Amphiphilic propane-l,2-diol derivatives incorporating calamitic structural units

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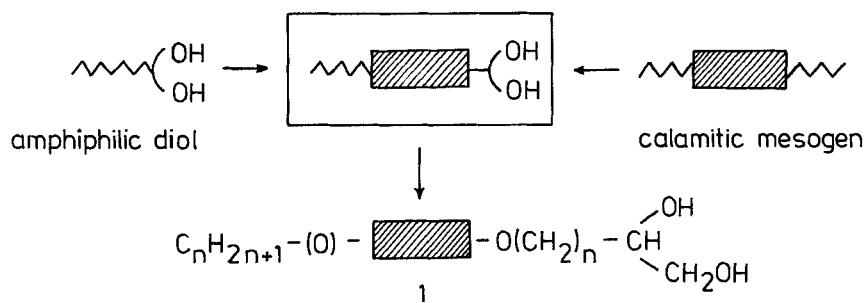G. BREZESINSKI and F. KUSCHEL

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Novel amphiphilic propane-1,2-diol derivatives incorporating a wide variety of calamitic structural units, like biphenyl, dicyclohexyl, phenylbenzoate, phenylpyrimidine and phenylthiadiazole, were synthesized and their mesomorphic behaviour studied. Most of these compounds exhibit broad smectic A and C mesophases in the water-free state. These mesophases could be stabilized further by addition of water. The transition temperatures depend mainly on the hydrophilic properties of the rigid core and on the length of the spacer by which the core is connected to the diol unit.

1. Introduction

Simple *n*-alkane-1,2-diols form both thermotropic and (after the addition of water) lyotropic liquid-crystalline phases consisting of bimolecular layers stabilized by an extended hydrogen bonding network between the diol groups [1, 2] when the *n*-alkyl chain is sufficiently long. More recently, it has been shown that the mesophase stability of both thermotropic and lyotropic mesophases of amphiphilic diols could be increased significantly by the appropriate introduction of rigid structural units such as the 1,4-disubstituted benzene ring or the *trans*-1,4-disubstituted cyclohexane ring into the *n*-alkyl chain [3–6]. These compounds illustrate how the combination of the structural characteristics of non-amphiphilic liquid-crystalline materials and surfactants gives rise to amphotropic compounds. We have, therefore, designed novel single chain amphiphilic diols by a combination of a diol structure and calamitic liquid-crystalline structures and have investigated their liquid-crystalline behaviour (see scheme 1).

amphiphilic diol

calamitic mesogen

$$C_nH_{2n+1}-(O)-\text{[core]}-O(CH_2)_n-CH\begin{smallmatrix}\diagup OH \\ \diagdown CH_2OH\end{smallmatrix}$$
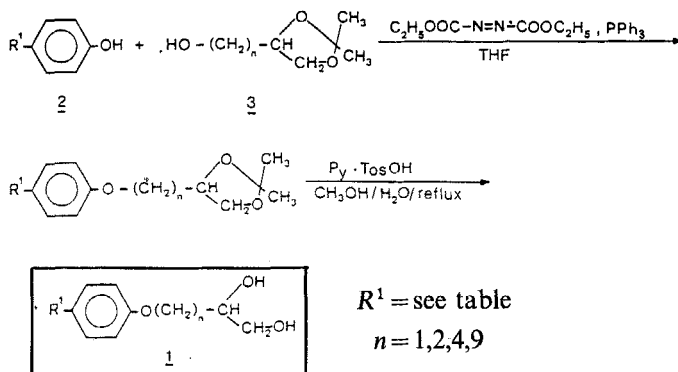
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Scheme 1. Single chain amphiphilic diols **1** formed by a combination of an amphiphilic diol and a calamitic mesogen.

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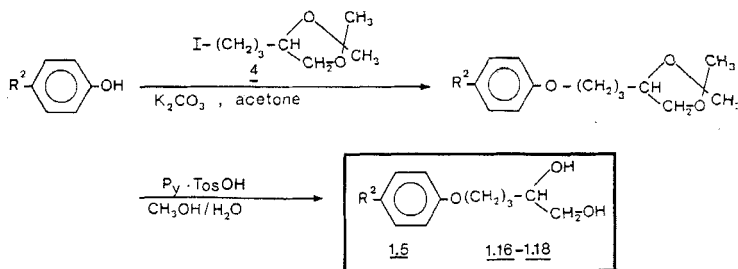## 2. Synthesis

The syntheses of the novel amphiphilic diol compounds **1**, which are summarized in the table, have been carried out using two different approaches. Most compounds were prepared by the Mitsunobu etherification reaction [7] of appropriate phenolic compounds **2** with 1,2-*O*-*iso*-propylidenealkanols **3** followed by acid catalysed deprotection of the diol units, using pyridinium-*p*-toluene-sulfonate (Py · TosOH) in wet methanol.

$$R^1\!\!-\!\!\bigcirc\!\!-OH \ + \ HO-(CH_2)_n-CH\!\!<^{O-C(CH_3)_2}_{CH_2O} \quad \xrightarrow[\text{THF}]{C_2H_5OOC-N=N-COOC_2H_5 \ , \ PPh_3}$$

$$\underline{2} \qquad\qquad\qquad \underline{3}$$

$$R^1\!\!-\!\!\bigcirc\!\!-O-(CH_2)_n-CH\!\!<^{O-C(CH_3)_2}_{CH_2O} \quad \xrightarrow[\text{CH}_3\text{OH}/\text{H}_2\text{O}/\text{reflux}]{Py \cdot TosOH}$$

$$R^1\!\!-\!\!\bigcirc\!\!-O(CH_2)_n-CH\!\!<^{OH}_{CH_2OH}$$

$$\underline{1}$$

$R^1 =$ see table

$n = 1,2,4,9$

On the other hand the 5-substituted pentane-1,2-diol derivatives **1.5**, and **1.16–1.18** were obtained by treatment of the appropriate phenols with 1,2-*O*-*iso*-propylidine-5-iodopentane **4** [8] and potassium carbonate in refluxing acetone, followed by the deprotection procedure.

$$R^2\!\!-\!\!\bigcirc\!\!-OH \quad \xrightarrow[\text{K}_2\text{CO}_3 \ , \ \text{acetone}]{I-(CH_2)_3-CH\!\!<^{O-C(CH_3)_2}_{CH_2O} \ \ \underline{4}} \quad R^2\!\!-\!\!\bigcirc\!\!-O-(CH_2)_3-CH\!\!<^{O-C(CH_3)_2}_{CH_2O}$$

$$\xrightarrow[\text{CH}_3\text{OH}/\text{H}_2\text{O}]{Py \cdot TosOH} \quad R^2\!\!-\!\!\bigcirc\!\!-O(CH_2)_3-CH\!\!<^{OH}_{CH_2OH}$$

$$\underline{1.5} \qquad\qquad \underline{1.16-1.18}$$

3. Results and discussion

The transition temperatures of the compounds synthesized are collected in the table. Inspection of the table indicates that all two ring compounds with the exception of the compounds **1.5**, **1.6** and **1.14** exhibit stable smectic mesophases with unexpectedly high clearing temperatures. The comparison given in figure 1 indicates the enormous mesophase stabilization caused by the replacement of the *n*-propyl chain of the phenyl benzoates **5** [9] by a 2,3-dihydroxypropyl group.

Furthermore the introduction of the diol unit gives rise to an amphiphilic molecular structure. Lyotropic mesomorphism could be observed after addition of water and the temperature ranges in which the liquid-crystalline phases occur grow larger with increasing water content. It is worth mentioning that the hydrophilic diol group shows only a limited uptake of water (2–3 water molecules per molecule of amphiphile). The values, given in the right hand column in the table, correspond to the transition

nonamphiphilic mesogen	amphiphilic mesogen
$C_8H_{17}O$ —⟨⟩— OOC —⟨⟩— OC_3H_7	$C_8H_{17}O$ —⟨⟩— OOC —⟨⟩— OCH_2 — CH $\overset{CH_2OH}{\underset{OH}{}}$
C 62 N 79 I 5.1	C 116 S_C^+ 138.5 S_A^+ 165 I 1.20
$C_8H_{17}O$ —⟨⟩— COO —⟨⟩— OC_3H_7	$C_8H_{17}O$ —⟨⟩— COO —⟨⟩— OCH_2 — CH $\overset{CH_2OH}{\underset{OH}{}}$
C 69 (S_A 59.5) N 81.5 I 5.2	C 120 S_C^+ 126.5 S_A^+ 131 I 1.22

Figure 1.   Comparison of the phase behaviour of amphiphilic (compounds **1.20** and **1.22**) and non-amphiphilic (compounds **5.1** and **5.2**) phenyl-benzoate mesogens. (Temperatures measured in °C.)

temperatures of the water saturated samples and were determined by observing a mixture of **1** with excess water in a sealed capillary on a hot stage with a polarizing microscope.
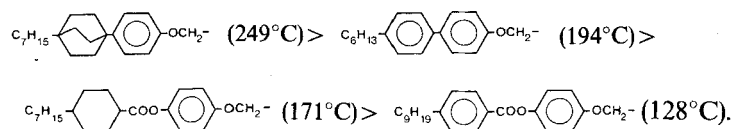
As another consequence of the amphiphilic structure these materials form smectic mesophases instead of the nematic phase observed for the non-amphiphilic analogous compounds **5.1** and **5.2**. We expect bimolecular smectic layers as found for the 2-(*trans*-4-*n*-alkylcyclohexyl)propane-1,3-diols [4].

The classification of the liquid-crystalline phases was made by texture observations in polarized light. All textures correspond to the known textures of conventional liquid crystals, e.g. the S_A^+ phases exhibit a fan shaped texture (see figure 2) or pseudo-isotropic texture, the S_C^+ phases a broken fan shaped texture or schlieren texture (see figure 3) and the S_B^+ phases mosaic textures with batonnets and pseudo-isotropic regions (see figure 4). In no case could the phase sequence $S_B^+ \to S_C^+ \to S_A^+$ be observed (see the table).

As for other calamitic mesogens, the kind of smectic mesophase observed below the smectic A phase is largely determined by the rigid core which means that cyclohexane and bicyclo[2.2.2]octane derivatives (compounds **1.1–1.3** and **1.25**) prefer a higher ordered mesophase (smectic B) whereas (hetero) aromatic derivatives preferably exhibit a tilted mesophase (smectic C). These mesophases are more dominant for amphiphilic derivatives and they are often induced by the diol unit.
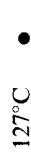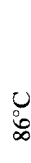
The mesophase stabilization, observed in line with the introduction of the diol group, depends strongly on the chemical structure of the rigid core. The clearing temperatures decrease with growing hydrophilic properties of this core

C_7H_{15}—⟨⟩⟨⟩—OCH_2— (249°C) > C_6H_{13}—⟨⟩⟨⟩—OCH_2— (194°C) >

C_7H_{15}—⟨⟩—COO—⟨⟩—OCH_2— (171°C) > C_9H_{19}—⟨⟩—COO—⟨⟩—OCH_2— (128°C).

Therefore, many heterocyclic derivatives do not exhibit thermotropic mesomorphism (compounds **1.5** and **1.6**). This behaviour agrees with our observation that the insertion of structural units which may participate in hydrogen bonding (hydrophilic structural units) disturbs the molecular self-organization of amphiphilic diols [10].

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Transition temperatures of the investigated propane-1,2-diol derivatives.

Parent structure:

$$R-\underset{\overset{|}{OH}}{\overset{\overset{|}{CH_2OH}}{CH}}$$

Compound	R	Water-free state					Water-saturated state		
		C	S_B^+	S_C^+	S_A^+	I	C	S^+	I
1.1	C_5H_{11}–⟨cyclohexyl⟩–⟨phenyl⟩–COO–$(CH_2)_9$–	●	● 85°C	107·5°C		●	●	● 52°C	● 128°C
1.2	C_7H_{15}–⟨phenyl⟩–O–$(CH_2)_9$–	●	● 92°C	144°C		●	●	●	● 165°C
1.3	C_7H_{15}–⟨phenyl⟩–⟨phenyl⟩–O–CH_2–	●	(● 106°C	99°C)	● 249°C	●			
1.4	C_6H_{13}–⟨phenyl⟩–O–CH_2–	●	160°C		● 194°C	●			
1.5	C_7H_{15}–⟨pyrimidine⟩–O–$(CH_2)_3$–	●	96°C			●	●	● 52°C	● 114°C
1.6	C_7H_{15}–⟨thiadiazole⟩–⟨phenyl⟩–O–CH_2–	●	109°C			●	●	● 64°C	● 131°C
1.7	$C_{11}H_{23}$–⟨thiadiazole⟩–⟨phenyl⟩–O–CH_2–	●	109°C		● 138°C	●	●	● 73°C	● 178°C
1.8	$C_{15}H_{33}$–⟨thiadiazole⟩–⟨phenyl⟩–O–CH_2–	●	110°C	● 115°C	● 148°C	●	●	● 76°C	● 193°C
1.9	C_7H_{15}–⟨thiadiazole⟩–⟨phenyl⟩–O–$(CH_2)_4$–	●	91°C	(● 81°C)		●	●	● 58°C	● 112°C
1.10	$C_{11}H_{23}$–⟨thiadiazole⟩–⟨phenyl⟩–O–$(CH_2)_4$–	●	92°C	● 110°C	● 125°C	●	●	● 60°C	● 147°C
1.11	C_8H_{17}–⟨thiadiazole⟩–⟨phenyl⟩–O–CH_2–	●	142°C	● 227°C	● 243°C	●			
1.12	$C_8H_{17}O$–⟨phenyl⟩–COO–⟨phenyl⟩–COO–$(CH_2)_9$–	●	83°C		● 100·5°C	●	●	● 59°C	● 115°C
1.13	C_4H_9O–⟨phenyl⟩–COO–⟨phenyl⟩–COO–$(CH_2)_9$–	●	74°C		● 98°C	●	●	● 56°C	● 120°C
1.14	$C_8H_{17}O$–⟨phenyl⟩–OOC–⟨phenyl⟩–O–$(CH_2)_9$–	●	117°C			●	●	● 99°C	● 124°C

No.	Structure					
1.15	C₈H₁₇O–⟨⟩–OOC–⟨⟩–O–(CH₂)₄–	• 86°C	• 127°C	• 130°C	• 60°C	• 151°C •
1.16	C₆H₁₃–⟨⟩–OOC–⟨⟩–O–(CH₂)₃–	• 96°C	• 118°C	•	• 37°C	• 156·5°C •
1.17	C₇H₁₅O–⟨⟩–OOC–⟨⟩–O–(CH₂)₃–	• 100°C	• 133°C	• 135°C	• 64°C	• 164°C •
1.18	C₈H₁₇O–⟨⟩–OOC–⟨⟩–O–(CH₂)₃–	• 105°C	• 140°C	• 142°C	• 68°C	• 168°C •
1.19	C₈H₁₇O–⟨⟩–OOC–⟨⟩–O–(CH₂)₂–	• 98°C	• 128°C	• 146°C	• 77°C	• 159°C •
1.20	C₈H₁₇O–⟨⟩–OOC–⟨⟩–O–CH₂–	• 116°C	• 138·5°C	• 165°C	• 60°C	• 179°C •
1.21	C₉H₁₉–⟨⟩–OOC–⟨⟩–O–CH₂–	• 96°C	• 124·5°C	• 156°C	• 46°C	• 189°C •
1.22	C₈H₁₇O–⟨⟩–COO–⟨⟩–O–CH₂–	• 120°C	• 126·5°C	• 131°C		• 164°C •
1.23	C₉H₁₉–⟨⟩–COO–⟨⟩–O–CH₂–	• 104°C	• 125°C	• 128°C	• 62°C	• 157°C •
1.24	C₇H₁₅–⟨⟩–CH₂O–⟨⟩–O–CH₂–	• 131°C	• 136·5°C	•	• 91°C	• 164°C •
1.25	C₇H₁₅–⟨⟩–COO–⟨⟩–O–CH₂–	• 83°C • 95°C		• 171°C	• 64°C	• 194°C •
1.26	C₇H₁₅–⟨⟩–CH₂O–⟨⟩–O–CH₂–	• 100°C		• 173°C	• 59°C	• 183°C •
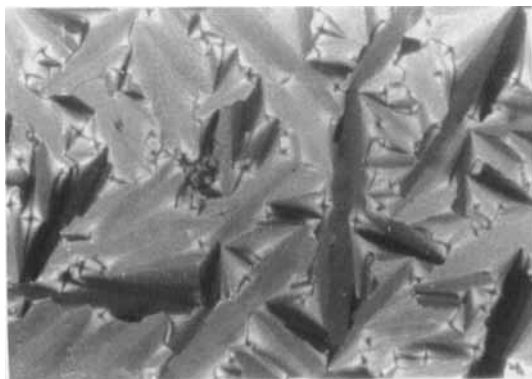
(a)
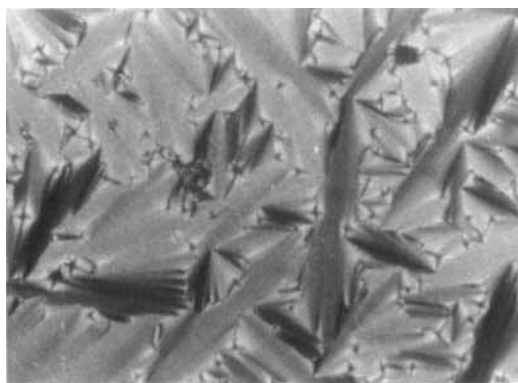
(b)

Figure 2. (a) S_A^+, fan-shaped texture. Crossed polarizers. Compound **1.25** at 105°C. Magnification ×150. (b) Fan-like texture of the smectic B^+ phase at 90°C with paramorphic boundaries, that is obtained by cooling the smectic A phase. Same section as in figure 2(a). Crossed polarizers. Magnification ×150.
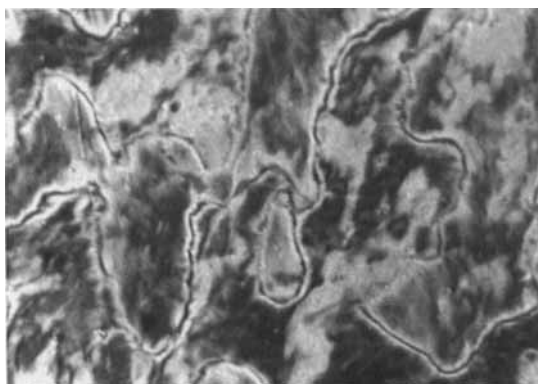

Figure 3. S_C^+ schlieren texture after cooling the pseudo-isotropic S_A^+ phase. Crossed polarizers. Compound **1.20** at 125°C. Magnification ×150.
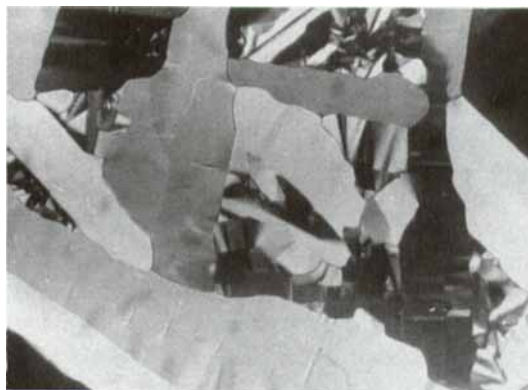
Figure 4. S_B^+ texture with double refracting lancets after cooling the isotropic melt. Crossed polarizers. Compound **1.1** at 95°C. Magnification $\times 150$.
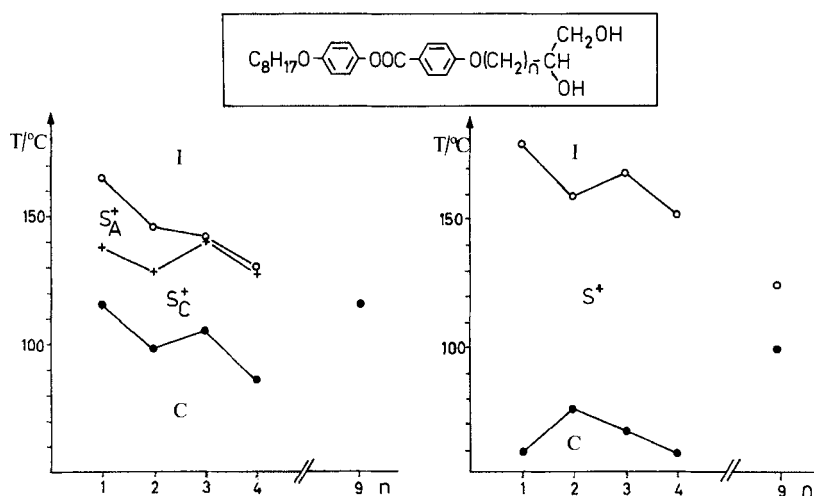
Figure 5. Transition temperatures plotted against the length of the alkylene spacer between the rigid core and the 1,2-diol unit in the water-free state (left) and the water-saturated state (right). ●, Melting temperatures; +, transition S_C^+–S_A^+; ○, clearing temperatures.

Figure 6. Comparison of the transition temperatures (°C) of 3-substituted propane-1,2-diol derivatives with different rigid cores. wf, Water-free state; ws, water-saturated state.

The mesophase degradation by heterocycles is diminished by elongation of the terminal (hydrophobic) alkyl chain (see compounds **1.6–1.8**). But there is another effect influencing the clearing temperatures; compounds **1.20** and **1.22**, as well as the compounds **1.21** and **1.23**, differ only in the direction of the carboxylate group between the rings (see also figure 1). It seems that the mesophase stability depends on the electron density at the ether oxygen near the diol structure in such a way that an increased electron density diminishes the clearing temperature due to increasing intramolecular hydrogen bonding.

Finally, the decoupling of the rigid core and the diol unit by a flexible spacer also diminishes the clearing temperatures considerably (see figure 5) accompanied by a significant odd–even effect. This odd–even effect is especially evident from the $S_C^+ \rightarrow S_A^+$ transition and the melting temperatures in the water-free state as well as the clearing temperatures of the lyomesophases whereby compounds with an odd numbered spacer show elevated transition temperatures. No mesophase could be observed for the long chain compound **1.14** due to rapid crystallization of the supercooled samples in the water-free state.

Until now, we have mainly looked upon the changes as caused by the replacement of one alkyl chain of non-amphiphilic mesogens by the diol unit. But there is also an inverse approach; the introduction of rigid structural units into the *n*-alkyl chain of amphiphilic diols stabilizes significantly the thermotropic as well as the lyotropic mesophases. From figure 6 we can conclude the larger the rigid unit, the more stable is the mesophase. In this way the combination of diol structure and calamitic liquid crystal structure is a powerful tool to facilitate the molecular self-organization of amphiphilic compounds. This principle need not be limited to thermotropic and lyotropic liquid-crystalline phases, but it could also be used to stabilize and to modify other self-assembling systems such as micelles, membranes and liposomes. For example, the phase behaviour of molecular membranes consisting of ionic surfactants incorporating liquid crystal structures has been investigated by Kunitake *et al.* [11–14].

4. Experimental

The synthesis of the compounds **1** by the Mitsunobu reaction has been carried out according to the following procedures.

4.1. [4-(2-n-*heptyl-1,3,4-thiadiazol-5-yl*)-*phenyloxy*]-*propane-1,2-diol* **1.6**

A 30 ml flask, fitted with a magnetic stirring bar, was charged with a solution of 3·0 mmol (0·4 g) 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolan, 3·0 mmol (0·79 g) triphenylphosphine and 2·0 mmol (0·55 g) of 2-heptyl-5-(4-hydroxyphenyl)-1,3,4-thiadiazol [15] in dry THF (15 ml). During 5 min 3·0 mmol (0·52 g) of diethyl azodicarboxylate (DEAD) was added dropwise to the stirred mixture while the temperature was maintained at 25°C. The resulting light yellow solution was stirred for 12 hours. The solvent was removed by rotary evaporation and the products were purified by crystallization from methanol/water (10:1). A solution of 50 mg pyridinium tosylate in a methanol/water mixture (10:1) was added and the resulting solution was refluxed until the hydrolysis of the acetal was completed (TLC analysis). The methanol was removed under vacuum and the residue dissolved in ethyl acetate. The solution was washed with water and brine, and dried over Na_2SO_4. Evaporation of the solvent and recrystallization from hexane/ethyl acetate gave the pure diol **1.6** (83 per cent yield).

^{13}C NMR (50 MHz, CDCl$_3$, ppm): 170·0 (quart. C), 168·2 (quart. C), 160·8 (quart. C), 129·3 (2C, =CH– atomatic), 123·1 (quart. C), 115·0 (2C, =CH– aromatic), 70·3 (–C–H), 69·3 (–CH$_2$–O–), 63·9 (–CH$_2$–O–), 31·6 (–CH$_2$–), 30·1 (–CH$_2$–), 30·0 (–CH$_2$–), 28·9 (–CH$_2$–), 28·8 (–CH$_2$–), 22·5 (–CH$_2$–), 14·0 (–CH$_3$).

The synthesis of the 5-substituted pentane-1,2-diol derivatives **1.5** and **1.16–1.18** is illustrated by the following example.

4.2. *5-[4-(5-n-heptylpyrimidine-2-yl)-phenyloxy]-pentane-1,2-diol* **1.5**

A mixture of 5 mmol (1·21 g) 5-*n*-heptyl-2-(4-hydroxyphenyl)-pyrimidine, 7 mmol (1·89 g) 4-(3-iodopropyl)-2,2-dimethyl-1,3-dioxolane [8], 10 g potassium carbonate and 150 ml dry acetone was stirred at reflux temperature, for 12 hours. Afterwards the solvent was evaporated and the residue dissolved in a mixture of 100 ml water and 100 ml diethyl ether. The aqueous layer was extracted twice with diethyl ether (2 × 50 ml) and the combined organic phases were washed with water (50 ml) and dried over sodium sulphate. After evaporation of the solvent, the crude product obtained was used for the deprotection of the 1,2-diol unit with pyridinium tosylate in wet methanol as described above. Repeated recrystallization from *n*-hexane/ethyl acetate gave the diol **1.5** (67 per cent yield).

^{1}H NMR (80 MHz, CDCl$_3$, ppm): 8·56 (s, 2 H, =CH– pyrimidine); 8·34 (d, $J = 9·0$ Hz, 2 H, =CH– aromatic); 6·95 (d, $J = 9$ Hz, 2 H, =CH– aromatic); 4·07 (t, $J = 5·8$ Hz, 2 H, –CH$_2$–O–); 3·3–3·9 (m, 3 H, =CHOH, –CH$_2$–OH); 2·59 (t, $J = 7·2$ Hz, 2 H, –CH$_2$– pyrimidine); 0·9–2·4 (m, 16 H, –CH$_2$–, –OH); 0·88 (t, $J = 5·3$ Hz, 3 H, –CH$_3$).

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