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Note

Direct syntheses of *S*-alkylthio-D-galactono-, D-mannono-1,4-lactones, *S*-alkylthio-L-galactitols and D-mannitols displaying amphiphilic and mesophasic properties

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Abstract—Alkylthio-L-galactitols and D-mannitols were obtained in good yields (70–81%) by reduction, with $NaBH_4$, of the corresponding 6-*S*-alkyl-6-thio-D-hexono-1,4-lactones.

Keywords: Unprotected bromohexolactones; *S*-alkylthiohexonolactones; *S*-alkylthiohexitols

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

It is now well established that such derivatives can form liquid crystals and also find practical uses as surfactants and nonionic detergents.[3,12] *S*-Alkylthiopolyols are a new group of amphiphilic carbohydrates.

The literature records a few methods for the preparation of alkyl 1-thioglycosides,[13] which can be converted into 1-*S*-alkyl-1-thiohexitols. These syntheses require tedious protection-deprotection steps and lead to substantially lower yields.[14]

We have previously described the preparation of 5-*S*-alkyl-5-thio-D-pentono-1,4-lactones and 1-*S*-alkyl-1-thiopentitols (70–90%),[15] in a two and three-step sequence, respectively, via the 5-bromo-5-deoxy-D-pentono-1,4-lactones as key intermediate. We have also studied the relationship between structure and tensioactive[16] and/or mesophasic[17] properties. These studies show that the surfactants containing an alditol moiety are more surface-active than the respective ones containing a ring. These derivatives give also lyotropic and thermotropic liquid crystals.

For these reasons, herein we extend our investigations to D-hexono-1,4-lactones: D-galactono- and D-mannono-1,4-lactones as starting materials. Our synthetic route is illustrated in Scheme 1.

We have previously described the preparation of 6-bromo-6-deoxy-D-galactono- (**1**) and D-mannono-1,4-lactones (**2**) from unprotected D-hexono-1,4-lactones in good yields (82; 69%, respectively) with PPh_3–CBr_4 in pyridine.[18]

To heptanethiol (1.2 equiv), sodium hydride (1.2 equiv) in 1:1 Me_2SO–THF was added at room temperature. The mixture was vigorously stirred for 1 h and the 6-bromo-6-deoxy-D-galactono-1,4-lactone (**1**) was then added. After 5 min, the 6-*S*-heptyl-6-thio-D-galactono-1,4-lactone (**3**) was obtained in 73% isolated yield (Scheme 1).

Using this method, 6-*S*-octyl, nonyl, decyl, undecyl and dodecyl-6-thio-D-galactono-1,4-lactones **4**–**8**, respectively, were obtained in good yields (Table 1).

When 6-bromo-6-deoxy-D-mannono-1,4-lactone (**2**) was treated in the same conditions, the 6-*S*-alkyl-6-thio-D-mannono-1,4-lactones (**9**–**14**) were obtained as the only products, in rather good yields (71–83%) (Table 1).

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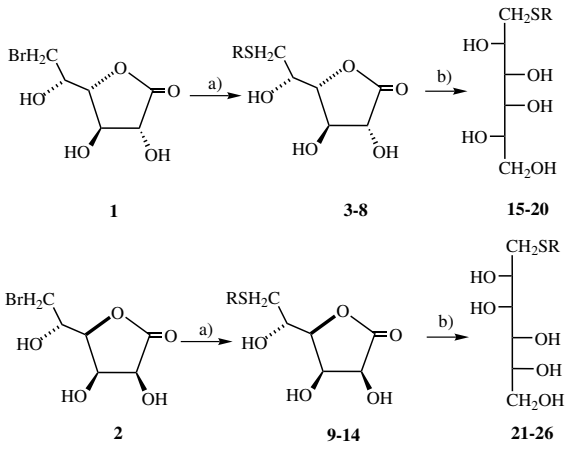

Scheme 1. Reagents and conditions: (a) RSH, NaH, Me_2SO/THF; (b) $NaBH_4$, EtOH.

Table 1. Yields and physical data of 6-*S*-alkyl-6-thio-D-galactono- and D-mannono-1,4-lactones

Substrate	Product [isolated yields (%)]	Mp (°C)	$[\alpha]_D^{24}$ (Me_2SO)
1	**3** (73)	153–159	−12 (*c* 0.7)
	4 (82)	144–149	−13 (*c* 0.8)
	5 (82)	139–145	−17 (*c* 1.00)
	6 (83)	150–155	−44 (*c* 0.8)
	7 (72)	91–96	−50 (*c* 0.8)
	8 (79)	104–109	−38 (*c* 0.4)
2	**9** (71)	61–65	+38 (*c* 0.9)
	10 (82)	59–62	+45 (*c* 0.8)
	11 (76)	61–66	+48 (*c* 0.6)
	12 (83)	69–74	+59 (*c* 0.6)
	13 (81)	65–70	+30 (*c* 0.2)
	14 (76)	58–63	+22 (*c* 0.2)

No epimerisation was observed at C-2, as in the case of D-ribono-1,4-lactone. We have observed such epimerisation, due to C-2 and C-3 configuration, during thioetherification and azidation of 5-bromo-5-deoxy-D-ribono-1,4-lactone.[15,19]

The reduction of the 6-*S*-alkyl-6-thio-D-galactono- (**3-8**) and D-mannono-1,4-lactones (**9–14**) was then investigated to access to 1-*S*-alkyl-1-thiohexitols. When 6-*S*-alkyl-6-thio-D-galactono- and D-mannono-1,4-lactones were treated with $NaBH_4$in EtOH at room temperature, for 1 h, 1-*S*-alkyl-1-thio-L-galactitols (**15–20**) and D-mannitols (**21–26**) were efficiently obtained in good yields (77–99%), as shown in Table 2.

1. Experimental

1.1. General

Melting points were determined on a Buchi 535 apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-370 digital polarimeter, using a sodium lamp ($\lambda = 589$ nm) at 24 °C. ^1H and ^{13}C NMR spectra were recorded in Me_2SO-d_6 or MeOD. 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 F254) and visualised under UV light and/or stained with phosphomolybdic acid–aqueous H_2SO_4 solution. Column chromatography was carried out on silica gel (E. Merck 230–400 mesh). All solvents were distilled before use.

Table 2. Yields and physical data of 1-*S*-alkyl-1-L-galactitols and D-mannitols

Substrate	Product [isolated yields (%)]	Mp (°C)	$[\alpha]_D^{24}$ (Me_2SO)
3	**15** (98)	140–148	−28 (*c* 0.6)
4	**16** (94)	128–132	−9 (*c* 1.00)
5	**17** (98)	149–154	−5 (*c* 0.6)
6	**18** (86)	194–199	−7 (*c* 0.5)
7	**29** (86)	150–153	−4 (*c* 0.7)
8	**20** (77)	137–144	−5 (*c* 0.7)
9	**21** (98)	143–147	+5 (*c* 0.2)
10	**22** (98)	134–138	+8 (*c* 0.3)
11	**23** (99)	117–121	+11 (*c* 0.3)
12	**24** (98)	76–82	+25 (*c* 0.6)
13	**25** (99)	91–97	+29 (*c* 0.2)
14	**26** (87)	90–92	+17 (*c* 0.6)

1.2. General procedure for thioalkylation of 6-bromo-6-deoxy-D-hexono-1,4-lactones

To a soln of alkanethiol (1.2 equiv) 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 6-bromo-6-deoxy-D-hexono-1,4-lactone (0.5–1 g) was then added and stirring was continued. After 5 min, MeOH (3 mL) was added and the soln was concentrated at diminished pressure heating with water at 50 °C. The crude product was chromatographed on Silica Gel (4:1 EtOAc–petroleum ether).

1.2.1. 6-*S*-Heptyl-6-thio-D-galactono-1,4-lactone (3). ^1H NMR: δ 4.41 (d, 1H, $J_{2,3}$ 8.2 Hz, H-2), 4.29 (m, 2H, H-3, H-4), 3.84 (t, $J_{4,5}$ 6.5 Hz, 1H, H-5), 2.75 (d, $J_{5,6}$ 6.9 Hz, 1H, H-6), 2.60 (t, 2H, H-α), 1.58–1.40 (m, 10H, H-β–Hω–1), 0.89 (t, 3H, H-ω); ^{13}C NMR: δ 175.4 (C-1), 74.8 (C-2), 73.5 (C-3), 81.0 (C-4), 67.9 (C-5), 35.2 (C-6), 32.5 (C-α), 32.1–22.9 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{13}H_{24}O_5S$: C, 53.40; H, 8.27; S, 10.97. Found: C, 53.32; H, 8.18; S, 10.55.

1.2.2. 6-*S*-Octyl-6-thio-D-galactono-1,4-lactone (4). ^1H NMR: δ 4.38 (d, 1H, $J_{2,3}$ 5.3 Hz, H-2), 4.30 (m, 2H, H-3, H-4), 3.84 (t, 1H, $J_{4,5}$ 6.9 Hz, H-5), 2.75 (d, 1H, $J_{5,6}$ 7.1 Hz, H-6), 2.59 (t, 2H, H-α), 1.61–1.33 (m, 12H, H-β–Hω–1), 0.91 (t, 3H, H-ω); ^{13}C NMR: δ 175.2 (C-1), 74.8 (C-2), 73.7 (C-3), 81.1 (C-4), 68.2 (C-5), 34.6 (C-6), 32.4

(C-α), 32.2–22.8 (C-β–C-ω–1), 14.7 (C-ω). Anal. Calcd for $C_{14}H_{26}O_5S$: C, 54.88; H, 8.55; S, 10.46. Found: C, 54.57; H, 8.71; S, 10.85.

1.2.3. 6-*S*-Nonyl-6-thio-D-galactono-1,4-lactone (5). ^{1}H NMR: δ 4.36 (d, 1H, $J_{2,3}$ 5.5 Hz, H-2), 4.27 (m, 2H, H-3, H-4), 3.82 (t, 1H, $J_{4,5}$ 7.1 Hz, H-5), 2.75 (d, 1H, $J_{5,6}$ 7.0 Hz, H-6), 2.59 (t, 2H, H-α), 1.60, 1.30 (m, 14H, H-β–Hω–1), 0.89 (t, 3H, H-ω); ^{13}C NMR: δ 175.4 (C-1), 74.8 (C-2), 73.6 (C-3), 81.0 (C-4), 68.0 (C-5), 35.3 (C-6), 32.6 (C-α), 32.1–22.9. (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{15}H_{28}O_4S$: C, 59.18; H, 9.27; S, 10.53. Found: C, 59.22; H, 10.65; S, 10.97.

1.2.4. 6-*S*-Decyl-6-thio-D-galactono-1,4-lactone (6). ^{1}H NMR: δ 4.26 (d, 1H, $J_{2,3}$ 8.3 Hz, H-2), 4.12 (m, 2H, H-3, H-4), 3.67 (m, 1H, H-5), 2.63 (d, 1H, $J_{5,6}$ 7.8 Hz, H-6), 2.51 (m, 2H, H-α) 1.50–1.27 (m, 16H, H-β–Hω–1), 0.84 (t, 3H, H-ω); ^{13}C NMR: δ 175.4 (C-1), 74.8 (C-2), 73.5 (C-3), 81.0 (C-4), 67.9 (C-5), 35.2 (C-6), 32.5 (C-α), 32.2–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{16}H_{30}O_5S$: C, 57.46; H, 9.04; S, 9.59. Found: C, 57.32; H, 9.32; S, 9.21.

1.2.5. 5-*S*-Undecyl-5-thio-D-galactono-1,4-lactone (7). ^{1}H NMR: δ 4.36 (d, 1H, $J_{2,3}$ 4.2 Hz, H-2), 4.33 (m, 2H, H-3, H-4), 3.86 (m, 1H, H-5), 2.75 (d, 1H, $J_{5,6}$ 7.3 Hz, H-6), 2.59 (m, 2H, H-α) 1.61–1.32 (m, 18H, H-β–Hω–1), 0.89 (t, 3H, H-ω); ^{13}C NMR: δ 175.4 (C-1), 74.8 (C-2), 73.5 (C-3), 81.0 (C-4), 68.0 (C-5), 35.3 (C-6), 32.6 (C-α), 32.2–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{17}H_{32}O_5S$: C, 58.59; H, 9.26; S, 9.20. Found: C, 58.45; H, 9.32; S, 9.62.

1.2.6. 5-*S*-Dodecyl-5-thio-D-galactono-1,4-lactone (8). ^{1}H NMR: δ 4.38 (d, 1H, $J_{2,3}$ 4.4 Hz, H-2), 4.31 (m, 2H, H-3, H-4), 3.84 (m, 1H, H-5), 2.76 (d, 1H, $J_{5,6}$ 7.4 Hz, H-6), 2.60 (m, 2H, H-α), 1.61–1.326 (m, 20H, H-β–Hω–1), 0.89 (t, 3H, H-ω); ^{13}C NMR: δ 175.1 (C-1), 74.8 (C-2), 73.7 (C-3), 81.0 (C-4), 68.1 (C-5), 34.8 (C-6), 32.4 (C-α), 32.1–22.8 (C-β–C-ω–1), 13.5 (C-ω). Anal. Calcd for $C_{18}H_{34}O_5S$: C, 59.64; H, 9.45; S, 8.85. Found: C, 59.48; H, 9.32; S, 8.35.

1.2.7. 6-*S*-Heptyl-6-thio-D-mannono-1,4-lactone (9). ^{1}H NMR: δ 4.54 (d, 1H, $J_{2,3}$ 4.4 Hz, H-2), 4.25 (m, 1H, H-3), 4.17 (dd, 1H, $J_{3,4}$ 2.4 Hz, H-4), 3.92 (m, $J_{4,5}$ 8.9 Hz, 1H, H-5), 2.78 (dd, $J_{5,6a}$ 2.65 Hz, $J_{6a,6b}$ 13.7 Hz, 2H, H-6a, H-6b), 2.56 (m, 2H, H-α), 1.54–1.32 (m, 10H, H-β–Hω–1), 0.84 (t, 3H, H-ω); ^{13}C NMR: δ 176.8 (C-1), 71.6 (C-2), 69.8 (C-3), 80.8 (C-4), 67.5 (C-5), 36.8 (C-6), 33.0 (C-α), 32.0–22.9 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{13}H_{24}O_5S$: C, 53.40; H, 8.27; S, 10.97. Found: C, 53.32; H, 8.18; S, 10.45.

1.2.8. 6-*S*-Octyl-6-thio-D-mannono-1,4-lactone (10). ^{1}H NMR: δ 4.44 (d, 1H, $J_{2,3}$ 4.3 Hz, H-2), 4.28 (m, 1H, H-3), 4.13 (dd, 1H, H-4), 3.91 (m, 1H, $J_{4,5}$ 8.9 Hz, H-5), 2.82 (dd, 2H, $J_{5,6a}$ 2.2 Hz, H-6a, $J_{6a,6b}$ 13.7 Hz, H-6b), 2.56 (m, 2H, H-α), 1.53–1.30 (m, 12H, H-β–Hω–1), 0.86 (t, 3H, H-ω); ^{13}C NMR: δ 175.2 (C-1), 74.8 (C-2), 73.7 (C-3), 81.1 (C-4), 68.2 (C-5), 34.6 (C-6), 32.4 (C-α), 32.2–22.8 (C-β–C-ω–1), 14.7 (C-ω). Anal. Calcd for $C_{14}H_{26}O_5S$: C, 54.88; H, 8.55; S, 10.46. Found: C, 54.92; H, 8.71; S, 10.62.

1.2.9. 6-*S*-Nonyl-6-thio-D-mannono-1,4-lactone (11). ^{1}H NMR: δ 4.44 (d, 1H, $J_{2,3}$ 4.5 Hz, H-2), 4.26 (m, 1H, H-3), 4.13 (dd, 1H, $J_{3,4}$ 2.5 Hz, H-4), 3.92 (m, 1H, $J_{4,5}$ 8.9 Hz, H-5), 2.82 (dd, 2H, $J_{5,6a}$ 2.7 Hz, $J_{6a,6b}$ 13.7 Hz, H-6a, H-6b), 2.55 (m, 2H, H-α), 1.50–1.30, (m, 14H, H-β–Hω–1), 0.85 (t, 3H, H-ω); ^{13}C NMR: δ 176.8 (C-1), 72.2 (C-2), 69.8 (C-3), 80.8 (C-4), 67.5 (C-5), 36.8 (C-6), 33.1 (C-α), 32.1–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{15}H_{28}O_4S$: C, 59.18; H, 9.27; S, 10.53. Found: C, 59.22; H, 9.32; S, 10.10.

1.2.10. 6-*S*-Decyl-6-thio-D-mannono-1,4-lactone (12). ^{1}H NMR: δ 4.50 (m, 1H, $J_{2,3}$ 4.4 Hz, H-2), 4.27 (m, 1H, H-3), 4.15 (dd, 1H, $J_{3,4}$ 2.4 Hz, H-4), 3.91 (m, 1H, $J_{4,5}$ 8.8 Hz, H-5), 2.79 (dd, 1H, $J_{5,6a}$ 2.7 Hz, H-6a), 2.53 (m, 2H, $J_{6a,6b}$ 11.1 Hz, H-6b, H-α), 1.52–1.32 (m, 16H, H-β–Hω–1), 0.84 (t, 3H, H-ω); ^{13}C NMR: δ 176.8 (C-1), 72.2 (C-2), 69.8 (C-3), 80.8 (C-4), 67.5 (C-5), 36.8 (C-6), 33.1 (C-α), 32.2–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{16}H_{30}O_5S$: C, 57.46; H, 9.04; S, 9.59. Found: C, 57.63; H, 9.25; S, 9.98.

1.2.11. 6-*S*-Undecyl-6-thio-D-mannono-1,4-lactone (13). ^{1}H NMR (MeOD): δ 5.21 (d, 1H, $J_{2,3}$3.6 Hz, H-2), 5.12 (m, 1H, H-3), 4.90 (dd, 1H, $J_{3,4}$2.5 Hz H-4), 4.73 (m, 1H, $J_{4,5}$ 8.9 Hz, H-5), 3.54 (dd, 2H, $J_{5,6a}$ 2.7 Hz, $J_{6a,6b}$ 12.7 Hz, H-6a, H-6b), 3.36 (m, 2H, H-α) 2.38–2.07, (m, 18H, H-β–Hω–1), 1.69 (t, 3H, H-ω); ^{13}C NMR (MeOD): δ 177.7 (C-1), 72.4 (C-2), 70.6 (C-3), 81.6 (C-4), 68.2 (C-5), 37.7 (C-6), 33.9 (C-α), 33.0–23.8 (C-β–C-ω–1), 15.6 (C-ω). Anal. Calcd for $C_{17}H_{32}O_5S$: C, 58.59; H, 9.26; S, 9.20. Found: C, 58.21; H, 9.43; S, 9.72.

1.2.12. 6-*S*-Dodecyl-6-thio-D-mannono-1,4-lactone (14). ^{1}H NMR: δ 4.49 (d, 1H, $J_{2,3}$ 2.3 Hz, H-2), 4.24 (m, 1H, H-3), 4.13 (dd, 1H, $J_{4,5}$ 8.7 Hz, H-4), 3.90 (m, 1H, H-5), 2.78 (dd, 2H, $J_{5,6a}$ 2.7 Hz, $J_{6a,6b}$ 12.9 Hz, H-6, H-b), 2.54 (m, 2H, H-α), 1.52–1.29 (m, 20H, H-β–Hω–1), 0.85 (t, 3H, H-ω); ^{13}C NMR: δ 176.9 (C-1), 71.5 (C-2), 69.8 (C-3), 80.8 (C-4), 67.4 (C-5), 36.8 (C-6), 33.1 (C-α), 32.2–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{18}H_{34}O_5S$: C, 59.64; H, 9.45; S, 8.85. Found: C, 59.81; H, 9.32; S, 8.56.

1.3. General procedure for reduction of 6-*S*-alkyl-6-thio-D-hexono-1,4-lactones

To a soln of 6-*S*-alkyl-6-thio-D-hexono-1,4-lactones (0.3–0.6 g) in EtOH (20 mL) was added $NaBH_4$ (1.6 equiv) at such a rate that the pH was maintained below 7. Then a further amount of NaBH4 (1.9 equiv) 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).

1.3.1. 1-*S*-Heptyl-1-thio-L-galactitol (15). ^{1}H NMR (MeOD): δ 3.78 (m, 1H, H-2), 3.62 (m, 3H, H-3, H-4, H-5), 3.60 (m, 1H, H-6), 2.74 (d, 1H, $J_{1,2}$ 7.2 Hz, H-1), 2.51 (m, 2H, H-α, H-β), 1.63–1.31 (m, 8H, H-γ–Hω–1), 0.91 (t, 3H, H-ω); ^{13}C NMR (MeOD): δ 35.6 (C-1), 69.8 (C-2), 71.3 (C-3), 71.1 (C-4), 70.9 (C-5), 64.1 (C-6), 32.4 (C-α), 31.9–22.6 (C-β–C-ω–1), 13.3 (C-ω). Anal. Calcd for $C_{13}H_{28}O_5S$: C, 52.67; H, 9.52; S, 10.82. Found: C, 52.47; H, 9.96; S, 10.51.

1.3.2. 1-*S*-Octyl-1-thio-L-galactitol (16). ^{1}H NMR: δ 3.72 (m, 1H, $J_{1,2}$ 7.3 Hz, H-2), 3.70 (m, 2H, H-3, H-4), 3.41 (m, 2H, H-5, H-6), 2.56 (d, 1H, H-1), 2.50 (t, 1H, H-α), 1.40–1.24 (m, 12H, H-β–H-ω–1), 0.85 (t, 3H, H-ω); ^{13}C NMR: δ 35.9 (C-1), 69.8 (C-2), 70.9 (C-3, C-4), 70.2 (C-5), 63.9 (C-6), 32.4 (C-α), 32.1–22.9 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{14}H_{30}O_5S$: C, 54.16; H, 9.74; S, 10.33. Found: C, 53.88; H, 9.59; S, 10.58.

1.3.3. 1-*S*-Nonyl-1-thio-L-galactitol (17). ^{1}H NMR: δ 3.78 (m, 1H, $J_{1,2}$ 7.0 Hz, H-2), 3.67 (m, 2H, H-3, H-4), 3.42 (m, 1H, $J_{5,6}$ 6.0 Hz, H-5), 3.37 (m, 1H, H-6), 2.53 (t, 1H, H-1), 2.45 (m, 2H, H-α, H-β), 1.48–1.23 (m, 12H, H-γ-H-ω–1), 0.84 (t, 3H, H-ω); ^{13}C NMR: δ 36.0 (C-1), 69.8 (C-2), 72.3 (C-3, C-4), 70.9 (C-5), 64.0 (C-6), 32.4 (C-α), 32.1–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{15}H_{32}O_5S$: C, 55.52; H, 9.94; S, 9.88. Found: C, 55.68; H, 9.64; S, 9.38.

1.3.4. 1-*S*-Decyl-1-thio-L-galactitol (18). ^{1}H NMR: δ 3.78 (m, 1H, $J_{1,2}$ 7.1 Hz, H-2), 3.70 (m, 2H, H-3, H-4), 3.41 (m, 2H, H-5, H-6), 2.56 (d, 1H, H-1), 2.50 (t, 1H, H-α), 1.40–1.24 (m, 16H, H-β–H-ω–1), 0.85 (t, 3H, H-ω); ^{13}C NMR: δ 36.0 (C-1), 69.8 (C-2), 70.9 (C-3, C-4), 70.2 (C-5), 63.9 (C-6), 32.4 (C-α), 32.1–22.9 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{16}H_{34}O_5S$: C, 56.77; H, 10.12; S, 9.47. Found: C, 56.59; H, 10.42; S, 9.65.

1.3.5. 1-*S*-Undecyl-1-thio-L-galactitol (19). ^{1}H NMR: δ 3.76 (m, 1H, $J_{1,2}$ 6.9 Hz, H-2), 3.70 (m, 2H, H-3, H-4), 3.43 (m, 2H, H-5, H-6), 2.58 (d, 1H, H-1), 2.49 (t, 1H, H-α), 1.42–1.23m, 18H, H-β–H-ω–1), 0.86 (t, 3H, H-ω); ^{13}C NMR: δ 36.0 (C-1), 69.8 (C-2), 70.9 (C-3, C-4), 70.2 (C-5), 64.0 (C-6), 32.5 (C-α), 32.2–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{17}H_{36}O_5S$: C, 57.92; H, 10.29; S, 9.10. Found: C, 57.39; H, 10.60; S, 9.58.

1.3.6. 1-*S*-Dodecyl-1-thio-L-galactitol (20). ^{1}H NMR: δ 3.78 (m, 1H, $J_{1,2}$ 7.1 Hz, H-2), 3.70 (m, 2H, H-3, H-4), 3.41 (m, 2H, H-5, H-6), 2.56 (d, 1H, H-1), 2.50 (t, 1H, H-α), 1.40–1.24 (m, 20H, H-β–H-ω–1), 0.86 (t, 3H, H-ω); ^{13}C NMR: δ 36.0 (C-1), 69.8 (C-2), 70.9 (C-3, C-4), 70.2 (C-5), 64.0 (C-6), 32.5 (C-α), 32.5–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{18}H_{38}O_5S$: C, 58.98; H, 10.45; S, 8.75. Found: C, 58.39; H, 10.50; S, 8.30.

1.3.7. 1-*S*-Heptyl-1-thio-D-mannitol (21). ^{1}H NMR: δ 3.42 (m, 4H, H-2, H-3, H-4, H-5), 3.29 (m, 1H, H-6), 2.85 (m, 2H, H-1a), 2.50 (m, 2H, H-1b, H-α), 1.44–1.28 (m, 10H, H-β–H-ω–1), 0.83 (t, 3H, H-ω); ^{13}C NMR: δ 35.1 (C-1), 70.7 (C-2), 73.7 (C-3), 73.5 (C-4), 72.8 (C-5), 62.9 (C-6), 33.0 (C-α), 31.7–22.9 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{13}H_{28}O_5S$: C, 52.67; H, 9.52; S, 10.82. Found: C, 52.47; H, 9.96; S, 10.67.

1.3.8. 1-*S*-Octyl-1-thio-D-mannitol (22). ^{1}H NMR (MeOD): δ 3.69 (m, 4H, H-2, H-3, H-4, H-5), 3.66 (m, 1H, H-6), 2.89 (m, 1H, H1a), 2.63 (d, 2H, H-1b, H-α), 1.60–1.38 (m, 12H, H-β–H-ω–1), 0.91 (t, 3H, H-ω); ^{13}C NMR (MeOD): δ 36.9 (C-1), 70.1 (C-2), 74.3 (C-3), 73.7 (C-4), 72.0 (C-5), 64.0 (C-6), 32.6 (C-α), 32.0–22.7 (C-β–C-ω–1), 13.5 (C-ω). Anal. Calcd for $C_{14}H_{30}O_5S$: C, 54.16; H, 9.74; S, 10.33. Found: C, 54.56; H, 9.43; S, 10.82.

1.3.9. 1-*S*-Nonyl-1-thio-D-mannitol (23). ^{1}H NMR: δ 3.59 (m, 2H, H-2, H-6a), 3.54 (m, 3H, H-3, H-4, H-5), 3.42 (m, 1H, H-6b), 2.84 (dd, 1H, $J_{1a,2}$ 3.4 Hz, H-1a), 2.58 (m, 1H, $J_{1a,1b}$ 11.9 Hz, H-1b, H-α), 1.49–1.26 (m, 14H, H-β–H-ω–1), 0.87 (t, 3H, H-ω); ^{13}C NMR: δ 37.5 (C-1), 70.3 (C-2), 72.3 (C-3), 72.2 (C-4), 71.4 (C-5), 64.7 (C-6), 32.9 (C-α), 32.1–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{15}H_{32}O_5S$: C, 55.52; H, 9.94; S, 9.88. Found: C, 55.43; H, 9.89; S, 10.21.

1.3.10. 1-*S*-Decyl-1-thio-D-mannitol (24). ^{1}H NMR: δ 3.61 (dd, 1H, $J_{6a,5}$ 3.0 Hz, H-6a), 3.56 (m, 2H, H-2, H-5), 3.46 (m, 2H, H-3, H-4), 3.39 (dd, 1H, $J_{5,6b}$ 6.8 Hz, $J_{6a,6b}$ 10.5 Hz, H-6b), 2.87 (dd, 1H, $J_{1a,1b}$ 12.5 Hz, $J_{1a,2}$ 3.5 Hz, H-1a), 2.50 (m, 1H, H-1b, H-α), 1.49–1.26 (m, 16H, H-β–H-ω–1), 0.89 (t, 3H, H-ω); ^{13}C NMR: δ 37.5 (C-1), 70.3 (C-2), 72.3 (C-3), 72.2 C-4), 71.4 (C-5), 64.7 (C-6), 33.0 (C-α), 32.7–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{16}H_{34}O_5S$: C, 56.77; H, 10.12; S, 9.47. Found: C, 56.55; H, 10.30; S, 9.12.

1.3.11. 1-*S*-Undecyl-1-thio-D-mannitol (25). ^{1}H NMR: δ 3.58 (dd, 1H, $J_{5,6a}$ 4.9 Hz, $J_{6a,6b}$ 12.1 Hz, H-6a), 3.45 (m, 5H, H-2, H-3, H-4, H-5, H-6b), 2.88 (dd, 1H, $J_{1a,2}$ 2.5 Hz, H-1a), 2.52 (m, 2H, $J_{1a,1b}$ 13.1 Hz, H-1b, H-α), 1.42–1.28 (m, 18H, H-β–H-ω–1), 0.90 (t, 3H, H-ω); ^{13}C NMR: δ 37.5 (C-1), 70.3 (C-2), 72.3 (C-3, C-4), 71.4 (C-5), 64.7 (C-6), 32.9 (C-α), 32.2–22.9 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{17}H_{36}O_5S$: C, 57.92; H, 10.29; S, 9.10. Found: C, 57.64; H, 10.51; S, 9.54.

1.3.12. 1-*S*-Dodecyl-1-thio-D-mannitol (26). ^{1}H NMR: δ 3.71 (m, 2H, H-3, H-4), 3.62 (m, 1H, H-2), 3.05 (m, 2H, H-5, H-6), 2.56 (dd, 1H, $J_{1a,2}$ 3.2 Hz, H-1a), 2.40 (m, 2H, $J_{1a,1b}$ 11.7 Hz, H-1b, H-α), 1.40–1.34 (m, 20H, H-β–H-ω–1), 0.83 (t, 3H, H-ω); ^{13}C NMR: δ 37.5 (C-1), 70.3 (C-2), 72.3 (C-3, C-4), 71.3 (C-5), 64.7 (C-6), 32.9 (C-α), 32.1–23.0 (C-β–C-ω–1), 14.8 (C-ω). Anal. Calcd for $C_{18}H_{38}O_5S$: C, 58.98; H, 10.45; S, 8.75. Found: C, 58.39; H, 10.60; S, 8.35.

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