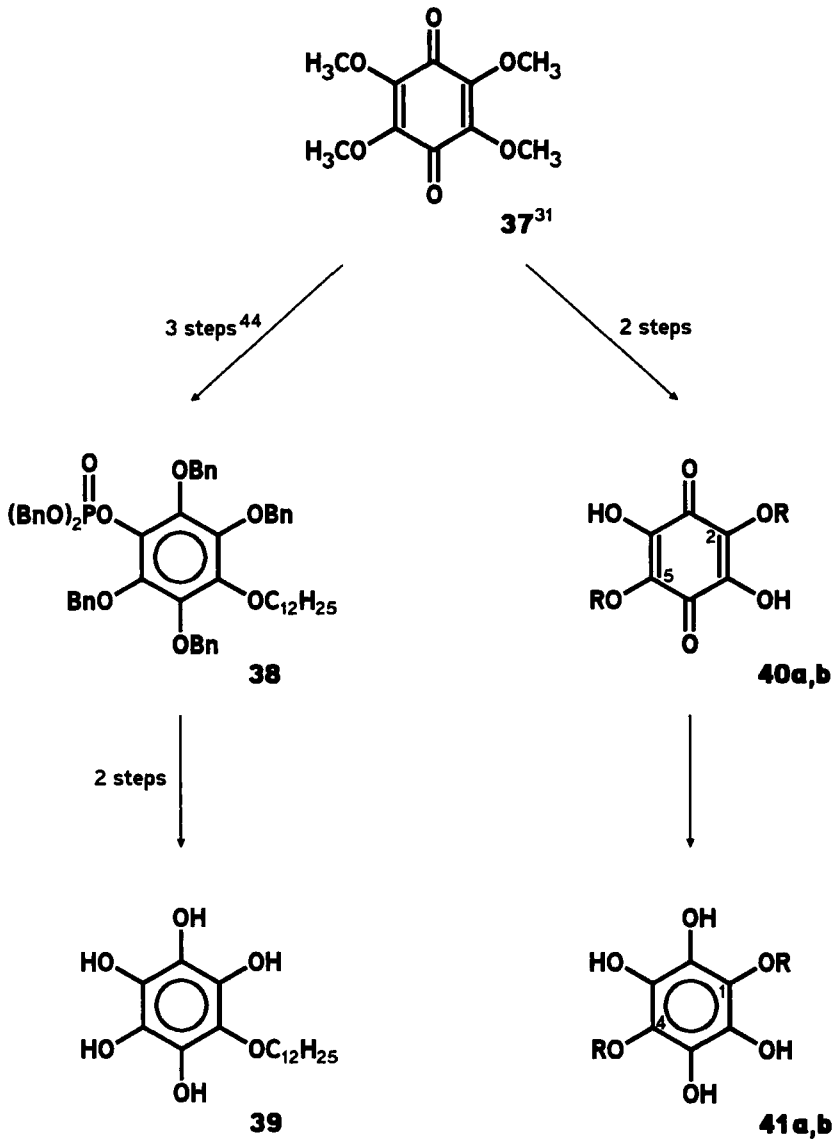


SCHEME 5 The synthetic route to the first liquid crystalline (smectic A phase forming) derivative **36** of **chiro**-(−)-inositol (**3**, see Figure 1) starting from the naturally occurring quebrachitol[28,29] (**33**), 2-O-methyl-(−)-inositol; see Experimental.

lack any liquid crystallinity, most probably due to insufficient space filling[14a] in the peripheries of their saturated (cyclohexane) cores and/or their inability to aggregate. Nevertheless, in view of the tetrol **32** this behaviour is somewhat strange since it is known[9a] that a few alkyl 6-O-acyl-glycopyranosides possessing a comparable substitution pattern, but differently functionalized (with an acetal and ester group) do exhibit columnar mesophases.

The largest group of compounds, eight in number, in this chapter is rod-shaped. Except one (**D**), the saturated members of it exhibit the smectic A phase on heating as already described[8c] in detail for three diethers of the types **C** and **D**. Again, they differ stereochemically and show as a result of it different thermotropic behaviour[8c] (cf. Table II), e.g., the **scyllo**-inositol dihexyl ether (**D**) melts at too high temperature to exhibit a mesophase; it is the highest melting compound discussed in this paper.

The triether **27a** (cf. Scheme 2) is a compound of special interest as it is liquid crystalline (S_A) despite of its unfavourable substitution pattern. It can be regarded as a relatively spacious derivative of the rod-shaped **C1**, but troubled by a bulky group at position 5 of the cyclohexane ring and, therefore, indicated with a marked loss of phase stability. The phase is now monotropic, but of identical type as of its parent 1,4-diether (**C1**), cf. Table II. In other words, the tetrol **C1**, a double vicinal diol, has been transformed into the triol **27a**, having one equatorial hydroxyl group less available for the formation of an intermolecular, dynamic, hydrogen bonding



Bn = benzyl, a: R = hexyl, b: R = octyl

SCHEME 6 Outline of the syntheses of the novel unsaturated/aromatic, but non-liquid crystalline multihydroxy model compounds of the three types **39–41** starting from tetramethoxy-1,4-benzoquinone[31] (**37**); see Experimental.

network. Most probably, both types of compounds (**C1** and **27a**) behave as rod-shaped multiols because the vicinal alkoxy chains in **27a** lie parallel in the monotropic smectic monolayer phase.

On the other hand, in contrast to the vicinal, now peg-shaped diether **25a**, the formation of a hexagonal columnar (H_X) phase by **27a** is impossible, because the alkoxy chain at ring position 1 would stay inside the hydrophilic section and hinder the construction of a columnar ordering of its molecules. Therefore, the peg-shaped half of the molecule **27a** does not control the kind of molecular aggregation. Rather, the rod-shape of the whole molecule dominates this process and no change in mesophase takes place: $S_A \nparallel H_X$. But, the formal transformation of **25a** into **27a** by etherification at position 1 does result in a change of mesophase from hexagonal columnar to smectic A: $H_X \rightarrow S_A$, the second case of this type of phase transformation presented in this paper.

Finally, we want to comment on an unpleasant surprise. Unfortunately, we have to realize that the unsaturated (quinoic or aromatic) analogues **40a,b** and **41a,b** of the inositol 1,4-diethers **C** and **D**, costly synthesized and presented here for the first time as model compounds for comparative reasons, are not thermomesomorphic (cf. Table II).

3.3. Cyclic Diols and Mono-ols/Inositol Tetra- and Pentaethers

Numerous tetraethers of **myo**- and **scyllo**-inositol with vicinal diol situations both in a cis- or trans-configuration have already been studied in great detail.[8b,d,e] They exhibit various types of columnar mesophases which are built up from hydrogen-bridged dimers of the respective vicinal diols. The stability of these mesophases is a function of the configuration of the diol groups. A rich multi-thermo-mesomorphism is also observed.[8b,d,e]

Various long-chained pentaethers of **myo**- and **scyllo**-inositol—not yet of **chiro**-inositol—having their remaining one hydroxyl function either axial or equatorial are known, but usually found not to be thermo-mesomorphic.[1,23b] However, a few exceptions have been published.[15] Even a kind of a "twofold mono-ol", the 1,4-diol, 1,2,4,5-tetra-O-hexyl-**scyllo**-inositol, $C_{30}H_{73}O_6$, m.w. 529.9, a colourless crystallizing compound, m.p. 90–92°C, has been synthesized in ten steps starting from **myo**-inositol (**2**), but also been found thermotropically not liquid crystalline.[47]

4. CONCLUDING REMARKS

This study of a great number of ether derivatives of three naturally occurring stereoisomers of inositol (1,2,3,4,5,6-hexa-hydroxycyclohexane) confirm earlier statements[8] that the appearance, the type, and the stability of their thermotropic mesophases, usually smectic A or hexagonal columnar, are determined by the number, the position, and the stereochemical arrangement of both the hydroxyl function and the alkoxy chains on the cyclohexane ring. However, analogous multiols having a quinoic or aromatic six-membered ring instead lack any kind of thermo-mesomorphism.

In general, axial functional groups weaken the stability of a mesophase exhibited by inositol derivatives. The more symmetric such a monoether derivative is concerning its functional groups the lower is its tendency to exhibit a mesophase of

the above mentioned types. The same seems to be true for a homologous series of D-glucopyranose monoether.

It is possible to transform a hexagonal columnar phase into a smectic A one in two ways: i) by changing two vicinal hydroxyl functions in a peg-shaped molecule from equatorial into axial positions, or ii) by blocking one equatorial hydroxyl function opposite to an ether group in a peg-shaped molecule through (formal) etherification. In our opinion, these two interesting phenomena deserve more detailed investigations.

5. EXPERIMENTAL

The chromatographies in various columns with their given inner diameters ∅ in cm were carried out on silica gel 60 (→SC 60, Merck, size: 0.063–0.2 mm, 70–230 mesh ASTM in case of flash chromatographies →SC 60, Merck, size: 0.040–0.063, 230–400 mesh ASTM) using the following solvents or mixtures of them in vol.-%, also applied for reactions and recrystallizations: chloroform (→CF), ethyl acetate (→EA), heptane (→HT), light petroleum, boiling range 30 – 70°C (→LP), methanol (→ML), *t*-butyl-methyl ether (→TBME). The melting points (m.p.) of non-liquid crystalline compounds were determined either by Et. (Elektrothermal apparatus), D.S.C., or P.M. (the latter two see below).

The selected, essential spectroscopic and phase transition data presented in this paper have been obtained with the following instruments, I.R.: Beckman I.R. 9; ^{1}H N.M.R. (400 MHz): Bruker AM 400; ^{13}C N.M.R. (67.9 MHz): Bruker AM 270; M.S. (direct inlet): VARIAN MAT 711; Polarizing Microscopy (P.M.): Leitz Laborlux 12 Pol with a hot stage Mettler FP 82 or Linkam THMS 600; Differential Scanning Calorimetry (D.S.C.): Mettler TA 3000/DSC 30 S with GraphWare TA 72.

*1,2,3,4,6-Penta(O-benzyl)-**myo**-inositol* (**10**). Here and in difference to an earlier route,[32] 2,4,6-tris-O-benzyl-**myo**-inositol[34] easily obtainable in three steps[33,34] from **myo**-inositol was used as the precursor. In a 250 ml flask 3.6 g (8 mmol) of it dissolved in 50 ml dry *N*,*N*-dimethylformamide (DMF) were first reacted with 0.23 g (9.6 mmol) sodium hydride, stirred at r.t. for 2 h, before 1.37 g (8 mmol) benzyl bromide had been added and the mixture stirred at r.t. over night. Thereafter, the same amounts of chemicals were added for a second time and the mixture treated as described and then concentrated in vacuo at about 25 mbar and 40°C bath temperature. A crystallization of the residue from ethanol in a fridge over night furnished 0.86 g (17%) colourless **10**. A column chromatography (∅ = 45 mm, 100 ml SC 60, LP/EA 4:1) of the residue from the mother liquor yielded a solid material from which further 0.65 g (13%) colourless **10** were obtained by crystallization from ethanol; total yield 1.51 g (30%) **10**, m.p. 178°C (Et.; Reference 32: m.p. 175–177°C from ML.

I.R. (CCl_4): ν = 3582 (hydroxyl, Reference 32: ν = 3535 in KBr). ^{1}H N.M.R. ($CDCl_3$): δ = 4.97–4.80 and 4.68–4.60 (2 ABq, $J \approx 11$ or 12 Hz, respectively; 2 OCH_2-phenyl at C-1 and C-3 or C-4 and C-6, without assignment), 4.90 (s, broad; OCH_2-phenyl at C-2), 4.07 (dd, $J \approx 2$ Hz; 2-H), 3.96 (dd, $J \approx 9.5$ Hz; 4-H and 6-H), 3.54 (ddd, $J \approx 2$, 9, and 9 Hz; 5-H), 3.38 (dd, $J \approx 2$ and 9.5 Hz; 1-H and

3-H), 2.49 (d, $J \approx 2$ Hz; 2-OH). ^{13}C N.M.R. ($CDCl_3$): δ = 138.93, 138.84, and 138.27 (3 s, ratio 1:1:2; 3 types of quart. arom. Cs), 81.12, 80.68, 75.15, and 74.47 (4 d, ratio 2:2:1:1; C-1 and C-3 or C-4 and C-6 as well as C-2 and C-5, without assignment), 75.38, 74.15, and 72.62 (3 t, ratio 1:1:2; 3 types of OCH_2). M.S. (200°C) m/z (%): no $M^{\oplus}$, 539 (30) $[M - 91]^+$, 181 (18), 91 (100) $[C_7H_7]^{\oplus}$. – $C_{41}H_{42}O_6$ (630.8); calculated C 78.06, H 6.71%; found C 77.64, H 6.97%.

*1-O-Dodecyl-3,4,5,6-tetra(O-benzyl)-**myo**-inositol* (**13**). A mixture of 1.08 g (2 mmol) of the 3,4,5,6-tetra-O-benzyl-**myo**-inositol[36] (**9**), 0.55 g (2.2 mmol) dodecyl bromide, and 5.6 g (0.1 mol) powdered potassium hydroxide in 50 ml toluene was refluxed for 12 h. After washing with water and diluted aqueous hydrochloric acid, drying over magnesium sulfate, the toluene was evaporated under reduced pressure. A flash chromatography (100 ml SC 60, $\emptyset$ = 3 cm, LP/EA 10:1) of the crude product yielded 470 mg (33%) yellowish oil. I.R. ($CHCl_3$): ν = 3570 (hydroxyl): ^{1}H N.M.R. ($CDCl_3$): δ = 4.27 (dd, each $J \approx 2.5$ Hz; 2-H), 4.00, 3.91, and 3.45 (3 dd, each $J \approx 9.5$ Hz; 4-, 5-, and 6-H without assignment), 3.65 and 3.56 (2 dt, each $J \approx 9$ or 7 Hz; OCH_2-alkyl), 3.42 and 3.23 (2 dd, each $J \approx 2.5$ or 9.5 Hz; 1-H and 3-H without assignment), 2.46 (s, broad; OH), 0.88 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 83.00, 81.11, 81.02, 80.46, 79.85, and 67.15 (6 d, ratio 1:1:1:1:1:1; 6 cyclohexane ring Cs), 75.89, 75.84, 75.79, 72.63, and 70.99 (5 t, ratio 1:1:1:1:1; 5 OCH_2), 14.06 (q; CH_3). M.S. (180°C) m/z (%): no $M^{\oplus}$, 617 (25) $[M - C_7H_7]^{\oplus}$, 616 (37) $[M - 92]^{\oplus}$, 181 (45), 91 (100) $[C_7H_7]^{\oplus}$. – $C_{46}H_{60}O_6$ (708.9); calculated C 77.93, H 8.53%; found C 77.06, H 8.32%.

*4-O-Dodecyl-**myo**-inositol orthoformate* (**14**, R = $C_{12}H_{25}$). A suspension of 240 mg sodium hydride (10 mmol) in 60 ml dry *N*,*N*-dimethylformamide was stirred for 20 min at r.t. and reacted with 1.9 g (10 mmol) **myo**-inositol orthoformate[33] (**14**, R=H), obtained by condensation[33] of **2** with triethyl orthoformate. After the dropwise addition of 2.49 g (10 mmol) 1-bromododecane the mixture was stirred during 20 min at r.t. and then for 24 h at 100°C. The usual work-up followed by flash chromatography (70 ml SC 60, $\emptyset$ = 2.5 cm, LP/EA 4:1) furnished 716 mg (20%) colourless oil which crystallized after weeks, m.p. 43.7°C (P.M.). IR (CCl_4): ν = 3520, 3588 (hydroxyl). ^{1}H N.M.R. ($CDCl_3$): δ = 5.46 (s, broad; formate H), 4.49–4.42, 4.34–4.28, 4.23–4.19, and 4.08–4.01 (4 m, ratio 1:3:1:1; the 6 inositol ring Hs), 3.83 and 3.14 (2 dd, $J \approx 1$ and 10 Hz or 1 and 12 Hz, respectively; 2-OH and 6-OH without assignment), 3.68–3.58 (m; OCH_2), 0.88 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 102.69 (d; formate C), 74.98, 74.75, 72.18, 67.78, 67.15 and 60.65 (6 d, equal intensity; inositol ring Cs without assignment), 71.45 (t; OCH_2), 14.08 (q; CH_3). M.S. (100°C) m/z (%): no $M^{\oplus}$, 283 (20), 241 (88), 73 (100), 57 (62). – $C_{19}H_{34}O_6$ (358.5); calculated C 63.66, H 9.56%; found C 63.76, H 9.38%.

*5-O-Dodecyl-1,2,3,4,6-penta(O-benzyl)-**myo**-inositol* (**15**). A solution of 20 ml dry DMF and 0.631 g (1 mmol) **10** was reacted with 48 mg (2 mmol) sodium hydride under stirring at r.t. during 2 h. After the addition of 748 mg (3 mmol) 1-bromododecane dissolved in 5 ml dry DMF the mixture was stirred at r.t. over night

and concentrated in vacuo leading to 1.52 g of a colourless, waxy crude product. Two flash chromatographies [1. $\emptyset$ = 45 mm, 100 ml SC 60, LP/EA 5:1, giving 1.15 g colourless, waxy intermediate material which was further purified by 2. $\emptyset$ = 30 mm, 60 ml SC 60, a) circa 600 ml LP and b) circa 600 ml LP/EA 1:1] yielded 727 mg (91%) colourless, waxy **15**, m.p. 64°C (P.M.). ^{1}H N.M.R. ($CDCl_3$): δ = 4.90–4.80 and 4.66–4.57 (2 ABq, $J \approx 10.5$ or 11.5 Hz; respectively; each 2 OCH_2-phenyl at C-1 and C-3 or C-4 and C-6, without assignment), 4.87 (s, broad; OCH_2-phenyl at C-2), 4.02 (dd, each $J \approx 2$ Hz; 2-H), 3.99 (dd, each $J \approx 9.5$ Hz; 4-H and 6-H), 3.81 (t, $J \approx 7$ Hz; OCH_2-alkyl), 3.30 (dd, $J \approx 2$ and 9.5 Hz; 1-H and 3-H), 3.26 (dd, each $J \approx 9.5$ Hz; 5-H), 0.88 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 139.00, 138.93, and 138.46 (3 s, ratio 2:1:2; 3 types of quart. arom. Cs), 83.69, 81.74, 80.86, and 74.44 (4 d, ratio 1:2:2:1; the first and the last signal C-2 or C-5, the middle ones C-1 and C-3 or C-4 and C-6, without assignment), 75.85, 74.20, 74.08, and 72.79 (4 t, ratio 2:1:1:2; 4 types of OCH_2-groups), 14.15 (q; CH_3). M.S. (270°C): m/z (%) = no $M^{\oplus}$, 709 (1), 600 (3), 345 (8), 267 (10), 181 (18), 91 (100). – $C_{53}H_{66}O_6$ (799.1); calculated C 79.66, H 8.33%); found C 79.11, H 8.69%.

*2-O-Dodecyl-penta(O-benzyl)-**myo**-inositol.* A mixture of 1.26 g (2 mmol) of the penta(O-benzyl)-**myo**-inositol[36] **12**, 2.81 g (50 mmol) powdered potassium hydroxide, and 10 ml (excess) dodecyl bromide in 50 ml benzene was refluxed for 24 h, thereafter cooled to r.t., and poured into water. The product was extracted with toluene from which after a usual work-up, chromatography (100 ml SC 60, $\emptyset$ = 3 cm, LP with growing amounts of EA up to a ratio of 4:1), and crystallization from ML 1.49 g (93%) colourless crystals were obtained, m.p. 60–61°C (Et.). ^{1}H N.M.R. ($CDCl_3$): δ = 4.01 (dd, each $J \approx 9.5$ Hz; 4-H and 6-H), 3.86 (dd, each $J \approx 2$ Hz; 2-H), 3.75 (t, $J \approx 7$ Hz; OCH_2-alkyl), 3.45 (dd, each $J \approx 9.5$ Hz; 5-H), 3.31 (dd, $J \approx 2$ or 9.5 Hz; 1-H and 3-H), 0.89 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 83.63, 81.67, 80.87, and 75.13 (4 d, ratio 1:2:2:1; 4 types of cyclohexane ring Cs), 75.97, 75.81, 73.39, and 72.63 (4 t, ratio 1:2:1:2; 4 types of OCH_2), 14.11 (q; CH_3). M.S. (240°C) m/z (%): no $M^{\oplus}$, 707 (7) $[M - C_7H_7]^{\oplus}$, 181 (40), 91 (100) $[C_7H_7]^{\oplus}$. – $C_{53}H_{66}O_6$ (799.1); calculated C 79.66, H 8.33%; found C 79.24, H 8.14%.

*2-O-Dodecyl-**myo**-inositol* (**17**). A mixture of 800 mg ($\approx$1 mmol) dodecyl-penta(benzyl)-**myo**-inositol hexaether described above, 1 ml boron trifluoride etherate, 7.5 ml ethanethiol, and 4 ml methylene chloride was stirred for 5 h at r.t. After evaporation of all volatile parts the residue was washed with a small amount of ether and crystallized 3 x from ML yielding 300 mg (86%) colourless product, m.p. see Table I. No I.R. due to blear looking KBr tablet. ^{1}H N.M.R. (D_6-DMSO): 1. hydroxyl, 2. selected alkyloxy, and 3. ring protons, δ = 4.57, 4.55, and 4.38 (3 d, ratio 1:2:2; $J \approx 4.5$, 4.5, and 5 Hz; 5-OH, 4- and 6-OH, and 1- and 3-OH, without assignment of the two hydroxyl pairs), 3.60 (t, $J \approx 6.5$ Hz; OCH_2), 0.85 (t, $J \approx 7$ Hz; CH_3), 3.46 (dd, each $J \approx 2.5$ Hz; 2-H), 3.30 (ddd, $J \approx 4.5$, 9, and 9 Hz; 4-H and 6-H), 3.15 (ddd, $J \approx 2.5$, 5, and 9 Hz; 1-H and 3-H), 2.87 (ddd, $J \approx 4.5$, 9, and 9 Hz; 5-H). ^{13}C N.M.R. (D_6-DMSO): δ = 81.75, 75.25, 72.98, and

71.96 (4 d, ratio 1:1:2:2; 4 types of ring Cs), 72.73 (t; OCH_2), 14.03 (q; CH_3). M.S. (215°C) m/z (%): 349 (<<1) $[M + 1]^{\oplus}$, 270 (25), 241 (27), 73 (100). – $C_{18}H_{36}O_6$ (348.5); calculated C 62.94, H 10.41%; found C 61.22, H 10.26%.

*1-O-Dodecyl-**myo**-inositol* (**18**). A hydrogenation (150 mg Pd/C catalyst, 10%, 3.5 bar) during 23 h of 709 mg (1 mmol) **13** in 30 ml acetic acid yielded 260 mg (75%) colourless crystalline material after crystallization from ML; its phase transition see in Table I. I.R. (KBr): ν = 3400, broad (hydroxyl). ^{1}H N.M.R. (D_6-DMSO): $\delta \approx$ 4.57, 4.5, 4.42, 4.38, and 4.34 [5 d, f.l.t.r. $J \approx$ 4, 4.5 (2x), 5.5, or 3.5; 5 OH without assignment], 3.85 (ddd, each $J \approx$ 3 Hz; 2-H), 3.29–3.56 (m, O–CH_2 and 2 ring Hs), 3.08 (ddd, $J \approx$ 3, 5.5, and 9 Hz; 3-H), 2.89 (dt, $J \approx$ 3.5 and 9 Hz; 2 ring Hs), 1.47 (q, $J \approx$ 7 Hz; β-CH_2), 0.85 (t, $J \approx$ 7 Hz; CH_3). ^{13}C N.M.R. (D_6-DMSO): δ = 80.23, 75.36, 72.50, 71.80, and 69.26 (5 d, ratio 1:1:1:2:1; 5 types of ring Cs), 69.12 (t; O—CH_2), 13.97 (q; CH_3). M.S. (270°C) m/z (%): 349 (100) $[M + 1]^{\oplus}$, 348 (8) $M^{\oplus}$, 181 (53), 109 (23). – $C_{18}H_{36}O_6$ (348.5); calculated C 62.94, H 10.41%; found C 62.21, H 10.24%.

*4-O-Dodecyl-**myo**-inositol* (**19**). A solution of 717 mg (2 mmol) **14** (R = $C_{12}H_{25}$) in 50 ml trifluoroacetic acid (80%) was stirred for 1 h at r.t., concentrated in vacuo, and the residue dissolved in CF. The product crystallized from this solution during 3 to 4 h in a fridge yielding 180 mg (26%) colourless crystals, its phase transition temperatures see Table I. No I.R. due to blear looking KBr tablet. ^{1}H N.M.R. (D_6-DMSO): 1. hydroxyl, 2. selected alkyloxy, and 3. ring protons, δ = 4.56, 4.51, 4.50, 4.37, and 4.34 (5 d of equal intensity, $J \approx$ 3, 2 × 4.5, 5.5, and 6 Hz; 2-OH and 4 more OH, respectively, without assignment), 3.59 (m; OCH_2), 0.86 (t, $J \approx$ 7 Hz; CH_3), 3.65 (ddd, 2 × $J \approx$ 2.5, 3 Hz; 2-H), 3.33 (ddd, $J \approx$ 4.5 and 2 × 9.5 Hz; 5-H or 6-H), 3.17 (ddd, $J \approx$ 2.5, 6, 9.5 Hz; 1-H or 3-H), 3.14 (dd, each $J \approx$ 9.5 Hz; 4-H), 3.07 (ddd, $J \approx$ 2.5, 5.5, 9.5 Hz; 3-H or 1-H), 3.07 and 2.95 (2 m; 6-H or 5-H). ^{13}C N.M.R. (D_6-DMSO): δ = 81.83, 74.78, 72.97, 71.59, and 71.33 (6 d of equal intensity; 6 ring Cs), 71.84 (t; OCH_2), 13.93 (q; CH_3). M.S. (290°C) m/z (%): 348 (<<1) $M^{\oplus}$, 270 (5), 241 (56), 109 (36), 73 (100). – $C_{18}H_{36}O_6$ (348.5); calculated C 62.04, H 10.41%; found: C 61.18, H 10.34%.

*5-O-Dodecyl-**myo**-inositol* (**20**). The hydrogenation (20 mg Pd/C catalyst, 10%, 4 bar) of 400 mg (0.5 mmol) **15** in a solvent mixture of 15 ml ML, 5 ml EA, and 1 ml glacial acetic acid was carried out in an autoclave at r.t. during 60 h. The usual work-up led to a colourless crystalline material which was recrystallized from ML, m.p. ≈ 250°C (P.M., dec.). Yield: 46 mg (26%). No I.R. due to blear looking KBr tablet. ^{1}H N.M.R. (D_6-DMSO): extremely broad resonances between δ = 4.5 and 4.3 as well as around 3.30 (all the OH), 3.67 (m; 2-H), 3.60 (t, $J \approx$ 7 Hz; OCH_2), 3.39 (dd, each $J \approx$ 9.5 Hz; 4-H and 6-H), 3.10 (dd, broad, $J \approx$ 1.5 and 9 Hz; 1-H and 3-H), 2.73 (dd, each $J \approx$ 9 Hz; 5-H), 0.84 (t, $J \approx$ 7 Hz; CH_3). ^{13}C N.M.R. (D_6-DMSO): δ = 83.94, 72.42, 72.32 and 71.94 (4 d, ratio 1:1:2:2; 4 types of inositol ring Cs, without assignment), 71.74 (t; OCH_2), 13.94 (q; CH_3). M.S. (230°C): m/z (%) = no $M^{\oplus}$, 239 (16), 73 (100). – $C_{18}H_{36}O_6$ (348.5); calculated C 62.04, H 10.41%; found C 62.26, H 10.39%.

*Mono-O-dodecyl-penta(O-benzyl)-**scyllo**-inositol.* This hexaether was prepared in an equal scale and purified accordingly to the **myo**-inositol stereoisomer **15** described above; the solvents applied here were toluene and TBME instead of benzene or toluene, respectively. The yield was 1.23 g (77%) colourless crystals, m.p. 71–72°C (Et., ML). ^{1}H N.M.R. ($CDCl_3$): δ = 3.82 (t, $J \approx 7$ Hz; OCH_2-alkyl), 3.45–3.57 (m; 2-H–6-H), 3.35 (dd, each $J \approx 9$ Hz; 1-H), 0.88 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 82.96, 82.86 and 82.82 (3 d, ratio 3:1:2; cyclohexane ring Cs), 75.93 and 74.26 (2 t, ratio 5:1; 5 OCH_2-phenyl and OCH_2-alkyl, resp.), 14.11 (q; CH_3). M.S. (280°C) m/z (%): no $M^{\oplus}$, 707 (<1) $[M - C_7H_7]^{\oplus}$, 181 (35), 91 (100) $[C_7H_7]^{\oplus}$. – $C_{53}H_{66}O_6$ (799.1); calculated C 79.66, H 8.33%; found C 79.34, H 8.42%.

*Mono-O-dodecyl-**scyllo**-inositol* (**21**). Its preparation in an equal scale was carried out likewise as described for the **myo**-inositol stereoisomer **17** yielding 90 mg (26%) colourless crystals from ML, m.p. see Table I. No. I.R. due to blear looking KBr tablet. ^{1}H (N.M.R. (D_6-DMSO): 1. hydroxyl, 2. selected alkyloxy, and 3. ring protons, δ = 4.68, 4.66 and 4.69 (3 d, ratio 2:1:2, $J \approx 3.5$, 3.5, and 4.5 Hz; 2- and 6-OH, 4-OH, and 3- and 5-OH, without assignment of the two hydroxyl pairs), 3.61 (t, $J \approx 7$ Hz; OCH_2), 2.86–3.05 (m; 2-H–6-H), 2.79 (dd, each $J \approx 9$ Hz; 1-H), 0.84 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. (D_6-DMSO): δ = 82.97, 74.29 and 73.84 (3 d, ratio 1:2:3; cyclohexane ring Cs), 71.88 (t; OCH_2), 13.94 (q; CH_3). M.S. (230°C) m/z (%): 349 (<<1) $[M + 1]^{\oplus}$, 270 (6), 241 (47), 239 (56), 73 (100). – $C_{18}H_{36}O_6$ (348.5); calculated C 62.04, H 10.41%; found C 61.76, H 10.40%.

*The dialkyl **myo**-inositol ethers* **23a** *and* **23b**. Mixtures of each 1.32 g (3 mmol) 1,4-di-O-benzyl-2,3-O-cyclohexylidene-**myo**-inositol[42] (**22**), 4 g powdered potassium hydroxide and 40 ml (excess) of hexyl or octyl bromide, respectively, were stirred for 2 h at 100°C. Usual work-up procedures followed by flash chromatographies (each 250 ml SC 60, Ø = 5 cm, LP/TBME 10: 1) yielded the corresponding products **23a** or **23b**, respectively, as yellowish, highly viscous oils.

a) *1,4-Di-O-benzyl-2,3-O-cyclohexylidene-5,6-di-O-hexyl-**myo**-inostiol* (**23a**), yield: 0.86 g (47%). ^{1}H N.M.R. ($CDCl_3$): δ = 4.87 – 4.70 (2 ABq, $J \approx 11$ or 12 Hz, respectively; 2 OCH_2-phenyl), 4.20 (dd, $J \approx 4$ and 5.5 Hz; 2-H), 4.01 and 3.54 (2 dd, $J \approx 5.5$ and 7 Hz or $J \approx 4$ and 8.5 Hz, respectively; 1-H and 3-H without assignment), 3.78–3.62 (m; 2 OCH_2-alkyl), 3.65, 3.62, and 3.10 (3 dd, $J \approx 7$ and 8.5, or each $J \approx 8.5$ and 9.5 Hz for the second and third doublett, respectively; 4-H, 5-H and 6-H without assignment), 0.89 and 0.88 (2 t, $J \approx 6$ Hz; 2 CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 138.49 (s; quart. arom. Cs), 110.21 (s; quart. aliph. C), 82.82, 82.27, 80.88, 78.65, 77.15, and 74.13 (6 d of equal intensity; the six inositol ring Cs), 74.03, 73.43, 73.15, and 73.11 (4 t of equal intensity; the four OCH_2), 14.03 (q; CH_3). M.S. (150°C) m/z (%): 608 (15) $M^{\oplus}$, 517 (4) $[M - 91]^{\oplus}$, 91 (100) $[C_7H_7]^{\oplus}$. – $C_{38}H_{56}O_6$ (608.8); calculated C 74.96, H 9.27%; found C 74.65, H 8.96%.

b) *1,4-Di-O-benzyl-2,3-O-cyclohexylidene-5,6-di-O-octyl-**myo**-inositol* (**23b**), yield: 1.28 g (64%). ^{1}H N.M.R. ($CDCl_3$): δ = 4.87–4.70 (2 ABq, $J \approx 11.5$ or 12.5 Hz,

respectively; 2 OCH_2-phenyl), 4.20 (dd, $J \approx 4$ and 5 Hz; 2-H), 4.01 and 3.54 (2 dd, $J \approx 5$ and 7 Hz or $J \approx 4$ and 8.5 Hz, respectively; 1-H and 3-H without assignment), 3.78 – 3.63 (m; 2 OCH_2-alkyl), 3.64, 3.62, and 3.10 (3 dd, twice $J \approx 7$ Hz, or each $J \approx 9$ Hz for the second and third doublett, respectively; 4-H, 5-H, and 6-H without assignment), 0.89 and 0.88 (2 t, $J \approx 6$ Hz; 2 CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 138.82 and 138.50 (2 s; quart. arom. Cs), 110.21 (s; quart. aliph. C), 82.82, 82.28, 80.89, 78.66, 77.16, and 74.13 (6 d of equal intensity; the six inositol ring Cs), 74.02, 73.42, 73.15, and 73.10 (4 t of equal intensity; the four OCH_2), 14.50 (q; CH_3). M.S. (140°C) m/z (%): 664 (41) $M^{\oplus}$, 573 (12) $[M - 91]^{\oplus}$, 91 (100) $[C_7H_7]^{\oplus}$. – $C_{42}H_{64}O_6$ (664.5); calculated C 75.86, H 9.70%; found C 72.55, H 9.93%.

*The dialkyl **myo**-inositol ethers* **24a** *and* **24b**. The hydrolyses each of 2 mmol of the inositol derivatives **23a** and **23b**, respectively, in each 50 ml acetic acid (80%) under stirring during 1 h at 90°C furnished after usual work-up procedures yellow oils which crystallized slowly.

a) *1,4-Di-O-benzyl-5,6-di-O-hexyl-**myo**-inositol* (**24a**), yield: 0.76 g (72%) colourless crystals from HT, m.p. 80.0°C (P.M.). I.R. (CCl_4): ν = 3590 hydroxyl. ^1H N.M.R. ($CDCl_3$): δ = 4.98–4.70 and 4.74–4.66 (2 ABq, each $J \approx 11.5$ Hz; 2 OCH_2-phenyl), 4.14 (dd, $J \approx 3$ Hz; 2-H), 3.85–3.73 (m; 2 OCH_2-alkyl), 3.71, 3.65, and 3.17 (3 dd, each $J \approx 9.5$ Hz; 4-H, 5-H, and 6-H without assignment), 3.4 (ddd, $J \approx 3$, 4, and 9.5 Hz; 3-H), 3.31 (dd, $J \approx 3$ and 9.5 Hz; 1-H), 2.44 (s, broad; 2-OH), 2.40 (d, $J \approx 4$ Hz; 3-OH), 0.89 and 0.88 (2 t, $J \approx 6.5$ Hz; 2 CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 138.64 and 138.01 (2 s; quart. arom. Cs), 83.35, 81.53, 81.22, 79.82, 71.56, and 69.28 (6 d of equal intensity; the six inositol ring Cs), 75.44, 74.01, 73.39, and 72.76 (4 t of equal intensity; the four OCH_2), 14.02 (q; CH_3). M.S. (150°C) m/z (%): 528 (11) $M^{\oplus}$, 437 (53) $[M - 91]^{\oplus}$, 91 (100) $[C_7H_7]^{\oplus}$. – $C_{32}H_{48}O_6$ (528.7); calculated C 72.69, H 9.15%; found C 72.49, H 8.96%.

b) *1,4-Di-O-benzyl-5,6-di-O-octyl-**myo**-inositol* (**24b**), yield: 0.59 g (50%) colourless crystals from HT, m.p. 71.5°C (P.M.). I.R. (CCl_4): ν = 3581 (hydroxyl). ^1H N.M.R. ($CDCl_3$): δ = 4.98–4.7 and 4.74–4.65 (2 ABq, each $J \approx 11.5$ Hz; 2 OCH_2-phenyl), 4.14 (m; 2-H), 3.85–3.73 (m; 2 OCH_2-alkyl), 3.70, 3.64, and 3.17 (3 dd, each $J \approx$ 9.5 Hz; 4-H, 5-H, and 6-H without assignment), 3.39 (ddd, $J \approx 3$, 4, and 9.5 Hz; 3-H), 3.31 (dd, $J \approx 3$ and 9.5 Hz; 1-H), 2.44 (s, broad; 2-OH), 2.41 (m; 3-OH). ^{13}C N.M.R. ($CDCl_3$): δ = 138.62 and 138.00 (2 s; quart. arom. Cs), 83.35, 81.54, 81.19, 79.81, 71.54, and 69.27 (6 d of equal intensity; the six inositol ring Cs), 75.45, 74.03, 73.91, and 72.78 (4 t of equal intensity; the four OCH_2), 14.11 and 14.06 (2 q; 2 CH_3). M.S. (205°C) m/z (%): 584 (0.1) $M^{\oplus}$, 493 (3) $[M - 91]^{\oplus}$, 91 (100) $[C_7H_7]^{\oplus}$. – $C_{36}H_{56}O_6$ (584.8); calculated C 73.93, H 9.65%; found C 74.04, H 9.31%.

*The dialkyl **myo**-inositol ethers* **25a** *and* **25b**. The hydrogenations (100 mg Pd/C catalyst, 10%, 3.5 bar) each of 1 mmol of the inositol diols **24a** and **24b**, respectively, in each 100 ml ML during 10 h at r.t. delivered after usual work-up procedures colourless products.

a) *4,5-Di-O-hexyl-myo-inositol* (**25a**), yield: 211 mg (61%) crystals from ML, its phase transitions see in Table II. No I.R. due to blear looking KBr tablet. ^{1}H N.M.R. (D_6-DMSO): δ = 4.57, 4.52, 4.43, and 4.41 (4 d of equal intensity, $J \approx$ 3.5, 5, 6, and 5.5 Hz, respectively; 4 hydroxyl), 3.7–3.61, 3.21–3.15, 3.1–3.05, and 2.78 (3 m and 1 dd, each $J \approx 9$ Hz; the inositol ring Hs without assignment), 3.53 (m; OCH_2), 0.85 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. (D_6-DMSO): δ = 83.61, 81.64, 72.85, 72.67, 71.70, and 71.63 (6 d of equal intensity; the six inositol ring Cs), 72.27 (1 t; 2 OCH_2), 31.37, 30.06, 25.41, and 22.16 (4 t of equal intensity; four types of CH_2), 13.93 (q; CH_3). M.S. (150°C) m/z (%): 348 (0.2) $M^{\oplus}$, 157 (100), 73 (66). – $C_{18}H_{36}O_6$ (348.5); calculated C 62.04, H 10.41%; found C 61.46, H 10.02%.

b) *4,5-Di-O-octyl-myo-inositol* (**25b**), yield: 323 mg (80%) crystals from ML, its phase transitions see Table II. No I.R. due to blear looking KBr tablet. ^{1}H N.M.R. (D_6-DMSO): δ = 4.57, 4.52, 4.43, and 4.41 (4 d of equal intensity, $J \approx$ 3.5, 5, 6, and 5.5 Hz, respectively; 4 hydroxyl), 3.7–3.61, 3.21–3.15, 3.1–3.05, and 2.78 (3 m and 1 dd, each $J \approx 9$ Hz; the inositol ring Hs without assignment), 3.52 (m; OCH_2), 0.84 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. (D_6-DMSO): δ = 83.59, 81.61, 72.84, 72.67, 71.68, and 71.64 (6 d of equal intensity; the six inositol ring Cs), 72.28 and 72.26 (2 t; 2 OCH_2), 31.32, 30.09, 29.10, 28.80, 25.76, and 22.13 (6 t of equal intensity; six types of CH_2), 13.94 (q; CH_3). M.S. (200°C) m/z (%): 405 (1) $[M + 1]^{\oplus}$, 294 (3), 186 (100), 73 (76), 71 (46), 57 (68). – $C_{22}H_{44}O_6$ (404.6); calculated C 65.31, H 10.92%; found C 65.21 H 10.65%.

1,4-Di-O-benzyl-3,5,6-tri-O-hexyl-myo-inositol (**26a**). A mixture of 793 mg (1.5 mmol) **24a**, 382 mg (1.8 mmol) iodohexane, and 8 g powdered potassium hydroxide in 25 ml benzene was stirred at 80°C for 6 hs. A usual work-up including a flash chromatography (100 ml SC 60, ∅ = 3 cm, HT/EA 5:1) led to 182 mg (20%) of a yellowish oil. I.R. (CCl_4): ν = 3570 (hydroxyl). ^{1}H N.M.R. ($CDCl_3$): δ = 4.84–4.76 and 4.78–4.68 (2 ABq, $J \approx$ 10.5 or 11.5 Hz, respectively; 2 OCH_2-phenyl), 4.19 (dd, broad, $J \approx 2.5$ Hz; 2-H), 3.85–3.5 (m; 3 OCH_2-alkyl and 2 inositol ring Hs), 3.26 and 3.14 (2 dd, $J \approx$ 2.5 and 9.5 Hz; 1-H and 3-H without assignment), 3.12 (t, $J \approx 9.5$ Hz; 1 inositol ring H), 2.40 (s, broad; 2-OH), around 0.87 (3 t, each $J \approx 6.5$ Hz; 3 CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 138.95 and 138.22 (2 s; quart. arom. Cs), 83.13, 81.07, 81.05, 83.38, 79.79, and 67.52 (6 d; 6 inositol ring Cs without assignment), 75.80, 74.12, 74.00, 72.82, and 71.05 (5 t; 5 OCH_2 without assignment), 14.01 (t; CH_3). M.S. (160°C) m/z (%): 613 (0.1) $[M + 1]^{\oplus}$, 521 (1) $[M - 91]^{\oplus}$, 254 (42), 170 (34), 91 (100) $[C_7H_7]^{\oplus}$, 57 (8). – $C_{38}H_{60}O_6$ (612.9); calculated C 74.47, H 9.87%; found C 74.34, H 9.70%.

1,4,5-Tri-O-hexyl-myo-inositol (**27a**). A hydrogenation (12 mg Pd/C catalyst, 10%, 3.5 bar) of 122 mg (0.2 mmol) of the preceding **26a** in 50 ml ML for 3 h at r.t. yielded 90 mg crude material. A crystallization from ML left 30 mg (35%) white crystals. The phase transition data see in Table II. I.R. (CCl_4): ν = 3587 (hydroxyl). ^{1}H N.M.R. ($CDCl_3$): δ = 4.23 (dd, each $J \approx 3$ Hz; 2-H), 3.85 (dd, $J \approx 9$ Hz; 6-H), 3.54 (dd, $J \approx 9$ Hz; 4-H), 3.45 (ddd, $J \approx$ 3.5, 3.5, and 9 Hz; 3-H), 3.14 (dd, $J \approx$ 3 and 9 Hz; 1-H), 3.09 (dd, $J \approx 9$ Hz; 5-H), between ≈3.5–≈3.89 (4 m; 3

OCH_2), 2.58, 2.51, and 2.45 (broad signals; 3 OH), 0.88 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 82.58, 80.77, 80.09, 72.37, 72.03, and 68.11 (6 d; the inositol ring Cs without assignment), 73.60, 73.31, and 70.61 (3 t; 3 OCH_2 without assignment), 14.02 (q; CH_3). M.S. (160°C) m/z (%); 432 (0.1) $M^{\oplus}$, 241 (36), 157 (100), 73 (50). – $C_{24}H_{48}O_6$ (432.6); high resolution, calculated 432.3451; found 432.3451.

*2,4,6-Tri-O-benzyl-1,3,5-tri-O-octyl-**myo**-inositol* (**29**). The alkylation was carried out with 0.90 g (2 mmol) 2,4,6-tris-O-benzyl-**myo**-inositol[34] (**28**) which was heated under stirring with 3 g powdered potassium hydroxide in 30 ml bromooctane for 14 h. After the addition of 100 ml water the product was extracted with CF and further worked up as usual. A subsequent flash chromatography on 100 ml SC 60 under the elution of LP/EA 40:1 yielded 1.27 g (81%) colourless oil. ^1H N.M.R. ($CDCl_3$): δ = 4.90–4.77 (ABq, $J \approx 10.5$ Hz; 2 OCH_2-phenyl at C-4 and C-6), 4.86 (s, broad; OCH_2-phenyl at C-2), 4.05 (dd, each $J \approx 2$ Hz; 2-H), 3.89 (t, $J \approx 9.5$ Hz; 4-H and 6-H), 3.79 (t, $J \approx 7$ Hz and m, ratio 1:2; 3 OCH_2-alkyl), 3.22 (dd, each $J \approx 9.5$ Hz; 5-H), 3.15 (dd, $J \approx 2$ and 9.5 Hz; 1-H and 3-H), 0.79 and 0.78 (2 t, $J \approx 7$ Hz, ratio 2:1; 3 CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 139.30 and 139.18 (2 s; quart. arom. Cs), 83.57, 81.69, 81.49, and 77.21 (4 d, ratio 1:2:2:1; the inositol ring Cs without assignment), 76.53, 75.73, 74.11, and 71.01 (4 t; 4 groups of OCH_2 without assignment), 14.09 (q; CH_3). M.S. (170°C) m/z (%): no $M^{\oplus}$, 288 (62), 105 (80), 91 (86) $[C_7H_7]^{\oplus}$, 71 (84), 57 (100). – $C_{51}H_{78}O_6$ (787.1); calculated C 77.82, H 9.99%; found C 77.96, H 9.67%.

*1,3,5-Tri-O-octyl-**myo**-inostiol* (**30**). A hydrogenation (300 mg Pd/C catalyst, 10%, 3.5 bar) of 3.15 g (4 mmol) of the above described precursor **29** in 50 ml glacial acetic acid during 12 h at r.t. and a usual work-up including a flash chromatography on 100 ml SC 60 under the elution with HT/EA 3:1 yielded 0.98 g (47%) **30** as a colourless oil. I.R. (CCl_4): ν = 3580 (hydroxyl). ^1H N.M.R. ($CDCl_3$): δ = 4.31 (dd, each $J \approx 3$ Hz; 2-H), 3.88 (dd, $J \approx 1.5$ and 9 Hz; 4-H and 6-H), 3.79, 3.69, and 4.51 (3 m; 3 OCH_2), 3.11 (dd, $J \approx 3$ and 9.5 Hz; 1-H and 3-H), 3.08 (t, $J \approx$ 9.5 Hz; 5-H), 2.52 (d, $J \approx 1.5$ Hz; 2 OH, 4-OH and 6-OH), 2.31 (s, broad; 2-OH), 0.88 and 0.87 (2 t, ratio 2:1, $J \approx 7$ Hz; 3 CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 82.24, 80.14, 71.67, and 65.62 (4 d, ratio 1:2:2:1; the inositol ring Cs without assignment), 72.82 and 70.52 (2 t, ratio 1:2, 3 OCH_2 without assignment), 14.06 (q; CH_3). M.S. (180°C) m/z (%): 516 (1) $M^{\oplus}$, 405 (1.5), 292 (100), 198 (91). – $C_{30}H_{60}O_6$ (516.8); calculated C 69.72, H 11.70%; found C 69.48 H 11.67%.

*4,6-Di-O-octyl-**myo**-inositol orthoformate* (**31**). A mixture of 11.4 g (60 mmol) of **myo**-inositol orthoformate[33] (**14**, R = H), 150 mg imidazol, and 3.24 g (135 mmol) sodium hydride was stirred in 300 ml dry *N,N*-dimethylformamide for 1 h at r.t. which was continued for further 24 h after 24.3 g (126 mmol) 1-bromooctane had been added. The work-up started with the addition of 15 ml saturated aqueous solution of ammonium chloride and 300 ml water, twice repeating extraction with each 300 ml dichloromethane, etc., and was followed by column chromatography (600 ml SC 60, LP/EA 4:1).

In between the most unpolar 2,4,6-triether of **14** (R = H) (3.4 g = 11%) and

the 4-(mono-)ether of **14** (R = H) (10.8 g = 60%) at the end a mixture of two diethers of **14** (R = H) (6.15 g) was isolated which could be separated by flash chromatography on 300 ml SC 60 (Ø = 5 cm, CF) furnishing next 4.24 g (17%) of the 4,6-diether **31** and finally 1.91 g (8%) of the 2,4-diether of **14** (R = H). The characterization of these four products are described below in the order of their isolation:

1) *2,4,6-Tri-O-octyl-myo-inositol orthoformate*, a colourless oil. ^{13}C N.M.R. ($CDCl_3$): δ = 103.14 (d; formate C), 74.37, 70.42, 68.22, and 67.94 (4 d, ratio 2:2:1:1; inositol ring Cs without assignment), 69.68 and 69.60 (2 t, ratio 2:1; 3 OCH_2), 13.98 (q; CH_3). – $C_{31}H_{58}O_6$ (526.8); calculated C 70.68, H 11.10%; found C 70.86, H 10.90%.

2) **31**, a colourless oil. I.R. (CCl_4): ν = 3585 (hydroxyl). ^1H N.M.R. ($CDCl_3$): δ = 5.47 (d, $J \approx 1$ Hz with 2-H; orthoformate H), 4.40 (tt, $J \approx 2$ and 3.5 Hz; 5-H), 4.27–4.17 (m; the four inositol Hs 1-H, 3-H, 4-H, and 6-H), 4.05 (ddt, $J \approx 1$ and 2 and 11 Hz; 2-H), 3.57–3.43 (2 m; 2 OCH_2), 3.04 (d, broad, $J \approx 11$ Hz; 2-OH), 0.88 (t, $J = 6.5$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 103.29 (d; formate C), 74.20, 73.02, 67.99, and 61.32 (4 d; ratio 2:2:1:1; inositol ring Cs without assignment), 69.73 (t; 2 OCH_2), 14.01 (q; CH_3). M.S. (50°C) m/z (%): 414 (2) $M^{\oplus}$, 185 (100). – $C_{23}H_{42}O_6$ (414.6); calculated C 66.63, H 10.21%; found C 65.44, H 10.28%.

3) *2,4-Di-O-octyl-myo-inositol orthoformate*, a colourless oil. ^{13}C N.M.R. ($CDCl_3$): δ = 102.48 (d; formate C), 75.09, 71.90, 69.80, 67.85, 67.43, and 67.13 (6 d of equal intensity; inositol ring Cs without assignment), 71.73 and 69.74 (2 t; 2 OCH_2), 13.97 and 13.95 (2 q; 2 CH_3). – $C_{23}H_{42}O_6$ (414.6); calculated C 66.63, H 10.21%; found C 66.10, H 10.30%.

4) *4-O-Octyl-myo-inositol orthoformate* (**14**, R = C_8H_{17}), m.p. 30.9°C (P.M.). I.R. (CCl_4): ν = 3511 and 3584 (hydroxyl). ^{13}C N.M.R. ($CDCl_3$): δ = 102.59 (d; formate C), 74.88, 74.68, 71.32, 67.71, 67.07, and 60.50 (6 d of equal intensity; inositol ring Cs without assignment), 71.32 (t; OCH_2); 13.96 (q; CH_3). – $C_{15}H_{26}O_6$ (302.4); calculated C 59.58, H 8.67%; found C 59.95, H 8.92%.

4,6-Di-O-octyl-myo-inositol (**32**). A solution of 829 mg (2 mmol) **31** in 30 ml trifluoro acetic acid (80%) was stirred for 1 h at r.t., concentrated, twice diluted with ML and each time again concentrated in vacuo (0.1 bar) at 80°C. A flash chromatography of the residue on 100 ml SC 60 (Ø = 2.8 cm, EA/LP/ML 10:10:1) yielded 400 mg (49%) highly viscous, colourless oil. I.R. (CCl_4): ν = 3578 and 3413, broad (hydroxyl). ^1H N.M.R. ($CDCl_3$): δ = 4.17 (dd, each $J \approx 2.5$ Hz; 2-H), 3.83–3.70 (m; 2 OCH_2), ≈ 3.6–≈3.4 (m; 5 inositol ring Hs), 0.88 (t, $J \approx 6.5$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 81.03 and 71.39 (2 d, ratio 1:3; inositol ring Cs), 72.78 (t; 2 OCH_2), 14.04 (q; 2 CH_3). M.S. (150°C) m/z (%): 404 (2) $M^{\oplus}$, 297 (50), 185 (100), 73 (98), 57 (98). – $C_{22}H_{44}O_6$ (404.6); high resolution, calculated 404.3138; found 404.3138.

3,4-Di-O-hexyl-1,2:5,6-di-O-cyclohexylidene-(–)-inositol (**35**). Into a mixture of 1.08 g (45 mmol) sodium hydride in 100 ml *N,N*-dimethylformamide (DMF) stirred

at r.t. for 30 min a solution of 3.06 g (9 mmol) 1,2:5,6-di-O-cyclohexylidene-(−)-inositol[43] (**34**) in 50 ml DMF was added and further stirred for 2 h. After the addition of 5.94 g (36 mmol) hexylbromide and heating of the mixture at 70°C for 2 d under anhydrous conditions the usual work-up (concentration, dissolution of the residue in CF, etc.) led to a syrup which was purified by column chromatography (300 ml SC 60, $\emptyset$ = 3 cm, LP/EA 10:1) yielding 1.09 g (24%) yellowish oil, $[\alpha]_D^{20} = -3°$ (CF). ^{13}C N.M.R. ($CDCl_3$): δ = 109.84 (s; the quart. Cs), 80.33, 78.78, and 76.20 (3 d; inositol ring Cs without assignment), 14.04 (q; CH_3). M.S. (120°C) m/z (%): 509 (13) $[M + 1]^{\oplus}$, 99 (68) $[C_6H_{11}O]^{\oplus}$, 85 (76) $[C_6H_{13}]^{\oplus}$, 55 (100). – $C_{30}H_{52}O_6$ (508.7); calculated C 70.82, H 10.30%; found C 70.89, H 9.98%.

3,4-Di-O-hexyl-(−)-inositol (**36**). 1.02 g (2 mmol) **35** was heated in a mixture of 55 ml glacial acetic acid and 14 ml water for 2 h at 100°C. The usual work-up (concentration, dissolution of the residue in ML, etc.) including a column chromatography (eluent: CF/ML 15:1) as described above yielded 168 mg (24%) colourless **36** as highly viscous oil which crystallized after few days at r.t., its phase transitions see Table II. $[\alpha]_D^{20} = -34°$ (ethanol). I.R. (CCl_4): ν = 3415, broad (hydroxyl). ^{1}H N.M.R. (D_6-DMSO): δ = 4.71 (d, $J \approx 3$ Hz; axial hydroxyls), 4.83 (d, $J \approx 6.5$ Hz, equatorial hydroxyls), 3.64 and 3.54 (each dt, with $J \approx 9$ and 7 Hz, respectively; H_a and H_b of two OCH_2), 3.58, 3.49, and 3.09 (3 m; 3 pairs of inositol ring Hs), 0.85 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 80.55, 71.34, and 70.77 (3 d; 3 pairs of inositol ring Cs), 73.02 (d; OCH_2), 31.70, 30.19, 25.71, and 22.58 (4, t; 4 CH_2), 13.99 (q; CH_3). M.S. (140°C) m/z (%): 349 (6) $[M + 1]^{\oplus}$, 348 (8) $M^{\oplus}$, 157 (100), 85 (80) $[C_6H_{13}]^{\oplus}$, 73 (88). – $C_{18}H_{36}O_6$ (348.5); calculated C 62.04, H 10.41%; found C 61.81, H 10.08%.

Tetrabenzyloxy-1,4-benzoquinone. A mixture of 4.56 g (20 mmol) tetramethoxy-1,4-benzoquinone[31] (**37**) and a catalytical amount of sodium benzyl alcoholate in an excess (35 ml) of benzyl alcohol was heated to 140°C. The remaining benzyl alcohol (plus the ML formed) was slowly destilled off under reduced pressure during 3 h, the oily residue deluted in CF, filtered (silica gel), and crystallized three times from LP/EA. Yield: 5.86 g (55%) yellow product, m.p. 114.1°C (P.M.). I.R. ($CHCl_3$): ν = 1680 (carbonyl). ^{1}H N.M.R. ($CDCl_3$): δ = 7.34 and 5.14 (2 s, broad; phenyl Hs and OCH_2). ^{13}C N.M.R. ($CDCl_3$): δ = 180.43 (s; CO), 142.91 and 136.04 (2 s; 2 types of quart. Cs), 71.46 (t, 4 OCH_2). M.S. (170°C) m/z (%): 532 (8) $M^{\oplus}$, 91 (100). – $C_{34}H_{28}O_6$ (532.6); high resolution, calculated 532.1886; found 532.1886.

Dibenzyl-[4-hydroxy-2,3,5,6-tetra(benzyloxy)]phenyl phosphate. In analogy to a related reaction[35] a mixture of 10.6 g (20 mmol) tetrabenzyloxy-1,4-benzoquinone and ≈14 g (≈40 mmol) tribenzyl phosphite in 200 ml LP was stirred for 3 d and the formed white precipitate filtered off. Crystallization from LP/EA yielded 14.7 g (92%), m.p. 98.9°C (P.M.). I.R. ($CHCl_3$): ν = 3510 (hydroxyl). ^{1}H N.M.R. (D_6-DMSO): δ = 4.89–5.04 (non-symmetric m; all the OCH_2), no detectable hydroxyl. ^{13}C N.M.R. ($CDCl_3$): selected features, δ = 75.66 and 69.49/69.44 (t and dt, ratio 2:1; phenyl-OCH_2 and P–OCH_2, respectively). M.S. (150°C) m/z (%):

794 (1) $M^{\oplus}$, 793 (1) $[M - H]^{\oplus}$, 91 (100). – $C_{48}H_{43}O_9P$ (794.8); high resolution, calculated 794.2645; found 794.2645.

Dibenzyl-[4-dodecyloxy-2,3,5,6-tetra(benzyloxy)]-phenylphosphate (**38**). The O-alkylation of the preceding substituted 4-hydroxylphenyl phosphate was carried out with 3.97 g (5 mmol) of it dissolved in 50 ml dry *N,N*-dimethylformamide. After the addition of 144 mg (6 mmol) sodium hydride and stirring of this mixture under Argon for 1 h it was reacted with 2.49 g (10 mmol) dodecyl bromide and newly stirred for 2 h at 60°C. A usual work-up using TBME as a solvent and purification by flash chromatography (100 ml SC 60, $\emptyset$ = 3 cm, LP/EA 10:1) yielded 2.1 g (44%) of a colourless oil which crystallized after few hours, m.p. 52.4°C (P.M.). ^{1}H N.M.R. ($CDCl_3$): δ = 4.92–5.14 (m; OCH_2-phenyl and P-OCH_2), 4.00 (t, $J \approx 7$ Hz; OCH_2-alkyl), 0.88 (q, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 75.92, 75.79 (2 t; OCH_2-phenyl), 74.60 (t; OCH_2-alkyl), 69.60/69.54 (t and dt; P–OCH_2); the ratio of these signals is 2:2:1:2; 14.10 (q; CH_3). M.S. (150°C) m/z (%): 963 (2) $[M + 1]^{\oplus}$, 872 (4) $[M + 1 - 91]^{\oplus}$, 271 (5), 181 (25), 91 (100). – $C_{60}H_{67}O_9P$ (963.2); high resolution, calculated 962.4523; found 962.4523.

4-Hydroxy-2,3-5-6-tetra(benzyloxy)-phenyl dodecyl ether. After 8.2 ml (13.2 mmol) of a methyl lithium solution (1.6 M in diethyl ether) had been added under Argon at −78°C to 2.12 g (2.2 mmol) **38** dissolved in 20 ml of dry tetrahydrofuran the mixture was first stirred for 2 h at −78°C and then for 1 h at r.t. The excess of the lithium organyl was destroyed by addition of 20 ml of ML, the mixture acidified with acetic acid and worked up in the usual way. A flash chromatography (150 ml SC 60, LP/EA 20: 1) of the crude material furnished 0.8 g (52%) of the desired pentaether as a colourless oil. I.R. ($CHCl_3$): ν = 3530 (hydroxyl). ^{1}H N.M.R. ($CDCl_3$): δ = 5.02 and 5.08 (2 s, broad; 2 groups of OCH_2), 3.96 (t, $J \approx 7$ Hz; OCH_2-alkyl), 0.89 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 75.15 and 75.61 (2 t; 2 types of OCH_2-phenyl), 74.54 (t; OCH_2-alkyl), 14.07 (q; CH_3). M.S. (300°C) m/z (%): 702 (2) $M^{\oplus}$, 239 (8), 183 (64), 140 (58), 96 (40), 57 (100). – $C_{46}H_{54}O_6$ (702.9); high resolution, calculated 702.3920; found 702.3920.

Pentahydroxyphenyl dodecyl ether (**39**). A hydrogenation (0.35 g Pd/C catalyst, 10%, 3.5 bar, 2 d) of 0.70 g (1 mmol) of the preceding dodecyl tetra(benzyloxy)phenyl ether dissolved in 40 ml EA yielded 0.19 g (55%) white crystals after a usual work-up and crystallization from HT/EA under Argon, m.p. see Table I; **39** is very sensitive to air. I.R. (KBr): ν = 3620 and 3690 (hydroxyl). ^{1}H N.M.R. (D_6-DMSO): δ = 7.4–7.8 (m, very broad, hydroxyl), 3.74 (t, $J \approx 7$ Hz; OCH_2), 0.85 (t, $J \approx 7$. Hz; CH_3). ^{13}C N.M.R. (D_6-DMSO): δ = 132.18, 131.53, 129.04 and 127.03 (4 s, ratio 2:1:1:2; quart. aromatic Cs), 72.28 (t; OCH_2), 14.04 (q; CH_3). M.S. (210°C) m/z (%): 342 (5) $M^{\oplus}$, 174 (100) $[M - C_{12}H_{24}]^{\oplus}$, 57 (25). – $C_{18}H_{30}O_6$ (342.4); high resolution, calculated 342.2042; found 342.2042.

The 2,5-dialkyl ethers **40a** *and* **40b** *of tetrahydroxy-1,4-benzoquinone.* Mixtures of each 4.56 g (20 mmol) tetramethoxy-1,4-benzoquinone[31] (**37**) and catalytical amounts of the corresponding sodium alkanolate in about 30 to 40 ml (excess) of

the respective primary alcohol, i.e. hexanol or octanol, were heated to 140°C. The alkanols were slowly destilled off under reduced pressure (3 h) and the oily residues were purified by chromatography (400 ml SC 60, LP/EA 40:1) yielding the corresponding two tetraalkoxy-1,4-benzoquinones (9.8 g = 96% or 12.2 g = 98%, respectively) as deep red, oily products, not characterized. The subsequent partial ether cleavages of these two intermediate tetraethers are described in the following example. A mixture of 4.07 g (≈8 mmol) of the above obtained crude tetrahexyloxy-1,4-benzoquinone, 80 mg adogen 464 (commercially available), 20 ml heptane, and 40 ml aqueous potassium hydroxide (40%) was refluxed for 2 h. After acidification with aqueous hydrogen chloride the product was extracted with ether, the combined extracts were washed with water, dried over magnesium sulfate, and the solvent was evaporated. Several crystallizations of the residue from HT yielded 1.13 g (≈42%) *2,5-dihexyloxy-3,6-dihydroxy-1,4-benzoquinone* (**40a**), brown in colour, m.p. 124.3°C (P.M.). I.R. ($CHCl_3$): ν = 3400, broad (hydroxyl), 1650 (carbonyl). ^1H N.M.R. ($CDCl_3$): δ = 6.81 (s; OH), 4.23 (t, $J \approx 7$ Hz; 2 OCH_2), 0.88 (t, $J \approx 7$ Hz; 2 CH_3). ^{13}C N.M.R. ($CDCl_3$): δ = 133.22 (s; 6 quart. arom. Cs), 72.97 (t; 2 OCH_2), 31.34, 29.75, 25.11, and 22.40 (4 t; 4 types of CH_2), 13.83 (q; 2 CH_3). M.S. (110°C) m/z (%): 340 (13) $M^{\oplus}$, 256 (12) $[M - C_6H_{12}]^{\oplus}$, 172 (100) $[M - 2\ C_6H_{12}]^{\oplus}$. – $C_{18}H_{28}O_6$ (340.4); high resolution, calculated 340.1886; found 340.1886.

A similar trial as described above, but starting from 9.31 g (≈15 mmol) of crude tetraoctyloxy-1,4-benzoquinone furnished 2.66 g (≈45%) *2,5-dioctyloxy-3,6-dihydroxy-1,4-benzoquinone* (**40b**), brown in colour, m.p. 113.0°C (P.M., HT). I.R. ($CHCl_3$): ν = 3400, broad (hydroxyl), 1650 (carbonyl). ^1H N.M.R. ($CDCl_3$): δ = 6.80 (s; OH), 4.23 (t, $J \approx 7$ Hz; 2 OCH_2), 0.88 (t, $J \approx 7$ Hz; 2 CH_3). ^{13}C N.M.R. ($CDCl_3$: δ = 133.26 (s; 6 quart. arom. Cs), 73.07 (t; 2 OCH_2), 31.73, 29.89, 29.21, 29.15, 25.54, and 22.59 (6 t; 6 types of CH_2), 14.02 (q; 2 CH_3). M.S. (120°C) m/z (%): 396 (36) $M^{\oplus}$, 284 (25) $[M - C_8H_{16}]^{\oplus}$, 172 (100) $[M - 2\ C_8H_{16}]^{\oplus}$. – $C_{22}H_{36}O_6$ (396.5); high resolution, calculated 396.2512; found 396.2512.

The 1,4-dialkyl ethers **41a** *and* **41b** *of hexahydroxybenzene.* Each of the two dialkoxybenzoquinone derivatives **40a** and **40b** described above were dissolved in EA and hydrogenated in presence of 20 mg platinum oxide during 15 min under normal pressure. A usual work-up procedure and crystallization from toluene (air has to be excluded!) yielded colourless products which easily get red-brown in the air. Therefore, their melting points must be determined in a quick way, e.g., advantageously between glass plates in a pre-heated hot stage using a (polarizing) microscope.

a) *1,4-Dihexyloxy-tetrahydroxybenzene* (**41a**), 0.15 g (88%), starting from 0.17 g (0.5 mmol) **40a** in 20 ml solvent, m.p. 112.2°C (P.M., toluene). I.R. ($CDCl_3$): ν = 3550 (hydroxyl). ^1H N.M.R. (D_6-DMSO): δ = 7.60 (s, broad; OH), 3.80 (t, $J \approx 7$ Hz; OCH_2), 0.86 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. (D_6-DMSO): δ = 132.68 and 131.77 (2 s; quart. arom. Cs, C–OR and C–OH, respectively, ratio 1:2), 72.15 (t; 2 OCH_2), 31.25, 29.43, 25.07, and 22.14 (4 t; 4 types of CH_2), 13.95 (q, 2 CH_3). M.S. (140°C) m/z (%): 342 (18) $M^{\oplus}$, 258 (5) $[M - C_6H_{12}]^{\oplus}$, 174 (100) $[M - 2\ C_6H_{12}]^{\oplus}$. – $C_{18}H_{30}O_6$ (342.4); high resolution, calculated 342.2042; found 342.2042.

b) *1,4-Dioctyloxy-tetrahydroxybenzene* (**41b**), 0.70 g (89%), starting from 0.79 g (2 mmol) **40b** in 20 ml solvent, m.p. 112.1°C (P.M., toluene), mixed m.p. with **41a** ≈ 99°C (P.M.). I.R. ($CHCl_3$): ν = 3550 (hydroxyl). ^{1}H N.M.R. (D_6-DMSO): δ = 7.59 (s, broad; OH), 3.80 (t, $J \approx 7$ Hz; OCH_2), 0.85 (t, $J \approx 7$ Hz; CH_3). ^{13}C N.M.R. (D_6-DMSO): δ = 132.65 and 131.75 (2 s; quart. arom. Cs, C–OR and C–OH, respectively, ratio 1:2), 72.13 (t; 2 OCH_2), 31.30, 29.46, 28.98, 28.76, 25.40, and 22.14 (6 t; 6 types of CH_2), 14.01 (q; 2 CH_3). MS. (100°C) m/z (%): 398 (24) $M^{\oplus}$, 286 (9) $[M - C_8H_{16}]^{\oplus}$, 174 (100) $[M - 2\ C_8H_{16}]^{\oplus}$. – $C_{22}H_{38}O_6$ (398.5); high resolution, calculated 398.2668; found 398.2668.

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15. It is well known that there is rarely any rule without exceptions. In fact, the pentahexylether[23b] of **scyllo**-inositol, m.p. −4.6°C (one hydroxyl group is free), the penta-O-hexanoyl derivative[13] of **scyllo**-thioinositol (the thiolo group is unsubstituted), and the *N*-hexanoyl-1-amino-1-deoxy-3,4,5,6-tetra-O-hexanoyl-**scyllo**-inositol[13] (again, one hydroxy group is free) are also thermomesomorphic: the first example monotropically below 0°C, the second and third one even enantiotropically,[13] m.p. ≈ 80°C, cl. p. ≈ 115°C or m.p. ≈ 95°C, cl. p. ≈ 117°C, respectively.
A hepta-O-derivative of β-D-cellobioside containing the sterically congested hydroxyl group in its 3-position unsubstituted, i.e. free, has also been found thermotropically liquid crystalline, m.p. not known, cl. p. 145°C, cf. Reference 26c.
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