

**Amphiphilic Carbohydrate-based Mesogens, 3 [1]**  
**D-Mannitol-1-O-*n*-Alkyl Ethers with Hydroxy and 1-O-D-Mannityl End-Groups: Novel Double-Headed Thermotropic Liquid Crystals**

Wilhelm Volker Dahlhoff\*

Max-Planck-Institut für Kohlenforschung,  
 Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a. d. Ruhr  
 Z. Naturforsch. **43b**, 1367–1369 (1988);  
 received May 9, 1988

Liquid Crystals, Double-headed 1-O-*n*-Alkyl-D-mannitol Amphiphiles

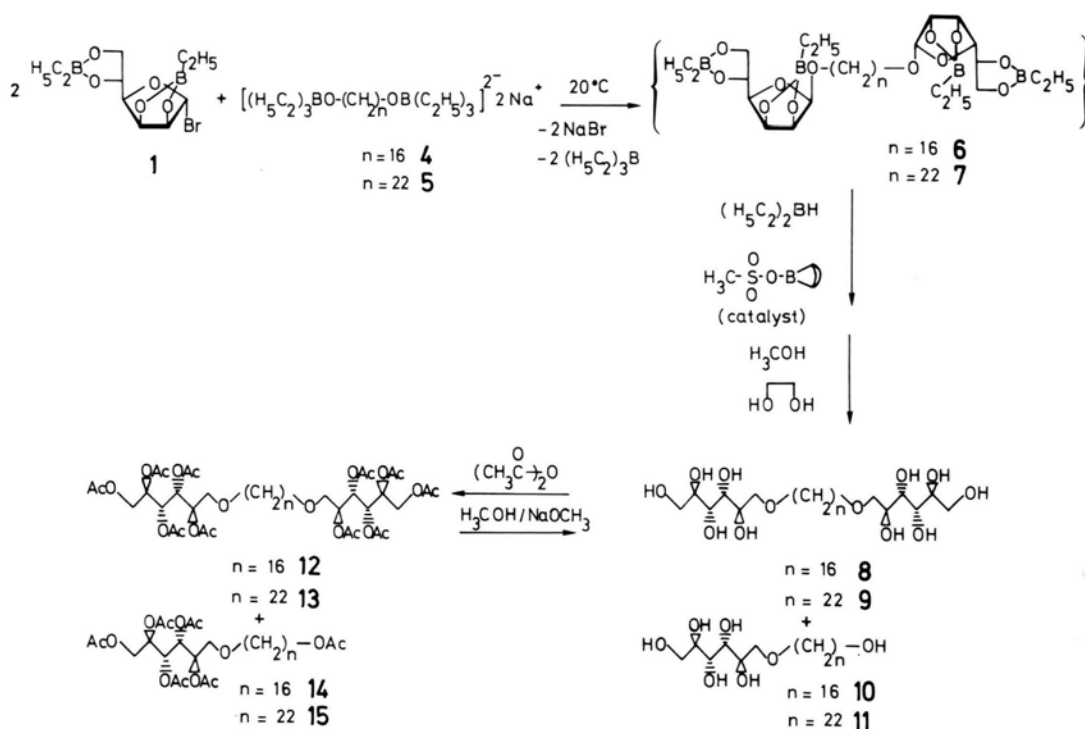
Mesogenic 1,16-di-(1-O-D-mannityl)-hexadecane (**8**), 1,22-di-(1-O-D-mannityl)-docosane (**9**), 1-(1-O-D-mannityl)-hexadecane-16-ol (**10**) and 1-(1-O-D-mannityl)-docosane-22-ol (**11**) are prepared from the respective  $\alpha,\omega$ -diols by glycosylation followed by glycoside reduction and deprotection.

In a recent compilation of mesogenic carbohydrates, it was concluded that the presence of a

polar or functional group at the terminus of the hydrophobic *n*-alkyl chain linked to the carbohydrate head-group inhibits thermotropic liquid crystal formation [2]. It has however been shown that some synthetic double-headed amphiphiles [“bolaamphiphiles”] are capable of forming monolayer lipid membranes [3]. Of particular interest are unsymmetric bolaamphiphiles, *i. e.* those having different sized head-groups thus inducing membrane curvature [4]. In order to ascertain whether or not such compounds can be thermotropic mesogens, new symmetric and unsymmetric alditol ether bolaamphiphiles were prepared as reported below.

The syntheses giving both types of double-headed amphiphiles can readily be achieved by glycosylation of sufficiently long,  $\alpha,\omega$ -diols followed by endocyclic acetal reductions. The two key steps in the synthetic approach involve

a) stoichiometric reactions of 2,3:5,6-di-O-ethylboranediyl- $\alpha$ -D-mannofuranosylbromide (**1**) [5] with of hexadecane-1,16-diol (**2**) or docosane-1,22-diol (**3**) after conversions to their reactive sodium triethylborates **4** and **5** [6, 7] and then



\* Reprint requests to Dr. W. V. Dahlhoff.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen  
 0932-0776/88/1000-1367/\$ 01.00/0



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

Compound <sup>b</sup>	$[\alpha]_D^{20}$ (c. solvent)	MS <sup>d</sup>	m.p. (°C)	$\Delta H$ (KJmol <sup>-1</sup> )	c.p. (°C)	$\Delta H$ (KJmol <sup>-1</sup> )
<b>8</b>	9.5° (0.4, (H <sub>3</sub> C) <sub>2</sub> SO)	586	148.7	127	196	6
<b>9</b>	10.6° (0.4, (H <sub>3</sub> C) <sub>2</sub> SO)	670	130	142	208	7
<b>10</b>	-6.7° (0.9, C <sub>5</sub> H <sub>5</sub> N)	422	1) 116 2) 129	20.5 60.0	122.5	5° -
<b>11</b>	-6.1° (0.9, C <sub>5</sub> H <sub>5</sub> N)	506	1) 120 2) 133	51.6 80.5	128	6 -

<sup>a</sup> Determined with a DuPont 1090-910 calorimeter; heating rate 10 °C min<sup>-1</sup>;  
<sup>b</sup> satisfactory C,H-analyses were obtained for **8–11**; <sup>c</sup> value found by cooling the isotropic liquid; <sup>d</sup> all compounds gave M+NH<sub>4</sub> parent ions by D.C.I./MS using ammonia as the reactant gas [12].

Table. Optical rotations, phase transition temperatures and their enthalpies for **8–11**<sup>a</sup>.

b) regioselective reductions of the intermediate dimannosides **6** and **7** by the new glycoside reducing method with ethyldiborane in the presence of 9-methanesulfonyloxy-9-borabicyclo[3.3.1]nonane (MSBBN) [8]. Following deprotection the double-headed **8** and **9** are obtained together with the monoethers **10** and **11**, respectively.

Pure **8–11** are easily obtained by per-O-acetylation of the product mixtures to give **12–15** and separating these by column chromatography. The acetates are converted to **8–11** by Zemplen saponification.

Having isolated the bolaamphiphiles **8**, **9**, and the unsymmetric **10** and **11** it is readily established by both D.S.C. and by polarizing microscopy [9], that all four compounds are indeed thermotropic mesogens (see Table).

Somewhat surprisingly, the symmetric **8** and **9** both have higher melting points and larger LC-ranges than the respective "halves" of these amphiphiles: *i. e.* **8** and **9** form stable mesophases having ranges over 47 °C and 78 °C, respectively, whereas 1-O-*n*-octyl-D-mannitol and 1-O-undecyl-D-mannitol have LC-ranges of 43 °C and 52 °C [10]. The unsymmetric **10** and **11** are dimorphic and only the lower melting modification is mesogenic in each case. The clearing points are best determined by D.S.C. on cooling the isotropic liquids.

Hence the presence of polar groups at the terminus of the lipophilic *n*-alkyl chain of amphiphilic carbohydrates does not necessarily prevent liquid crystal formation. A discogenic double-headed scyllitol ether has also been reported [13], but in contrast to **8–11**, it is a non-hydrogen bonding monotropic mesogen.

## Experimental Section

All experiments were carried out under an atmosphere of dry argon. Hexadecane-1,16-diol was purchased from Aldrich and docosane-1,22-diol was kindly donated by Dr. Roland Rienäcker of this Institute.

### *1,16-Di-(1-O-D-mannityl)-hexadecane (8) and 1-(1-O-D-mannityl)-hexadecane-16-ol (10)*

A solution of sodium triethylborate (1.58 g, 12.5 mmol) in diethyl ether (5 ml) is added dropwise at room temperature to a stirred mixture of **2** (1.6 g, 6.2 mmol) and diethyl ether (10 ml), liberating 285 Nml (103%) hydrogen. The slightly cloudy mixture is then cooled to 0 °C and a solution of **1** (3.8 g, 11.9 mmol) in diethyl ether (10 ml) is added dropwise in the course of 2 h. After 18 h at ~20 °C the sodium bromide is filtered off and the filtrate concentrated (10<sup>-3</sup> torr, 40 °C) to give a colourless viscous sirup (3.8 g) with  $[\alpha]_D -28.1^\circ$  (c 1.4, CHCl<sub>3</sub>).

To some of the product mixture (2.44 g), ethyldiborane (4 ml with 12.55% H<sup>-</sup> ≈ 40 mmol) and MSBBN (0.18 g, 6.8 mmol) is added and the stirred mixture is heated to 120 °C (bath temperature) for 5 h. The clear solution is concentrated (60 °C, 10<sup>-3</sup> torr) and the residue deboronated with portions of methanol (5 ml) and ethane-1,2-diol (5 ml). The crude mixture of **8** and **10** (1.71 g) is treated with ethanol (10 ml) and the solid filtered off and dried giving 1.02 g which is acetylated with acetic anhydride (8 ml) in pyridine (8 ml) for 30 h at 60 °C. The mixture of **12** and **14** obtained (1.7 g containing 44.5% **12** and 40.5% **14**) is separated by column chromatography [silica gel 60/70–230 mesh Merck,

column  $\varnothing$  30 cm, length 18 cm; eluents ethyl acetate/pentane mixtures 1:3 (500 ml) and 1:2 (500 ml); 5 ml fractions are collected]. Fr. 25–75 contained **14** (0.7 g) of 99.7% purity (GC); Fr. 120–180 eluted with 1:2 solvent mixture gives **12** (0.51 g) of 98.1% purity (GC). The  $R_f$  values of **12** and **14** are 0.23 and 0.61, respectively (solvent, ethyl acetate/pentane, 1:2).

Deacetylations are then carried out by standard Zemplen saponifications [11] to give **8** and **10** from **12** and **14** resp.

**9** and **11** are prepared from docosane-1,22-diol by the same reaction sequence as described above for obtaining **8** and **10**

Step 1. Yield 86%;  $[\alpha]_D^{20} -29.3^\circ$  (c 0.9,  $\text{CHCl}_3$ ).  
Steps 2 and 3. Overall yield 77%.

Step 4. Per-O-acetylation gives a mixture containing 51% **13** and 37% **15** by HPLC. **13** and **15** are then separated by column chromatography.  $R_f$  values for **13** and **15** are 0.22 and 0.36 resp., ethyl acetate/pentane 3:1.

Deacetylations then give **9** and **11**.

- 
- [1] Part 2: See W. V. Dahlhoff, Z. Naturforsch. **42b**, 661 (1987). A preliminary report of this work was given at the XIII Int. Carbohydrate Symposium, p. 27, Ithaca, N.Y. (1986).
- [2] G. A. Jeffrey, Acc. Chem. Res. **19**, 168 (1986).
- [3] J.-H. Fuhrhop, H.-H. David, J. Mathieu, U. Liman, H.-J. Winter, and E. Boekema, J. Am. Chem. Soc. **108**, 1785 (1986).
- [4] J.-H. Fuhrhop and J. Mathieu, Angew. Chem. **96**, 124 (1984); Angew. Chem., Int. Ed. Engl. **23**, 100 (1984).
- [5] W. V. Dahlhoff, A. Geisheimer, and R. Köster, Synthesis **1980**, 935.
- [6] W. V. Dahlhoff, A. Geisheimer, G. Schroth, and R. Mynott, Z. Naturforsch. **39b**, 1004 (1984).
- [7] W. V. Dahlhoff and A. Geisheimer, Z. Naturforsch. **40b**, 141 (1985).
- [8] R. Köster, S. Penades-Ullate, and W. V. Dahlhoff, Angew. Chem. **97**, 508 (1985); Angew. Chem., Int. Ed. Engl. **24**, 519 (1985).
- [9] G. W. Gray and J. W. Goodby, Smectic Liquid Crystals, Leonard Hill, Glasgow and London (1984).
- [10] W. V. Dahlhoff, Abstr. III, Europ. Symposium on Carbohydrates, p. 96, Grenoble, 16.–20. 9. 1985.
- [11] Methods in Carbohydrate Chem. Vol. II, 215, Ed. R. L. Whistler, M. L. Wolfrom, Academic Press, New York (1963).
- [12] D. Henneberg, H. Damen, W. Joppek, and W. Schmöllner, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr.
- [13] B. Kohne, P. Marquardt, K. Praefcke, P. Psaras, W. Stephan, and K. Turgay, Chimia **40**, 360 (1986).