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M. Veber^a; E. Cheylan^b; S. Czernecki^b; J. Xie^b

^a Laboratoire de Physique des Solides, Université Paris-Sud, Orsay Cedex, France ^b Laboratoire de Chimie des Glucides, Université Pierre et Marie Curie, Paris, France

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Synthesis and mesomorphic properties of some aryl β -D-C-glycosides

by M. VEBER*, E. CHEYLAN†, S. CZERNECKI† and J. XIE†

Laboratoire de Physique des Solides, Bâtiment 510, Université Paris-Sud, 91405 Orsay Cedex, France

†Laboratoire de Chimie des Glucides, Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France

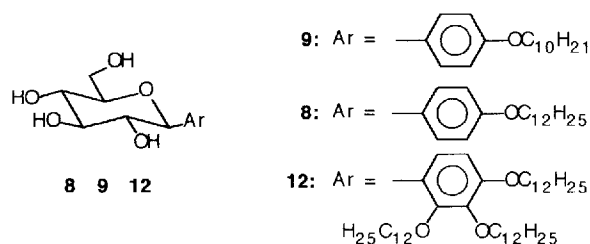
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The synthesis of some aryl β -D-C-glycosides bearing long alkoxy chains (grafted on the carbohydrate moiety through the intermediate of an aromatic core) is described. Their mesomorphic properties (studied by microscopic observations under polarized light, DSC and X-ray diffraction) are presented.

1. Introduction

Interest in the synthesis and in studies of the liquid crystalline properties of amphiphilic carbohydrates has increased in the past few years [1]. Indeed, some of these materials can exhibit thermotropic and lyotropic properties due to their amphiphilic character and a few (the more soluble) have been used as non-ionic surfactants [2,3]. However, only few studies of structure-property relationships have yet been performed. On the other hand, it has been shown that *p*-alkylphenyl- β -D- and *p*-alkylcyclohexyl- β -D-glucopyranosides exhibit mesomorphic properties [4]. Recently, some results have been published concerning the synthesis and mesomorphic properties of trioxadecalin compounds in which S_A and cholesteric phases have been obtained [5]. It has to be noted that in such compounds no hydrogen bonds can occur.

Until now, to our best knowledge, no studies have been performed concerning the synthesis and the mesomorphic properties of β -D-C-glucopyranosides in which the aliphatic chains are grafted on the sugar moiety by the intermediate of an aromatic core directly linked to the sugar through a C-C bond. In order to elucidate what could be the influence on the mesomorphic properties of this C-C link (instead of a C-O link) in position 1 of the glucopyranoside system, we have synthesized the β -D-C-glucopyranosides **8**, **9** and **12**, bearing an aryl group substituted with one or three alkoxy chains:



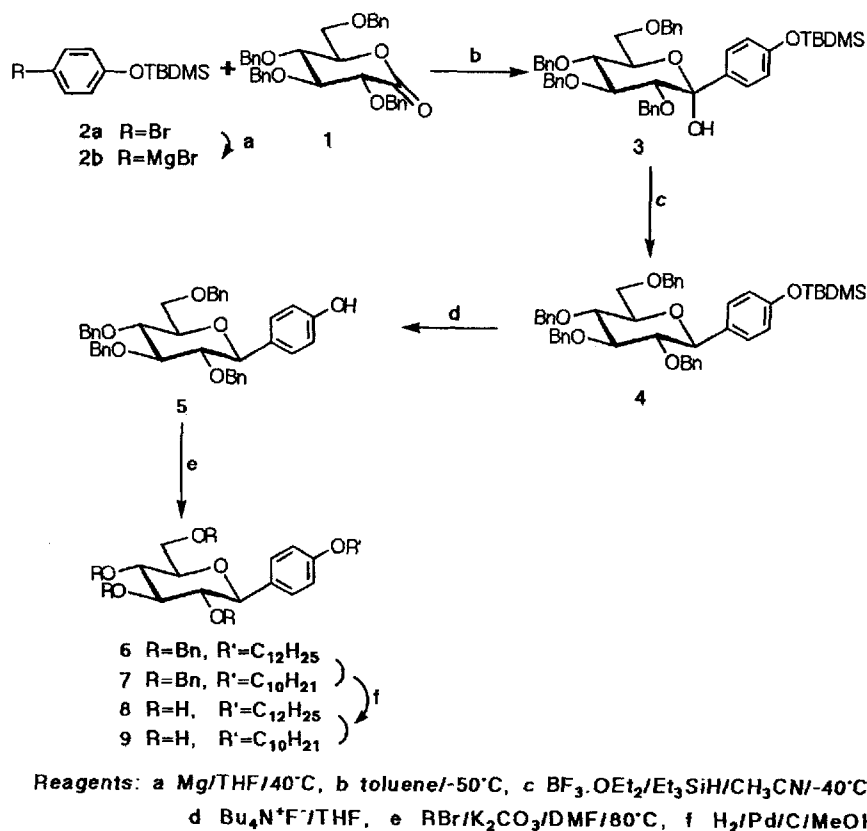
The aim of this paper is to describe the synthesis of such compounds and the studies of their mesomorphic properties.

2. Synthesis

The monoalkylated derivatives, 4-dodecyloxy-1-(β -D-glucopyranosyl)benzene (**8**) and 4-decyloxy-1-(β -D-glucopyranosyl)benzene (**9**) were prepared from the same intermediate, 4-hydroxy-1-(2',3',4',6'-tetra-*O*-benzyl- β -D-glucopyranosyl)benzene (**5**) (scheme 1). The latter was obtained by a methodology which affords aryl β -C-glycosides by condensation of an organometallic derivative with perbenzylated D-gluconolactone (**1**), followed by reduction of the hemiacetal [6].

Transfer of a solution of 4-[(*tert*-butyldimethylsilyloxy]phenylmagnesium bromide (**2b**) (1.7 equivalents) in THF to a solution of **1** in toluene at -50°C gave **3** after hydrolysis with a saturated aqueous solution of ammonium chloride (scheme 1). Crude **3** was treated with $\text{BF}_3 \cdot \text{OEt}_2$ and triethylsilane in CH_3CN at -40°C . After work-up and desilylation with tetrabutylammonium fluoride in THF, the crystalline perbenzylated compound **5** was obtained in 90% overall yield from **1**. Assignment of the β -configuration was based upon the observed 9.4 Hz coupling constant between the

* Author for correspondence.

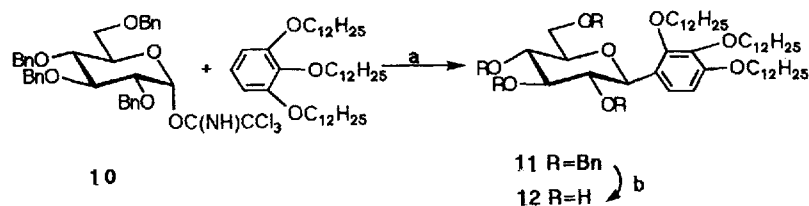


Scheme 1.

H-1' and axial H-2' using ¹H/¹H shift correlation spectra. Compounds **8** and **9** were obtained by alkylation of **5** with *n*-dodecyl bromide or *n*-decyl bromide in DMF, in the presence of potassium carbonate at 80°C, followed by hydrogenolysis in MeOH, in 60% and 67% yield, respectively.

For the preparation of the trialkylated derivative, another route involving a Friedel-Crafts reaction between a glycosyl donor and an electron rich aromatic derivative was followed [7]. For that purpose, 2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl-trichloroacetamide (**10**) [8] was employed (scheme 2).

Treatment of 1,2,3-tri-dodecyloxybenzene with 3 equivalents of **10** in the presence of BF₃·OEt₂ (3 equivalents) in anhydrous CH₂Cl₂ during 24 h at room temperature afforded **11** in 40% yield. The regioselectivity of the coupling was demonstrated by examination of the ¹H NMR spectrum, where two doublets at 6.85 and 7.00 ppm with ³J = 8.7 Hz were observed. Debenzylation of **11** in MeOH afforded **12** in 82% yield. The β -configuration of the C-C bond at the anomeric centre of **12** was determined by the coupling constant of 8.9 Hz (*J*_{1,2}), agreeing with the literature values for a β -oriented phenyl C-glucoside. The purity of all the compounds



Reagents: a BF₃·OEt₂, CH₂Cl₂; b H₂, Pd/C, MeOH.

Scheme 2.

was checked by elementary analysis and ^1H and ^{13}C NMR spectroscopy.

3. Mesomorphic properties: results and discussion

Microscopic observations were performed with a Leitz Orthoplan polarizing microscope equipped with a Mettler FP5 variable temperature stage. Transition temperatures and enthalpies were determined with a DSC7 Perkin Elmer apparatus.

X-ray patterns of aligned smectic phases were made using a previously described set-up [9]. An aligned sample of compound **12** was obtained by spreading a small amount of the product onto a thin single crystal sheet of mica with a spatula and a Guinier powder camera was used to measure accurately the structural parameter of the mesophase of this compound.

3.1. Microscopic observations and DSC results

The transition temperatures as well as the transition enthalpies for the three compounds studied are given in table 1. Compounds **8** and **9**, bearing only one alkoxy chain, have a strong tendency to give large homeotropic domains on untreated glass, by cooling from the isotropic phase. However, we have been able to obtain textures such as those presented in figure 1 (taken upon heating compound **8** to 166°C), which shows the oily strikes characteristic of a molten S_A phase. Compound **12**, bearing three alkoxy chains, exhibits textures such as that presented in figure 2 (taken upon cooling, at 70°C). This pseudo-focal-conic fan texture, with large homeotropic domains, as well as some line defects, seems to be characteristic of a D_h phase.

All those sugars exhibit peculiar behaviour on examining by DSC. For example, in the case of compound **9**, the peak corresponding to the transition to the S_A phase slowly vanishes upon annealing, while the transition to the isotropic phase remains almost unchanged in temperature as well as in enthalpy. This behaviour could be

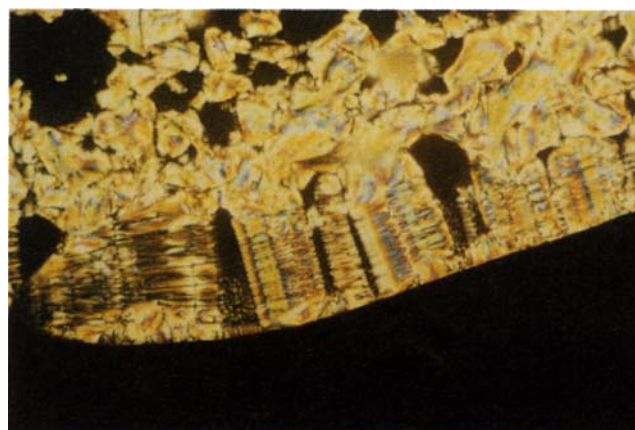


Figure 1. Compound **8**: texture obtained at 166°C upon heating.



Figure 2. Compound **12**: texture obtained at 70°C upon cooling.

Table 1. Transition temperatures, transition enthalpies and interlayer spacings for compounds **8**, **9** and **12**

Compounds	Transition temperatures/ $^\circ\text{C}$ (Transition enthalpies/ J g^{-1})	$d/\text{\AA}$
8	$\text{Cr} \xrightarrow{102 (60.7)} S_A \xleftarrow[165^a]{169^a} \text{I}$	39.0
9	$\text{Cr} \xrightarrow{107 (46.0)} S_A \xleftarrow[171 (4.1)]{173 (4.0)} \text{I}$	35.3
12	$\text{Cr} \xrightarrow{24.9 (1.5)} D_h \xleftarrow[102.3 (2.5)]{103.9 (2.1)} \text{I}$	^b

^a Determined by microscopic observations.

^b See text.

due to the existence in the crystal of strong hydrogen bonds which are not always reformed in the same way upon reaching the crystalline phase (at 50°C as the starting temperature and using 5°C min^{-1} as the heating and cooling rate).

Concerning compound **8**, the transition to the S_A phase could only be detected by DSC on the first heating, with no peak corresponding to the clearing point; therefore the temperature given in Table 1 results from the microscopic observations. Finally, for compound **12**, the transition enthalpy to the D_h phase slowly decreases upon annealing, without reaching a zero value as in the case of compound **9**. The transition to the isotropic phase remains constant in temperature and enthalpy.

3.2. X-ray diffraction studies

3.2.1. Compounds bearing one alkoxy chain

A pattern of an aligned mesophase has been obtained only in the case of compound **9**. It exhibits, at small

angles and along the direction of the magnetic field (meridian), two Bragg peaks corresponding to reflections from the smectic layers (interlayer spacing $d=35.3 \text{ \AA}$). At wide angles, a diffuse ring corresponding to the molten paraffinic chains can be seen at $s=1/4.7 \text{ \AA}^{-1}$. This pattern is characteristic of a smectic A phase. In the case of compound **8** the powder pattern obtained exhibits a first and a second order reflection in a 1:2 ratio (interlayer spacing $d=39.0 \text{ \AA}$). At wide angles the diffuse ring corresponding to the molten chains is detected at $s=1/4.6 \text{ \AA}^{-1}$.

3.2.2. Compounds bearing three alkoxy chains

An aligned pattern, taken at room temperature and obtained by spreading a small amount of compound **12** on a mica sheet is presented in figure 3. At small angles, two reflections can be detected in a spacing ratio 1:2, corresponding to a distance of 32.6 \AA . No extra reflection due to core to core interactions can be detected. At wide angles, a diffuse ring corresponding to the molten chains can be seen at $s \approx 1/4.6 \text{ \AA}^{-1}$. Such a pattern could be characteristic of either a smectic phase or a columnar phase.

In order to get more information about the mesophase, a powder pattern, presented in figure 4, was taken at 45°C . At small angles, five reflections can be detected, the spacing ratios of which are $1:3^{1/2}:4^{1/2}:7^{1/2}:9^{1/2}$. At

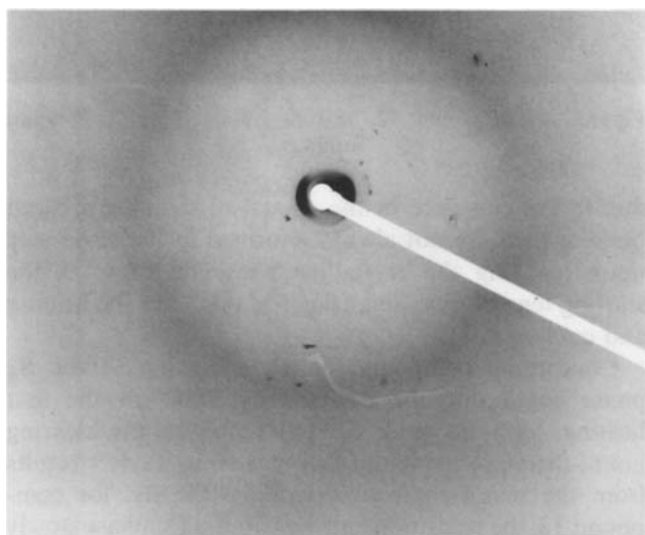


Figure 3. X-ray pattern obtained at room temperature for the aligned sample of compound **12**.

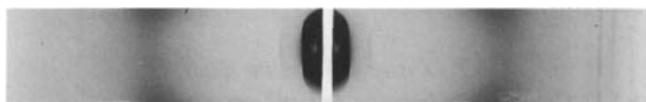


Figure 4. Powder pattern of compound **12** recorded at 45°C in the columnar hexagonal phase D_h .

wide angles, a diffuse ring corresponding to the molten aliphatic chains can be detected at $s=1/4.46 \text{ \AA}^{-1}$. No sign of core to core interactions appears on this pattern. A proposed indexation, given in table 2 allowed us to conclude that the mesophase presented by compound **12** is columnar hexagonal (D_h), with $a=40.1 \pm 0.2 \text{ \AA}$.

3.3. Discussion

Usually, carbohydrate compounds bearing one alkoxy chain directly grafted on the sugar moiety exhibit partially bilayered S_A phases in which the *paraffinic chains* are interdigitated. In our case, the core length measured using a model has been estimated as 9.7 \AA (from the oxygen atom of the aryl group to O_4 of the sugar core) and the total molecular length of compound **8** is $\approx 25 \text{ \AA}$ (the length of the paraffinic chain has been estimated using the parameters given by Skoulios *et al.* [10]). Therefore, the interlayer spacings are 1.6 times greater than the length of the fully extended molecule (the same value is found for compound **9**) and an interdigitated model seems to represent the organization of the molecules in the layers.

Nevertheless, in order to learn if the chains are fully or partially interdigitated, we decided to calculate the area per chain. Assuming that the density of a liquid crystalline phase is close to one, we have: $S = nM_w/N_A d$, where S is the area occupied by the paraffinic chains, M_w is the molecular mass of the compound **8** or **9**, n is the number of molecules arranged perpendicular to the lamellae (2 for a bilayered or a partially bilayered model), d is the interlayer spacing deduced from X-ray measurements and N_A is the Avogadro number. This leads to an area per chain of 36 \AA^2 for both compounds. If the paraffinic chains were fully interdigitated, this would mean that the area occupied by one chain would be $36 \text{ \AA}^2/2 = 18 \text{ \AA}^2$, which is a too small a value for molten paraffinic chains [5]. Therefore, it seems that the paraffinic chains are only slightly interdigitated (if at all), contrary to the model proposed by Jeffrey and Wingert [11,12].

Adding more chains to the rigid core leads, as usual, to the formation of a columnar hexagonal D_h phase. Since we have no sign of core to core interactions, we

Table 2. Proposed indexation for the powder pattern of compound **12** recorded at 45°C ; $a=40.1 \pm 0.2 \text{ \AA}$.

$h k$	Measured lattice spacings/ \AA	Calculated lattice spacings/ \AA
1 0	34.75	34.90
1 1	20.19	20.15
2 0	17.47	17.45
2 1	13.18	13.19
3 0	11.70	11.63

have to evaluate the linear chain density to obtain more insight into the organization of the molecules inside the columns (as has been done in the case of some vinamidinium salts [13]). First of all, let us estimate the axial molecular density $1/d_{\text{core}} = (\rho N_A 3^{1/2} / 2M_W) a^2$, where a is the hexagonal lattice parameter, M_W is the molecular mass of compound **12** (792) and N_A is the Avogadro number, provided that the density of the mesophase is close to one (which is usually the case for columnar hexagonal phases [13]). So, $1/d_{\text{core}} = 1/0.94 \text{ \AA}^{-1}$.

In order to compare the columnar phases of different compounds, it is better to compare the linear chain density $1/d_{\text{ch}} = n_{\text{ch}}/d_{\text{core}}$ in which n_{ch} represents the number of paraffinic chains grafted onto the rigid core (three in the case of compound **12**). This leads to $1/d_{\text{ch}} = 1/0.31 \text{ \AA}^{-1}$. Usually, in mesomorphic compounds, the mean inter-chain distance is of the order of 4.5–4.7 \AA , which means that, in our case, in a column slice with $c' = 4.65 \text{ \AA}$, we should find 5 molecules. Now, the volume per methylene group can be estimated according to: $V_{\text{CH}_2} = [3^{1/2} a^2 / 2] (\pi l_{\text{core}}^2) c' / n_{\text{CH}_2}$ with $l_{\text{core}} = 9.7 \text{ \AA}$ and $c' = 4.65 \text{ \AA}$. Then, $V_{\text{CH}_2} \approx 28.4 \text{ \AA}^3$, which is a typical value in the case of columnar phases [13].

4. Conclusions

We have presented here some results concerning the synthesis and mesomorphic properties of some β -D-C-glycosides bearing one or three paraffinic chains. The originality of this work is that the chains have been added through the intermediate of an aryl group directly linked through a C–C bond to the sugar core.

Compounds bearing one alkoxy chain exhibit a bilayered S_A phase, with only a slight (if it exists) interdigitation of the paraffinic chains. In such a case, we cannot deduce the position of the sugar head groups in the layers as proposed by Jeffrey and Wingert [11,12]. Work is in progress through varying the chain length in order to propose a better model of this S_A phase.

Concerning β -D-C-glycosides bearing three chains, a columnar hexagonal phase D_h has been identified which

may be surprising, since a model shows that the aromatic core and the sugar moiety are almost perpendicular to each other. In the absence of any core to core interactions, the evaluation of the axial chain density allowed us to propose a model in which a slice of 4.65 \AA of column contains five molecules. The central rigid part of each column, constituted by the sugar head groups, probably associated by hydrogen bonds, is surrounded by a dense crown of paraffinic chains, almost as in the case of some inverted cylindrical micelles of lipids [14]. The synthesis of compounds bearing different chain lengths should help us to obtain more insight into the organization of the molecules inside the columns.

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