Carbohydrate Research, 115 (1983) 53–58
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CARBOHYDRATE LIQUID-CRYSTALS*

GEORGE A. JEFFREY AND SARAMA BHATTACHARJEE
Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260 (U.S.A.)
(Received November 1st, 1982; accepted for publication, November 22nd, 1982)

ABSTRACT

Certain alkyl glycosides and 1-thioglycosides are shown to have thermotropic, liquid-crystal phases between room temperature and their melting points. In the alkyl 1-thio-β-D-xylopyranoside series, liquid-crystal phases occur with heptyl and octyl chains, but not with hexyl, or lower, members of the series. Heptyl 1-thio-α-D-mannopyranoside forms liquid crystals, but the substitution of terminal OH, Cl, and $C\equiv N$ groups on the alkyl chains inhibits liquid-crystal formation. Octyl, nonyl, and decyl α- and β-D-glucopyranosides form liquid crystals. This property is associated with crystal structures in which the carbohydrate moieties are hydrogen-bonded and the alkyl chains intercalated.

INTRODUCTION

In Part I of this series[1], the crystal structure of heptyl 1-thio-α-D-mannopyranoside was reported, and a transition to a liquid-crystal phase at 61° was noted. Closer examination has since revealed that this compound also has a solid-to-solid phase-transition at 39°. These phase transitions and the molecular packing in the crystal structure are analogous to those observed in the smectogenic *p*-(*n*-alkyl)benzoic acids[2]. Decyl α-D-glucopyranoside has an analogous crystal structure[3], with a liquid-crystal phase between 76° and a melting point of 138°. The crystal structures of octyl α- and β-D-glucopyranoside have been studied by electron diffraction, and have been shown[4] to have liquid-crystal phases with major, endothermic transitions at 71.8 and 68.2°; this suggests that mesogenic properties may be common among the general class of alkyl glycosides, and we have explored this hypothesis further by examining a variety of these compounds for their liquid-crystal properties.

EXPERIMENTAL

The compounds examined were as follows: a series of alkyl 1-thio-β-D-xylopyranosides (from methyl to octyl[5]), provided by Dr. M. Claeyssens, Rijks Universiteit, Ghent, Belgium; heptyl 1-thio-α-D-mannopyranoside and derivatives there-

---

*Part II. For Part I, see ref. 1.

0008-6215/83/$ 03.00

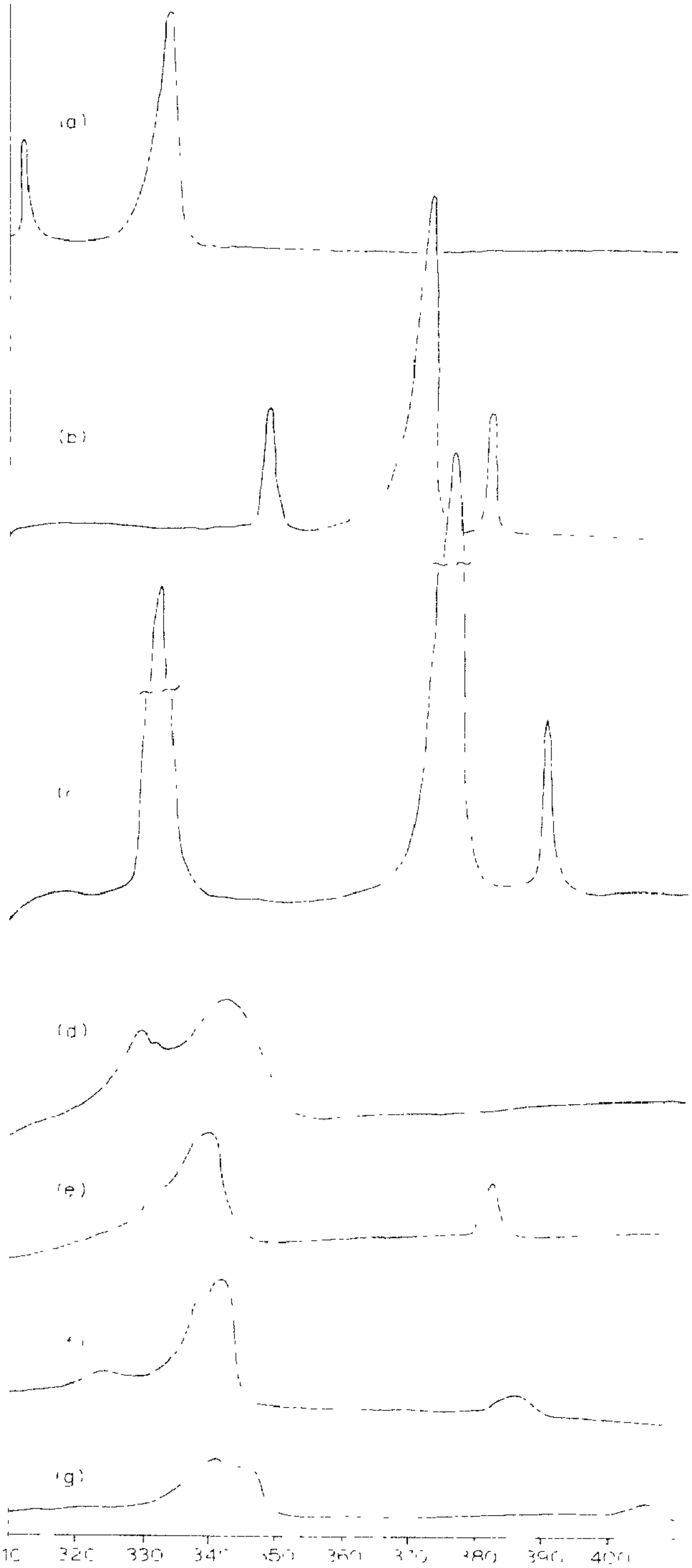

Fig. 1. Differential-scanning-calorimeter thermograms of some alkyl glycosides and 1-thioglycosides. [Key: (a) heptyl 1-thio-α-D-mannopyranoside; (b) heptyl 1-thio-β-D-xylopyranoside; (c) octyl 1-thio-β-D-xylopyranoside; (d) heptyl β-D-glucopyranoside; (e) octyl β-D-glucopyranoside; (f) nonyl β-D-glucopyranoside; and (g) decyl β-D-glucopyranoside.]

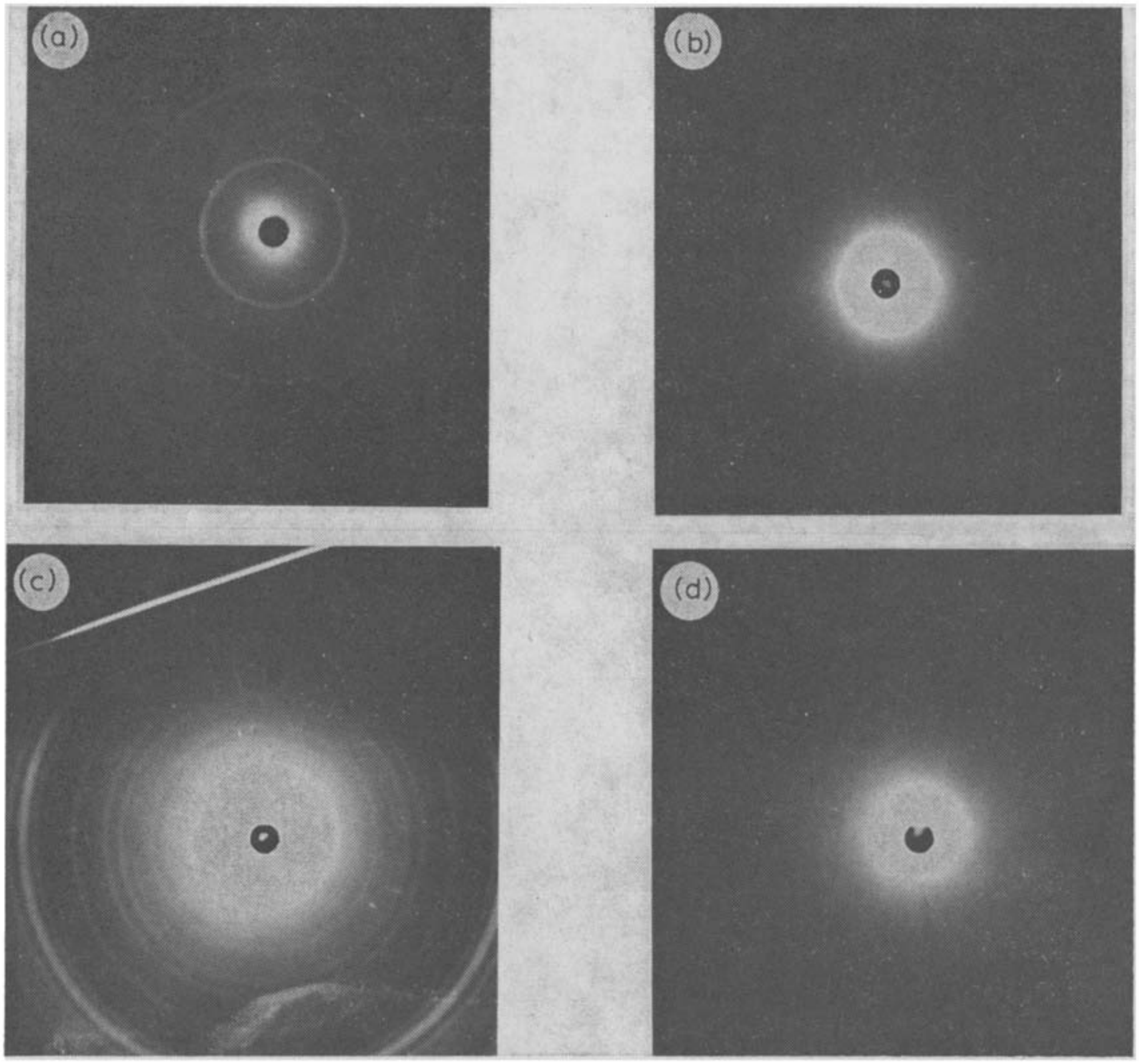

Fig. 2. Crystal and liquid-crystal diffraction-patterns of some alkyl pyranosides. [(a) Crystalline powder diffraction pattern of heptyl 1-thio-α-D-mannopyranoside at 25°. (b) Liquid-crystal diffraction-pattern of heptyl 1-thio-α-D-mannopyranoside at 70°. (c) Crystalline powder diffraction-pattern and liquid-crystal pattern of octyl β-D-glucopyranoside at room temperature. (d) Liquid-crystal diffraction-pattern of octyl β-D-glucopyranoside at 70°.]

of[6] from Dr. P. Durette, Merck Sharp and Dohme, Rahway, New Jersey, USA; and heptyl to decyl β-D-glucopyranoside from the Sigma Chemical Company. Preliminary recognition of mesophase formation was made by observing the successive appearance and disappearance of bifringence with temperature, using a polarizing microscope with a heated stage. The more-precise measurements of the transition temperatures, reported in Table I, were made from the differential scanning thermograms shown in Fig. 1, using a Perkin–Elmer differential scanning calorimeter, Model DSC 1B. The X-ray diffraction patterns, examples of which are shown in Fig. 2, were obtained with a flat-plate camera by using Ni-filtered CuKα radiation with a 450-mm collimator having crossed slits. The powder specimens, contained in thin-walled, glass capillaries, were heated in a furnace controlled to ±1 °, with incident and diffracted X-ray beam apertures.

TABLE I

TRANSITION TEMPERATURES (°C) AND d-SPACINGS (IN Å) OF SOME ALKYL GLYCOPYRANOSIDES[a]

	Crystalline phase	*(degrees)*	*Intermediate phase*	*(degrees)*	*Mesophase*	*(degrees)*	*Liquid*
Heptyl 1-thio-α-D-mannopyranoside	15.12 [30.24]	39	22.87 [18.84]	61	22.7	151	
Heptyl 1-thio-β-D-xylopyranoside	23.2	72	—	97	23.5	105	
Octyl 1-thio-β-D-xylopyranoside	20.48	57	24.9	100	25.2	114	
β-D-Glucopyranosides							
heptyl	27.9	56	---	59	22.9	69	
octyl	29.4 (29.0)	57 (55, 57)	--	68 (68)	26.1	110 (105)	
nonyl	32.6	51	33.02 [28.01]	68	27.6	113	
decyl	34.0	68	34.00 [29.28]	72	29.5	133	

---

[a] Values without brackets are at d_{max}; with square brackets, at d_{100}. Values in parentheses were taken from ref. 4.

RESULTS

The results are summarized in Table I, which shows the transition temperatures derived from the differential-scanning-calorimeter thermograms shown in Fig. 1, and d-spacings measured from the X-ray diffraction patterns. For the crystalline phases, the maximum d-spacing (d_{max}) observed is given. When single-crystal data are available, the maximum d_{100}-spacing is also reported. For the intermediate phase, the two largest d-spacings are listed. For the liquid-crystal phase, the d-spacing of the single, intense ring is reported.

For the alkyl 1-thio-β-D-xylopyranosides, no evidence of liquid-crystal formation was obtained for the methyl, ethyl, propyl, butyl, pentyl, and hexyl glycosides. There is a corresponding discontinuity in the melting points between the pentyl (m.p. 114–115°), the hexyl (m.p. 158–160°), and the heptyl glycoside (m.p. 105°). We have not yet established whether there is a corresponding change in the type of molecular packing in the crystals, but this seems likely. As shown in Fig. 1b and c, the thermograms for the heptyl and octyl 1-thio-D-xylosides show a sharp peak at the respective transition temperature. Those transitions from intermediate phase to liquid crystal are the most endothermic, and those from liquid crystal to liquid, the least.

The phase behavior of heptyl 1-thio-α-D-mannopyranoside (Fig. 1a) is similar, except for the wider range of temperature over which the liquid-crystal phase is stable.

Derivatives of heptyl 1-thio-α-D-mannopyranoside in which the terminal methyl group of the alkyl chain was replaced by a hydroxyl, chloro, or cyano group did not have mesogenic properties. Neither did a fully acetylated derivative, octyl tetra-*O*-acetyl-β-D-glucopyranoside, indicating the essential role of the carbohydrate hydrogen-bonding for liquid-crystal formation in these compounds. The alkyl β-D-glucopyranosides gave differential-scanning-calorimeter thermograms (Fig. 1 d–g) having peaks broader than those of the D-xylosides, and the temperatures of the two phase-changes are closer together, being unresolved for the octyl glycoside. In the thermogram of octyl β-D-glucopyranoside[4], these peaks were resolved, and two minor transitions were reported at 54.5 and 57.2°, with the main endotherm at 68.2°. For the nonyl glycoside, there is also evidence of two intermediate phases, before the main transition to the liquid crystal.

DISCUSSION

These results support the hypothesis that there is a large class of alkyl glycosides that are thermotropic mesogens, and they indicate that the carbohydrate moiety may be derived from any monosaccharide, or possibly, reducing disaccharide, and that the alkyl chains can range from heptyl upwards. The octyl and decyl β-D-glucopyranosides are well known detergents[7], and are used as solubilizing agents for bacterial membranes[8,9]. This suggests that the longer-chain alkyl glycosides will have both thermotropic and lyotropic properties[10].

The appearance of a single, well-defined, diffraction ring on the flat-plate X-ray photographs, and the evidence of intercalated hydrocarbon layers in those crystal structures that have been determined, suggest that the liquid-crystal phases so far examined are *smectic*. However, the outer ring at higher diffraction angles, characteristic of unoriented smectic phases, has not hitherto been observed. Presumably, essential clues to the structure of the mesophase will come from knowing that of the intermediate phase, and from the change in structure that takes place in the first transition into that phase.

A compilation of thermotropic mesogens made in 1973 listed over 5,000 compounds[11], none of which were carbohydrates. Because of their technological importance, there are now probably more than 10,000 of these compounds known; however, this interesting class of carbohydrate liquid-crystals does not seem to have received the attention it deserves, considering the fact that their transition temperatures are close to those of life processes.

ACKNOWLEDGMENTS

We are grateful to Dr. M. Claeyssens and Dr. P. L. Durette for supplying us with samples, and to Dr. J. Magill of the Department of Metallurgical and Materials Engineering, University of Pittsburgh, for use of a differential scanning calorimeter. This research was supported by the U.S. Public Health Service, National Institutes of Health, Grant No. GM-24526.

REFERENCES

1 D. C. Carter, J. R. Ruble, and G. A. Jeffrey, *Carbohydr. Res.*, 102 (1982) 59–67.

2 R. F. Bryan, P. Hartley, R. W. Miller, and M.-S. Shen, *Mol. Cryst. Liq. Cryst.*, 62 (1980) 281–310.

3 P. C. Moews and J. R. Knox, *J. Am. Chem. Soc.*, 98 (1976) 6628–6633.

4 D. L. Dorset and J. P. Rosenbusch, *Chem. Phys. Lipids*, 29 (1981) 299–307.

5 F. Deleyn, M. Claeyssens, J. van Beeumen, and C. K. de Bruyne, *Can. J. Biochem.*, 56 (1978) 43–50.

6 P. L. Durette and T. Y. Shen, *Carbohydr. Res.*, 83 (1980) 178–186.

7 W. J. de Grip and P. H. M. Bovee-Geurts, *Chem. Phys. Lipids*, 23 (1979) 321–335.

8 C. Baron and T. E. Thompson, *Biochim. Biophys. Acta*, 382 (1975) 276–285.

9 G. W. Stubbs, H. G. Smith, and B. J. Litman, *Biochim. Biophys. Acta*, 426 (1976) 46–56.

10 Compare, G. M. Brown, P. Dubreuil, F. M. Ichhaporia, and J. E. Desnoyers, *Can. J. Chem.*, 48 (1970) 2525–2531.

11 D. Demas, H. Demas, and H. Zaschke, *Fliessige Kristallen in Tabellen*, Verlag Grundstoffindustrie, Liepzig, DDR (1973).