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Mesophase characterization of some long chain vicinal multihydroxy amphiphiles [1, 2]

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The mesophase characterization of three stereoisomeric multihydroxy compounds, the 1, 2(*S*), 3(*R*), 4(*R*)-, 1, 2(*R*), 3(*S*), 4(*R*)-, and 1, 2(*S*), 3(*S*), 4(*R*)-icosanetetrols, as well as of an octadecafuranose derivative has been carried out by means of polarizing microscopy, X-ray diffraction etc. The four multiols with their very long flexible alkyl chains are mono-thermomesomorphic; their single mesophases are miscible with each other, with a typical carbohydrate derivative, and are characterized by X-ray diffraction having a layer structure without order in it. The phase transition data of the three icosanetetrols are strongly dependent on their stereochemistry. The measurements of the refractive indices of one of the tetrols show a typical behaviour known for S_A phases or for lamellar phases, i.e. the sign of the birefringence is positive.

1. Introduction

Interest in the physical properties of multihydroxy amphiphiles derived from synthetic materials [3] or from natural products, e.g. carbohydrates and related compounds, is growing steadily [1, 4–16]. Thus, the influence of changes in the stereochemistry, the position and number of hydroxyl groups, and the length and number of (linear or branched) alkyl chains on the occurrence, the type and the stability of a mesophase has been studied intensively and found to be dramatic. However, the vast majority of the thermomesomorphic compounds investigated were rod-shaped, and their observed mesophase was designated as smectic A_d [4, 5, 11, 17], characterized by a bilayer structure due to partially overlapping molecules.

In the course of our work regarding the relationship between the shape and properties of multiols derived from sugars [6] and inositols [1, 7, 13–16] it became of interest to study the liquid-crystalline properties and in particular to determine the type of mesophases of the four long chain, vicinal multiols **1**–**4** (selected from a larger series

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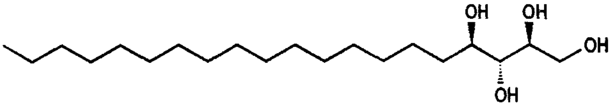

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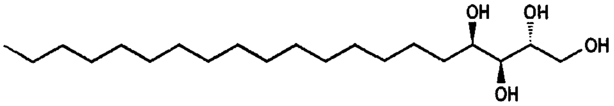

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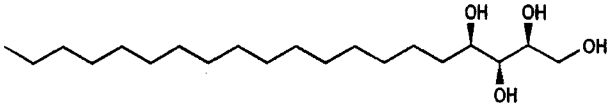

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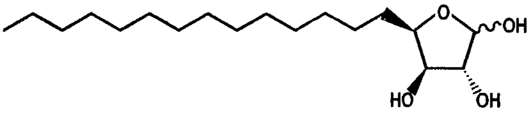

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of such multihydroxy amphiphiles [18]). These four multiols, partly encountered as entities of natural products, synthesized a few years ago [18], were then described as affording "liquid crystals on heating", but were not studied in detail. Moreover, no attention was drawn at all to the obvious liquid-crystalline behaviour of the same compounds or their homologues by Kumar and Dev [19]. We have looked into this problem in some detail and report our results here.

2. Results and discussion

2.1. *Origin of the compounds*

The synthetic sequences leading to the three stereoisomeric linear vicinal tetrols [2] (1) 1,2(*S*),3(*R*),4(*R*)-('D-ribo'-)icosanetetrol (**1**), (2) 1,2(*R*),3(*S*),4(*R*)-('D-lyxo'-) icosanetetrol (**2**), (3) 1,2(*S*),3(*S*),4(*R*)-('D-xylo'-)icosanetetrol (**3**), or to the sugar derivative **4** (5-*C*-tridecyl-5-deoxy-D-xylofuranose) are described elsewhere [18]. These four selected model compounds were placed at our disposal from that source and studied here without additional purification.

2.2. *Characterization of the mesophases*

Polarizing microscopy and differential scanning calorimetry bear out the previous assertion [18] that the multiols **1**–**4** are indeed all thermotropic liquid crystals (see the table). There are only minor variations between our precisely determined phase transition temperatures and the rough estimates presented earlier [18]. Moreover, our microscopic investigations of the compounds **1**–**4** each reveals a single mesophase which shows complete miscibility (contact method) with each other as well as with the mesophase of the commercially available 1-*O*-octyl-β-D-glucopyranoside used here as a typical carbohydrate liquid crystal [4]. Their texture is that of an oily streak type with homeotropic domains (illustrated in figure 1). This definitely proves that the type of mesophases formed here is of the smectic A class known for the great majority of single

Table 1. Transition temperatures (°C) and enthalpies (kJ/mol)—in parenthesis—for the long chain vicinal multihydroxy amphiphiles [2] (multiols) 1–4; heating rate 5 K/min.

Multiol	C		S_A		I	Stable mesophase range ΔT/K
1	●	107·8 (46·0)	●	155·8 (1·1)	●	48·0
2	●	† 140·1 (88·7)	●	159·2 (1·4)	●	19·1
3	●	88·7 (47·2)	●	137·7 (1·2)	●	49·0
4	●	117·3 (32·1)	●	149·2 (1·9)	●	31·9

† A further higher melting modification, m.p. 145°C probably exists.

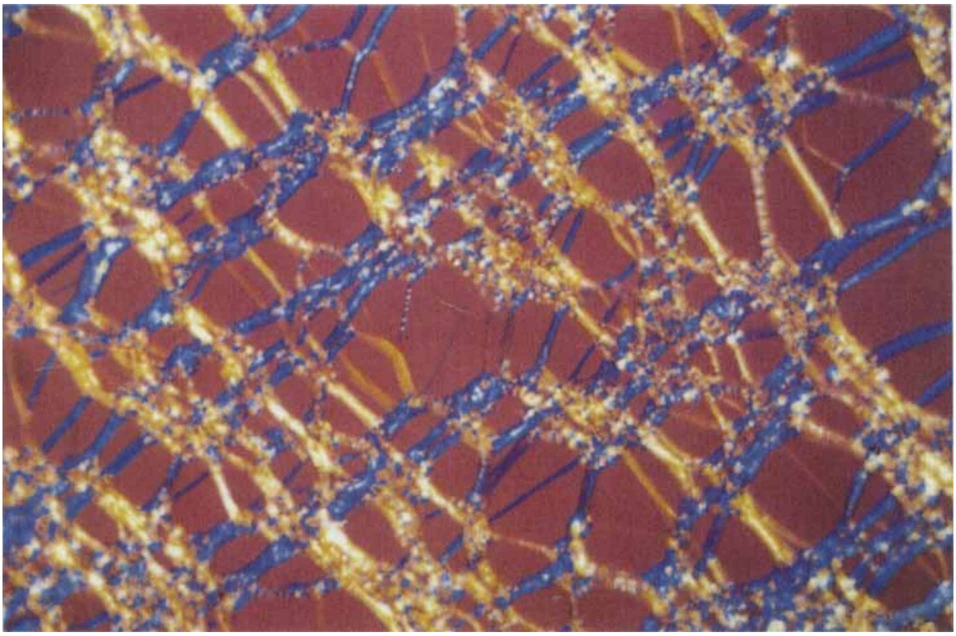

Figure 1. The mesophase texture with oily streaks and homeotropic domains of the 1, 2(*S*), 3(*S*), 4(*R*)-('D-xylo'-)icosanetetrol (3) [2] on heating at 88·3°C (heating rate 1 K/min, crossed polars, λ-plate, magnification × 32 in a 24 × 36 mm camera, see experimental).

tailed thermomesogenic carbohydrate derivatives [4]. (The term smectic A class shall also include the $L\alpha$ phases.)

However, it seems interesting to note that neither one of our four multiols is miscible with 4-nonylphenyl 4-nitrocinnamate known to form a smectic A_d phase [20]. Therefore, the designation of our smectic-like phases of **1**–**4** by S_{A_d} should be done cautiously; the ratio $d/L > 1$ alone does not allow us to assign the phases in the same class.

Our X-ray studies, performed by means of a Guinier camera with an un-oriented sample of **3**, disclose a liquid-crystalline bilayer structure without order in the hydrogen-bonded structure. The microdensitometer curve of a Guinier pattern (cf. figure 2) shows the layer reflection up to the third order and a diffuse scattering maxima

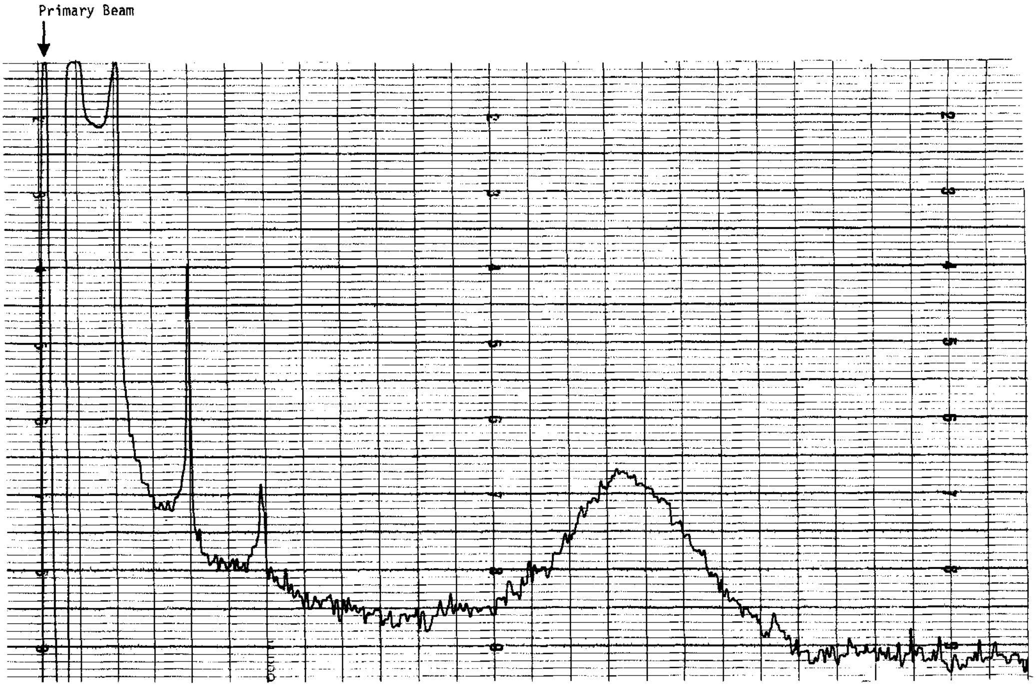

Figure 2. The microdensitometer curve of a Guinier pattern obtained for 1, 2(*S*), 3(*S*), 4(*R*)-('D-xylo'-)icosanetetrol (**3**) [2] in its smectic A phase at 93°C.

at Bragg angles of about 10°. The *d*-value (layer thickness) calculated via Bragg's law is essentially greater than the length of molecules (e.g. $L \approx 2{\cdot}8$ nm for **1**–**3**, measured from space filling models), $L < d < 2L$; it is mostly found in similar chemical systems [5, 21, 22].

Furthermore, these *d*-values are clearly a function of temperature (cf. figure 3). The decrease of *d* with increasing temperature agrees with the behaviour observed in fluid lamellar (Lα) phases [for example in thermotropic thallium salts [23] or in amphiphilic systems consisting of molecules with a long aliphatic chain]. Hence, the flexibility of these alkyl chains increase with increasing temperature.

The measured *d*-values of substances **1** and **2** were found to be different to those of **3** although the length of the three molecules are identical. However, taking into account the different temperatures of the measurements and comparing the values in corresponding rates by a plot $d = f(T - T_{S_A I})$ in figure 4, the values fit one curve quite well. This result strongly supports the influence of temperature on the proposed structure of the mesophase under discussion.

In this point with respect to the temperature dependence, the results under discussion are different to those found for liquid-crystalline phases of derivatives of other diols [24], in which no temperature dependence could be observed. This was explained by the dense packing in the region of the interdigitated alkyl chains. It was assumed that the lack of free volume in the aliphatic region presents a conformational variety of the chains. Therefore, a structural explanation in the form presented as model II [17] with rigid interdigitated chains seems to be unable to explain the observed temperature dependence in our multiol cases studied here. The question as to whether

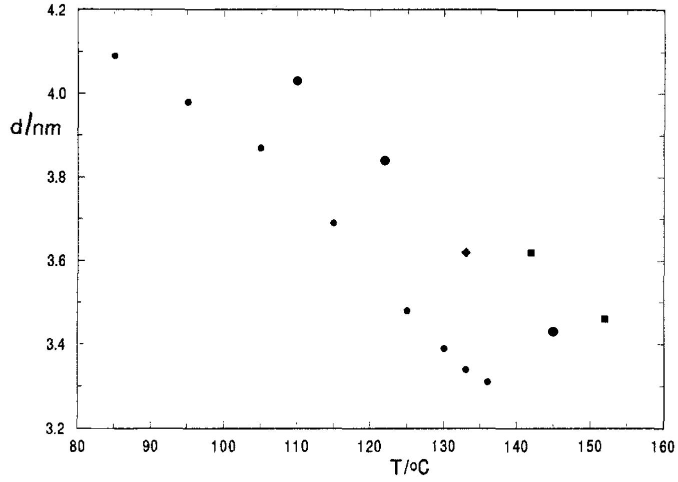

Figure 3. The *d*-values (layer thickness) of the tetrols **1** (◆) **2** (■) and **3** (●) as a function of temperature.

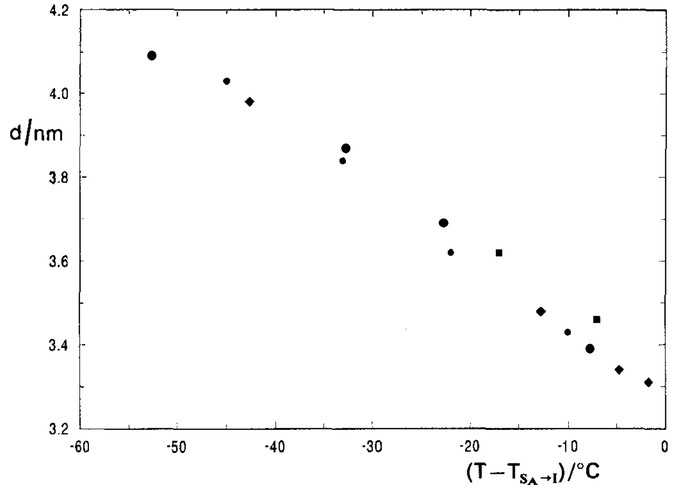

Figure 4. The comparison of the *d*-values of the tetrols **1** (◆), **2** (■) and **3** (●) in corresponding states at the same shifted temperatures $T-T_{S_A \to I}$. ($T=155$°C of tetrol **1** has been used because of a small decomposition during the measurements.)

the multiol moieties of the molecules **1**–**4** are arranged parallel or antiparallel (meaning overlapped) clearly cannot be answered unambiguously on the basis of the results obtained here. Nevertheless, the phase structure should be similar to that of the well-known Lα phase which is characterized by a bilayer structure formed by alternatingly arranged sublayers of polar groups and liquid-like aliphatic regions.

The measurements of the refractive indices (cf. figure 5) show a behaviour typical for S_A phases or for lamellar phases [25], i.e. the sign of the birefringence (n_e-n_o) is positive. However, the extreme low birefringence (0·023 at $T_{S_A \to I}-T$ of 38 K) is obviously the result of the low molecular polarizability anisotropy. Generally, the reduction of the birefringence with increasing temperature can be interpreted by the decrease of the molecular order; here, especially by the higher mobility of the long aliphatic chains [26].

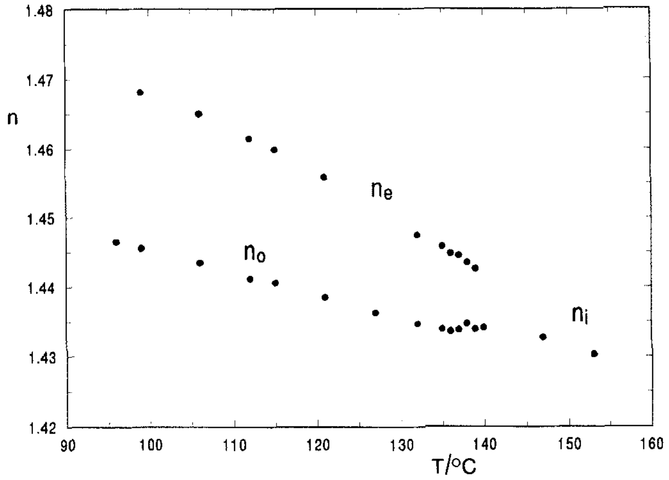

Figure 5. The temperature dependence of the refractive indices of 1,2(*S*),3(*S*),4(*R*)-('D-xylo'-)-icosanetetrol (3) [2] in its smectic A phase (n_e and n_o) as well as in the isotropic phase (n_i) at the wavelength 589 nm; n_o designates the refractive index of the ordinary ray whereas n_e is the refractive index of the extraordinary one.

As the data collected in the table demonstrate the transition temperatures of the three stereoisomeric 1,2,3,4-icosanetetrols **1**–**3** are strongly dependent on their stereochemistry. Interestingly, the 2(*R*),3(*S*),4(*R*)-configuration in **2** leads to the most stable, but, because of its high melting point, smallest mesophase, whereas the steric situation in the 2(*S*),3(*S*),4(*R*)-isomer **3** gives rise to the weakest, but, due to its low melting point, widest one. This is an example of remarkable difference in relative and absolute stabilities of mesophases due to stereochemical alteration at only one carbon centre (C-2). For the 2(*S*),3(*R*),4(*R*)-configuration in the tetrol **1** the two transition temperatures are enhanced by about 20 K compared to the 1,2(*S*),3(*S*),4(*R*)-tetrol **3**.

The enthalpy values for the melting process ($C \to S_A$) of all four compounds **1**–**4** are of the characteristic magnitude for multihydroxy amphiphiles [8, 10]; the same is true for the enthalpy values of each of the clearing processes [8, 10] ($S_A \to I$) which in the four tetrols **1**–**4** are very much similar.

3. Conclusions

Since our four smectic A phase exhibiting multiols (each possessing more than two [1, 14] vicinal hydroxyl groups) studied here are closely related in structure to several other, including some naturally derived, long chain multihydroxy compounds [18, 19] we predict that all, or most of them, form this type of thermotropic mesophase. Hence, we conclude that all of these multiols most probably belong to the swiftly growing family of so-called single tailed thermotropic, liquid-crystalline carbohydrate-related amphiphiles which aggregate via hydrogen bonding networks.

It is our intention to synthesize homologues of the tetrols **1**–**4** in order to study in more detail the influence of the ring system and in particular of the chain-length on the mesophase behaviour of this type of compound.

4. Experimental

The thermomicroscopy was performed with a polarizing microscope Leitz Laborlux 12 Pol on a Mettler hot stage FP 82 (heating/cooling rate 1 K min^{-1}, the photographs were taken with a photoautomat Wild MPS 51). Quantitative thermal analyses were performed with a Mettler TA 3000/DSC 30 S with GraphWare TA 72. The X-ray studies were carried out using a Guinier camera (diameter 114 mm) equipped with a self-made hot stage; Cu Kα radiation was used in all cases. The refractive indices were measured by means of Abbe's double prism method in which the liquid crystal is used as a homeotropically oriented film between the hypotenuse areas of two prisms allowing the calculation of the refractive index from the boundary angles of the total reflection. The double prism was mounted in an electrically heated device which provided the temperature control [27].

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