Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Preliminary Communications First liquid crystalline derivatives of umbelliferyl β-D-glucoside [1]

Dirk Blunk[a]; Klaus Praefcke[a]; Günter Legler[b]
[a] Institute of Organic Chemistry, Technische Universität Berlin, Berlin, Germany [b] Institute of Biochemistry, Universität Köln, Köln, Germany

To cite this Article Blunk, Dirk , Praefcke, Klaus and Legler, Günter(1995) 'Preliminary Communications First liquid crystalline derivatives of umbelliferyl β-D-glucoside [1]', Liquid Crystals, 18: 1, 149 — 150
To link to this Article: DOI: 10.1080/02678299508036603
URL: http://dx.doi.org/10.1080/02678299508036603

LIQUID CRYSTALS, 1995, VOL. 18, NO. 1, 149–150

Preliminary Communications

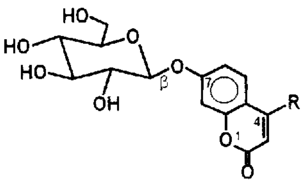
First liquid crystalline derivatives of umbelliferyl β-D-glucoside [1]

by DIRK BLUNK, KLAUS PRAEFCKE* and GÜNTER LEGLER†
Institute of Organic Chemistry, Technische Universität Berlin,
Straße des 17. Juni 135, D-10623 Berlin, Germany
† Institute of Biochemistry, Universität Köln, Zülpicher Straße 47,
D-50674 Köln, Germany

(Received 15 August 1994; accepted 20 August 1994)

Three examples of a new series of carbohydrate liquid crystals incorporating a coumarin unit are reported. A steric effect influencing their smectic A phase formation is discussed in comparison with structurally unaffected amphiphilic carbohydrate-based mesogens.

In the course of our work on natural product liquid crystals [2–5], mainly on multihydroxy amphiphiles, we had access to 4-alkyl derivatives of umbelliferyl β-D-glucoside (**1 a–c**, 4-alkyl-7-(β-D-glucopyranosyloxy)-2H-1-benzopyran-2-ones), and were tempted to examine the anticipated thermomesogenic properties of these bioactive representatives.



1 a: R = C_7H_{15}
b: R = C_9H_{19}
c: R = $C_{13}H_{27}$

The molecular structure of the 4-alkyl derivatives **1 a–c** of umbelliferyl β-D-glucoside, investigated here.

The middle part of this type of glucoside **1**, the rigid and relatively flat coumarin unit, is flanked by a hydrophilic tetrol (carbohydrate) head group and a lipophilic tail *R* causing a somewhat bent molecular shape. Despite the humpbacked situation created by positions 1 to 3 of the coumarin sub-structure, our compounds can apparently exist in a conformation that is stretched enough to allow the systems to exhibit mesogenity on heating. Naturally, compounds without such a steric burden, for example, the closely related 1-*O*-trans-4′-alkylcylohexyl or 1-*O*-4′-substituted-phenyl derivatives of β-D-glucopyranoside, are much better favoured to be thermotropically liquid crystalline over considerably wider ranges of temperature [6]. For instance, whereas **1 a** is not thermomesogenic, the 4-octyl- and 4-heptyloxy-phenyl β-D-glucosides [6] are; interestingly, the melting points of these three carbohydrate aryl ethers are nearly identical (107–108°C). Our recent findings on the liquid crystalline behaviour of the three derivatives **1 a–c** of umbelliferyl glucopyranoside, as the parent compound of a new mesogen family, are reported here.

The synthesis of **1 a–c** has been described elsewhere [7], but relevant information is given later in this article; their structures were proved by IR and NMR spectroscopy.

Whereas the heptyl derivative **1 a** is not liquid crystalline, neither thermo- nor lyo-tropically (in water), both the nonyl and tridecyl homologues **1 b** and **c** are—see the table. Miscibility studies (contact method) of the mesophases of **1 b** and **1 c** with 4-*O*-dodecyl-*myo*-inositol

The phase transition data* for the three 4-alkyl derivatives (**1 a–c**) of umbelliferyl β-D-glucoside; the type of thermotropic mesophase exhibited is smectic A(S_A).

Tetrol	Alkyl, *R*	m.p. (Δ*H*)	cl.p. (Δ*H*)
1 a	Heptyl	107·1/107·2 (64·3)	Not liquid crystalline
1 b	Nonyl	159·5/163·2 (33·5)	{158·8/158·8 (2·2)}
1 c	Tridecyl	163·0/163·4 (32·9)	200·0/198·0 (1·3)

* The temperatures for the melting and clearing processes (m.p. or cl.p., respectively) are given in °C and were those obtained by polarizing microscopy/differential scanning calorimetry (Δ*H* = transition enthalpy is given in kJ mol^{-1}); the data marked in { } relate to a monotropic transition. Melting points of **1 a** and **b** determined earlier using a normal m.p. apparatus used in chemical laboratories can be looked up in reference [7]. The new compound **1 c** is the first enantiotropic member of this novel series of mesogens.

---

* Author for correspondence.

0267-8292/95 $10·00 © 1995 Taylor & Francis Ltd.

[2 (d)] or 1-*O*-octyl-*β*-D-glucopyranose [8]—two typical members of the so-called single tailed family of carbohydrate liquid crystals—show clearly that they both are of the smectic A type. Between lipophilized glass plates, samples of our umbelliferyl glucopyranoside derivatives **1 b** and **c** form focal-conic textures, including wide homeotropic areas, on cooling from their isotropic phases. In contact preparations with water, myelin structures are observable, indicating the formation of a lyotropic mesophase, probably lamellar in type.

Microscopic investigations were carried out with a Leitz Laborlux 12 Pol polarizing microscope equipped with a Mettler FP 82 hot stage. The DSC measurements were performed with a Mettler TA 3000/DSC 30 S with GraphWare TA 72. The heating/cooling rates applied in both methods were 5 K min^{-1}.

The lipophilized microscopic slides and cover glasses were prepared by treating the carefully cleaned glass plates in a sealed vessel with some drops of dichlorodimethylsilane for 2 hours.

4-Tridecylumbelliferyl β-D-glucopyranoside [9] (***1 c***). Ethyl 3-oxohexadecanoate [10] (10 g, m.p. 41–42°C) was condensed [11] with resorcinol (4·5 g) to give 4-tridecylumbelliferone (5·5 g, m.p. 98–100°C) after recrystallization from ethyl acetate/ether/ethanol 1/1/1. Its reaction with 1-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl) trichloracetamidate in dichloromethane, using BF_3Et_2O as catalyst [12], gave, after purification by MPLC on silica gel in toluene/ethyl acetate 95/5 → 60/40, 4-tridecylumbelliferyl *β*-D-glucopyranosyl tetra-acetate in 35 per cent yield. The free glucoside was obtained by catalytic deacetylation (sodium methanoate in methanol) and recrystallization from ethanol/water. IR (Beckman I.R. 9, KBr, cm^{-1}): n = 3405 (OH, very broad), 1696 (C=O), 1612 (C=C), 1073 (aliph. C–O). ^{1}H NMR (Bruker AM 400, $CDCl_3/CD_3OD$, ppm): d = 0·68 (t, 3 H, J = 7 Hz; CH_3), 1·03–1·28 (m, 20 H; 10 alkyl-CH_2), 1·50 (tt, 2 H, each J = 7 Hz; *β*-CH_2), 2·57 (t, 2 H, J = 7 Hz; α-CH_2), 3·28–3·40, 3·58–3·63 and 3·69–3·74 (3m, 4 H, 1 H and 1 H, respectively, glucosyl-Hs without assignment), 4·81 (d, 1 H, J = 8 Hz; anomeric H), 5·98 (s, 1 H; 3-H), 6·84–6·88 and 7·40–7·44 (2m, 2 H and 1 H, respectively; 5-H, 6-H and 8-H without assignment). Our phase transition data for **1 c** are compiled in the table.

K.P. is grateful to the following institutions for their financial support of our liquid crystal work: Deutsche Forschungsgemeinschaft (Sonderforschungsbereich Sfb 335 'Anisotrope Fluide', project C3), Bonn, Fonds de Chemischen Industrie, Frankfurt/Main, Technische Universität Berlin, and Gesellschaft von Freunden der Technischen Universität Berlin (travelling funds to Dipl.-Chem. D. Blunk). Furthermore, we thank Mr A. Eckert, technical assistant in our laboratory for his skilled collaboration.

References

[1] Part 92 of liquid crystalline compounds; part 91: PRAEFCKE, K., BILIGIN, B., and USOL'TSEVA, N., 1995, *J. mater. Chem.* (submitted in August 1994).

[2] *Inositol derivatives*: (a) KOHNE, B., and PRAEFCKE, K., 1985, *Chem.-Ztg.*, **109,** 121. (b) ECKERT, A., KOHNE, B., and PRAEFCKE, K., 1988, *Z. Naturf.* (*b*), **43,** 878. (c) MIETHCHEN, R., PRADE, H., HOLZ, J., PRAEFCKE, K., and BLUNK, D., 1993, *Chem. Ber.*, **126,** 1707. (d) PRAEFCKE, K., BLUNK, D., and HEMPEL, J., 1994, *Molec. Crystals liq. Crystals*, **243,** 323.

[3] *Sugar derivatives* (a) KOHNE, B., and PRAEFCKE, K., 1984, *Angew. Chem.*, **96,** 70; 1984, *Angew. Chem. Int. Ed. Engl.*, **23,** 82. (b) PRAEFCKE, K., and BLUNK, D., 1993, *Liq. Crystals*, **14,** 1181. (c) reference [2 (d)].

[4] *Guggultetrols and related multiols*: PRAEFCKE, K., KOHNE, B., DIELE, S., PELZL, G., and KJAER, A., 1992, *Liq. Crystals*, **11,** 1.

[5] *Deoxynojirimycin derivatives*: BLUNK, D., PRAEFCKE, K., and LEGLER, G., 1994, *Liq. Crystals*, **17,** 841.

[6] TSCHIERSKE, C., LUNOW, A., and ZASCHKE, H., 1990, *Liq. Crystals*, **8,** 885.

[7] LEGLER, G., and LIEDKE, H., 1985, *Biol. Chem. Hoppe-Seyler*, **366,** 113.

[8] GOODBY, J. W., 1984, *Molec. Crystals liq. Crystals*, **110,** 205.

[9] STACHORA, A., 1990, Diploma Thesis (Chemistry), University of Cologne, Germany.

[10] VISCONTINI, A., and ADANK, K., 1952, *Helv. chim. Acta*, **35,** 1342.

[11] RUSSEL, A., and FRYE, J. F., 1941, *Org. Synth.*, **21,** 22.

[12] SCHMIDT, R. R., and STUMPP, M., 1983, *Justus Liebigs Annln Chem.*, 1249.