Journal of Thermal Analysis and Calorimetry, Vol. 74 (2003) 77–83

MESOMORPHISM OF S-ALKYLTHIOPENTONOLACTONES AND THEIR ITOL DERIVATIVES

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(Received December 27, 2002; in revised form March 14, 2003)

Abstract

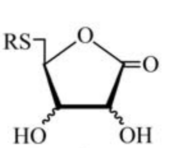
Mesophasic properties of S-alkylthiopentonolactones (*D*-ribono, *D*-arabinono and *D*-xylono) and the corresponding itol derivatives with general formula Su-SR (R=n-C_nH_{2n+1}) are studied. It was shown that the thermotropic and lyotropic phase transition temperatures are influenced by the following structural parameters: alkyl chain length, free OH group number, cyclic or acyclic Su structure and itol conformation.

Keywords: 5-S-alkyl-5-thio-*D*-pentonolactones, 1-S-alkyl-1-thiopentitols, DSC, glycoamphiphiles, liquid crystals, lyotropy, POM, thermotropy

Introduction

It was shown that glycoderivatives with general formula Su-ZR, in which a hexose or itolic unit Su, is linked by an atom or an atom group Z=O, S, OCO to R alkyl chains (R=n-C_nH_{2n+1}; n=6–18) constitute a wide range of nonionic amphiphilic compounds abundantly studied in the last years [1–11].

Few examples on pentoses and corresponding pentitols derivatives have been studied. We report herein some new thermotropic and lyotropic mesophase properties of 5-S-alkyl-5-thiopentonolactones (Type **I**) (*D*-ribono, *D*-arabinono and *D*-xylono) and the corresponding itol derivatives (Type **II**) with general formula Su-S-R (R=n-C_nH_{2n+1}; n=6; 8; 10; 12).



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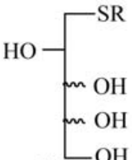

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1388–6150/2003/ $ 20.00

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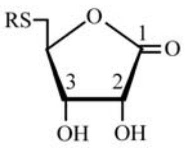
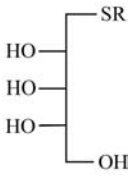
Materials and methods

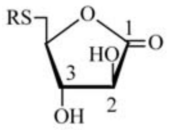
Materials



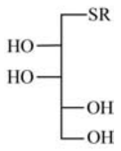
5-S-alkyl-5-thio-*D*-ribono-1,4-lactones



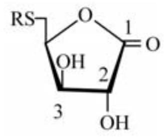
1-S-alkyl-1-thio-*L*-ribitols



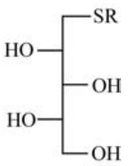
5-S-alkyl-5-thio-*D*-arabinono-1,4-lactones



1-S-alkyl-1-thio-*D*-lyxitols



5-S-alkyl-5-thio-*D*-xylono-1,4-lactones



1-S-alkyl-1-thio-*L*-xylitols

General analytical methods

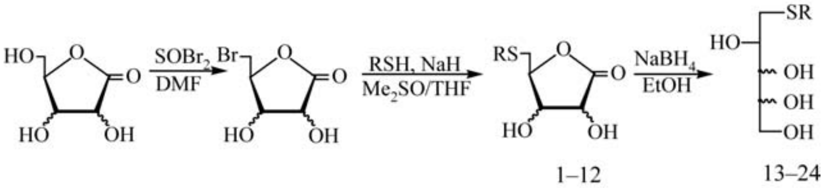
Optical rotations were measured with a digital polarimeter DIP-370 (JASCO), using a sodium lamp (λ=589 nm) at 25°C. ^{1}H and ^{13}C NMR spectra were recorded in D_2O or $CDCl_3$. Me_4Si was used as an internal standard on a Bruker 300 MHz spectrometer. Thin-layer chromatography (TLC) was performed on E. Merck glass plates silica gel sheets (Silica Gel F_{254}) and visualised under UV light and stained with phosphomolybdic acid–H_2SO_4 solution. Column chromatography was performed on Kieselgel (E. Merck 230–400 mesh) with the appropriate gradient elution.

Phase transition temperatures were determined by DSC using a Mettler FP85 microfurnace and/or by thermal polarized optic microscopy (POM) using Olympus BX50 polarizing transmitted light equipped with a Mettler FP82 micro furnace. Both Mettler apparatus were connected to a FP90 central processor. For thermotropic liquid crystals, transition temperatures, noted *MP* (melting point: solid→liquid crystal) and *CP* (clearing point: liquid crystal→isotropic liquid) are T_{onset} measured by DSC in aluminium crucibles of 40 μL. The apparatus was calibrated with indium, benzophenone and benzoic acid. All the products were lyophilised before the study. The lyotropic liquid crystal (LLC) transition temperatures, noted T_1 (liquid crystal apparition) and T_2 (liquid crystal disappearance) are determined by dissolving the crystals into the water, and thereby creating a concentration gradient which supports mesophase formation. When T_2 is upper 100°C, ethylene glycol replaces water. This qualitative experiment shows if mesophases can exist.

Synthesis

Synthesis of the different compounds was reported in a preceding paper [12]:

Type **I** and **II** compounds were prepared using Scheme 1.



Scheme 1

Type **I** compounds:

To a solution of alkanethiol (2.8 mM) in 1:1 Me_2SO–THF (8 mL) was added sodium hydride (1.2 equiv.). The mixture was vigorously stirred at room temperature for 1 h. The 5-bromo-5-deoxy-*D*-pentono-1,4-lactone (0.5 g; 2.37 mM) was then added and stirring was continued. After 5 min, MeOH (3 mL) was added and the solution was concentrated and co-concentrated with water, at 50°C, under reduced pressure. The crude product was chromatographed on silica gel (4:1 EtOAc–petroleum ether).

Type **II** compounds:

To a solution of 5-S-alkyl-5-thio-*D*-pentono-1,4-lactones (0.2 g, 0.91 mM) in EtOH (20 mL) was added $NaBH_4$ (1.6 equiv., 350 mg) at such a rate that the pH was maintained below 7. Then a further amount of $NaBH_4$ (1.9 equiv., 415 mg) was added to increase the pH to 9. Stirring was continued at room temperature, for 1 h, before adding more ion exchange resin (Dowex 50×8–100 ion) to decrease the pH to 3. The resin was then removed by filtration. The filtrate was concentrated and co-concentrated with MeOH (3×18 mL) to give the crude mixture which was chromatographed on Silica Gel (95:5 EtOAc–MeOH).

Results and discussion

The majority of the studied compounds have shown thermotropic liquid crystal behaviour and the most of them gave also lyotropic mesophases. The reported DSC phase transition temperatures were obtained at a 5°C min^{-1} heating rate (Fig. 1). A previous investigation of heating rate, from 1 to 10°C min^{-1} showed that the best DSC data was observed at a heating rate of 5°C min^{-1}.

The thermotropic liquid crystal transition temperatures of the 5-S-alkyl-5-thiopentonolactones and their itol derivatives and, in the similar way, the existence of lyotropic liquid crystals are collected in Table 1.

Table 1 Phase transition temperatures (°C) and corresponding enthalpies (J g^{-1}) of S-alkylthiopentonolactones and the corresponding itol derivatives, measured at 5°C min^{-1}

Su	ref	n	Thermotropy		Lyotropy	
			$MP[\Delta H]$	$CP[\Delta H]$	T_1	T_2
	1	6	99.5 [121]		no	LLC
	2	8	104.5 [107]		no	LLC
	3	10	102.7 [107]		no	LLC
	4	12	108.2 [111]		no	LLC
	5	6	45.8 [46]	80.0 [7.77]	<RT	84
	6	8	54.8 [50.8]	110.4 [4.84]	<RT	107
	7	10	45.9 [72.6]	123.2 [3.83]	<RT	104
	8	12	54.0 [84.6]	129.5 [2.90]	36	106
	9	6	20.7 [33.1]	80.9 [6.21]	<RT	85
	10	8	46.6 [71.3]	106.3 [4.16]	30*	123
	11	10	48.5 [108]	122.4 [5.04]	29*	116
	12	12	58.0 [126]	125.7 [2.62]	40*	127
	13	6	32.5 [107]**	110.7 [6.3]	<RT	104
	14	8	77.0 [120]	131.4 [5.6]	<RT*	109
	15	10	83.6 [133]	135.5 [38]	<RT*	106
	16	12	87.2 [115]	141.0 [1.5]	<RT*	87
	17	6	64.8 [91.2]	113.7 [8.3]	23	37
	18	8	62.0 [88.8]	135.8 [4.5]	33	116
	19	10	57.8 [84.4]	130.2 [3.5]	27	116
	20	12	52.7 [304]**	144.7 [2.5]	50	98
	21	6	9.6 [128]**	102.8 [31.1]	<RT	116
	22	8	53.2 [94.6]	130.9 [7.6]	<RT	111
	23	10	40.9 [97.5]	147.2 [32]	<RT	82
	24	12	60.8 [95.5]	140.0 [3.3]	43	123

*lyotropic liquid crystal (LLC) in cooling at room temperature
**double peak

Lyotropic liquid crystals

No lyotropic liquid crystal is detected for ribonolactone (**1–4**) derivatives. The hydroxyl group positions promote intramolecular hydrogen bonds. All the other compounds exist

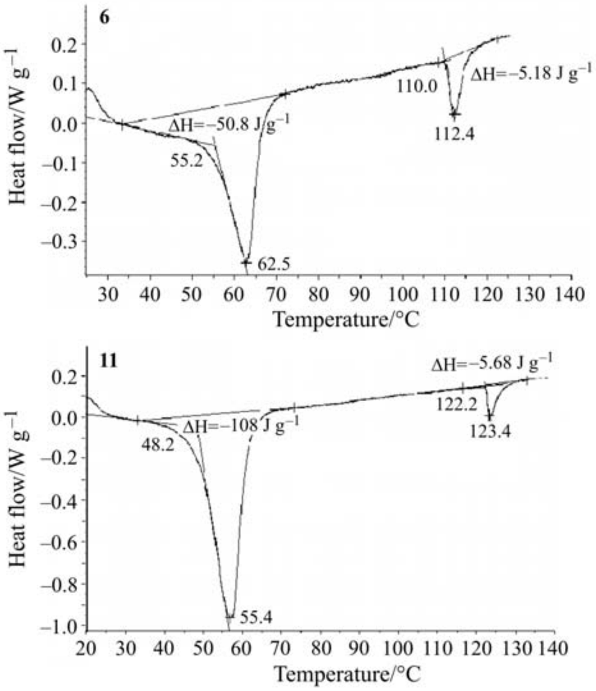


Fig. 1 DSC curves of compounds **6** and **11** at 5°C min^{-1} heating rate, sample mass: 10 mg

in a temperature domain from about room temperature (*RT*=20°C), at the formation or after temperature cycle, to temperature often superior to 100°C; it is large domain.

Thermotropic liquid crystals

For the same reason, ribono derivatives have not thermotropic liquid crystals. *MP* is almost independent of chain length (*n*), whereas *CP* increases from low values for short alkyl chain length to reach a maximum and would decrease for *n*>12 [13].

For arabinono- (**5–8**) and xylonolactone (**9–12**) derivatives, it seems that the symmetric position of the hydroxyl groups *vs.* cycle gives close *MP* and *CP* values, the little differences proceeding of the surrounding atoms, thus molecular modelisation of 5-*S*-hexyl-5-thio-*D*-pentono-1,4-lactones [14] gives:

Compound	$d_{\text{OH-2, OH-3}}$	$d_{\text{OH-2, O-1}}$
Arabinono	3.58 Å	3.03 Å
Xylono	3.22 Å	2.81 Å

For the itol derivatives, the temperature domains of mesophase and *MP* are higher than those of pentonolactone derivatives. Apparently, the stiffness of the head leads to a higher instability of aggregates for the second.

For the different diastereoisomers, *CP* is close to the same *n* (Table 2) but *MP* are different with the temperature domains roughly in the order:

Arabinitol (**13–16**)<xylitol (**17–20**)<xylitol (**21–24**)

Because the hydroxyl groups are more dispersed in the molecule, as it was already shown for the erythritol/threitol derivatives [15]. We also think that the conformation differences have only a little effect. If we compare 1-*D*-xylitol derivatives with 1-*D*,*L* ones (Table 3) [16], *CP* are close and *MP* higher in the second case.

Table 2 Variation of *CP* with *n* for itol derivatives

n	6	8	10	12
CP/°C	108±6	133.4±2.5	138.7±8.5	142.4±2.4

Table 3 Phase transition temperatures (°C) and corresponding enthalpies (J g^{-1}) of 1-*D*, *L*-itols derivatives from [16]

n	*MP*/°C [Δ*H*/J g^{-1}]	*CP*/°C [Δ*H*/J g^{-1}]
6	56.7 [125.1]	105.8 [8.65]
8	49.9 [151.8]	128.7 [7.8]
10	58.0 [153]	141.9 [3.97]
12	66.7 [177]	139.3 [4.36]

Conclusions

All S-alkylthiopentonolactones (*D*-ribono, *D*-arabinono and *D*-xylono) and the corresponding itol derivatives with general formula Su-*S*-R ($R=n\text{-}C_nH_{2n+1}$, $6\leq n\leq 12$) give lyotropic liquid crystals when the two hydroxyl groups are not planar. This is also applied for the thermotropic liquid crystals which follow the properties already seen for hexose and hexitol derivatives.

* * *

We thank the Conseil Régional de Picardie and the Ministère de la Recherche for financial support.

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