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SYNTHESES OF SODIUM 2-ACYLAMINO-2,6-DIDEOXY-D-GLUCO-PYRANOSE-6-SULPHONATES*

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ABSTRACT

Sodium 2-acylamino(octanamido, dodecanamido, hexadecanamido)-2,6-dideoxy-D-glucopyranose-6-sulphonates (**14–16**) were synthesised by *N*-acylation of 2-amino-2,6-dideoxy-D-glucopyranose-6-sulphonic acid. Compound **14** was also obtained by oxidation of 1,3,4-tri-*O*-acetyl-6-*S*-acetyl-2-deoxy-2-octanamido-6-thio-α-D-glucopyranose with hydrogen peroxide followed by deacetylation, and **15** by oxidation of 6,6′-dithiobis(2,6-dideoxy-2-dodecanamido-D-glucopyranose) with hydrogen peroxide.

INTRODUCTION

Sulphoglycolipids are rare compounds. Sulphoquinovosyl diglyceride, a component of photosynthetic tissues of plants and micro-organisms[2], was isolated from green plants by Benson *et al.*[3] and synthesised by Gigg *et al.*[4]. We now describe the preparation of sulphoglycolipids having the 2-acylamino-2,6-dideoxy-D-glucopyranose-6-sulphonate structure. Derivatives of amino sugars *N*-acylated with fatty acids are potent immunostimulants[5–8]. Synthetic glycolipids (neo-glycolipids)[9] are useful in studies of biological receptors[10] and they can form micellar and vesicular microaggregates[10,11] which are of interest as carriers of drugs, devices for photochemical solar-energy conversion, and models for biological membranes[12].

RESULTS AND DISCUSSION

1,3,4-Tri-*O*-acetyl-6-*S*-acetyl-2-deoxy-2-octanamido- (**3**) and -2-dodecanamido-6-thio-α-D-glucopyranose (**4**) have been prepared as intermediates in the synthesis of the sulphonates **14** and **15**, by acetylation of **1** and **2** followed by nucleophilic displacement of the tosyloxy group with potassium thiolacetate[13]. The i.r.

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TABLE I

CHEMICAL SHIFTS (δ) FOR **3**[a], **9**[a], **13**[b], AND **14**[b] AT 200 MHz

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*NH*	*OH-1*	*OH-3*	*OH-4*	*SAc*	*OAc-1*	*OAc*	*Fatty chain*
3	6.11d	4.42ddd	5.21t	5.08t	4.01m	←3.14m→		5.55d				2.33s	2.17s	2.10s	2.11m (2 H), 1.25m (8 H)
														2.00 s	1.54m (2 H), 0.87m (3 H)
10	5.63d	4.31q	5.03t	5.14t	3.76ddd	3.24dd	3.10dd	5.79d				2.34s	2.10s	2.10s	2.04m (2 H), 1.24m (16 H)
														2.00s	1.53m (2 H), 0.87m (3 H)
13α	4.89d	4.01ddd	5.16dd	4.61t	4.35ddd	←2.6m→		7.73d	7.12[c]					1.95s	2.05m (2 H), 1.24m (8 H)
														1.87s	1.44m (2 H), 0.88m (3 H)
13β	4.02d	3.70m	4.99t	4.58t	3.81m	←2.6m→		7.82d	7.82[c]					1.95s	2.14m (2 H), 1.24m (8 H)
														1.87s	1.44m (2 H), 0.88m (3 H)
14α	4.85dd	3.54m	3.46m	3.04m	4.03ddd	2.85dd	2.67dd	7.51d	6.45d	4.56d	5.85d				2.08m (2 H), 1.24m (8 H)
															1.45m (2 H), 0.88m (3 H)
14β	4.40dd	3.36m	3.23m	3.04m		2.95dd	2.67dd	7.62d	6.49d	4.77d	5.69d				2.18m (2 H), 1.24m (8 H)
															1.45m (2 H), 0.88m (3 H)

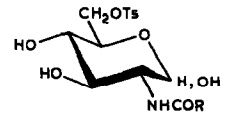
[a]In $CDCl_3$. [b]In $(CD_3)_2SO$. [c]Broad singlet.

TABLE II

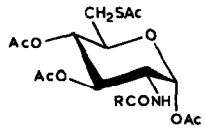
COUPLING CONSTANTS[a] FOR **3**, **9**, **13**, AND **14**

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{NH,2}$	$J_{OH,1}$	$J_{OH,3}$	$J_{OH,4}$
3	3.8	9.5	9.5	9.5				8.9			
10	8.8	9.5	9.5	9.5	3.1	6.3	14.4	9.5			
13α	3.4	10.9	9.5	10.0	5.8	3.8		9.5			
13β	3.4	10.0	10.0	10.0				9.5			
14α	3.2		9.0	9.0	7.1	4.1	13.9	7.7	4.3	4.8	2.0
14β	7.9	10.2	8.8		7.6	4.1	13.9	7.6	6.4	4.9	2.9

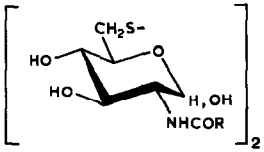
[a]Determined by first-order analysis (Hz, ±0.5 Hz).



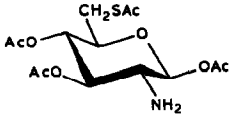
1 R = C_7H_{15}
2 R = $C_{11}H_{23}$



3 R = C_7H_{15}
4 R = $C_{11}H_{23}$



5 R = C_7H_{15}
6 R = $C_{11}H_{23}$



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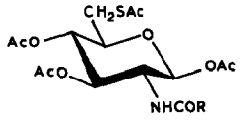
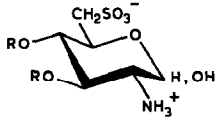
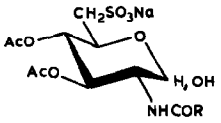


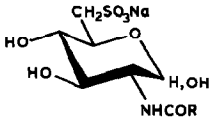
8 R = Me
9 R = C_7H_{15}
10 R = $C_{11}H_{23}$



11 R = H
12 R = Ac



13 R = C_7H_{15}



14 R = C_7H_{15}
15 R = $C_{11}H_{23}$
16 R = $C_{15}H_{31}$

spectra of **3** and **4** each showed a strong absorption at 1685 cm^{-1} for thioester. The $J_{1,2}$ value (3.8 Hz) for **3** (Table II) is consistent with an α anomer. Deacetylation of **3** and **4** with methanolic sodium methoxide afforded the crystalline disulphides **5** and **6**, and **5** was characterised as the hexa-acetate. *N*-Acylation of 1,3,4-tri-*O*-acetyl-6-*S*-acetyl-2-amino-2-deoxy-6-thio-β-D-glucopyranose[14] (**7**) with octanoyl and dodecanoyl chlorides in chloroform gave **9** and **10**, respectively. The ^{1}H-n.m.r. spectrum of **10** (Tables I and II) were consistent with the assigned structure.

Oxidation[15] of **8** with hydrogen peroxide in acetic acid gave 3,4-di-*O*-acetyl-2-amino-2,6-dideoxy-D-glucopyranose-6-sulphonic acid (**12**). When **3** was oxidised with hydrogen peroxide in acetic acid containing sodium acetate, there was no hydrolysis of the *N*-acyl linkage, and the octanamidosulphonate **13** was obtained. Deacetylation of **13** with methanolic sodium methoxide gave sodium 2,6-dideoxy-2-octanamido-D-glucopyranose-6-sulphonate (**14**). The structures of **13** and **14** were assigned on the basis of elemental analyses and i.r. and ^{1}H-n.m.r. (Tables I and II) data. The 3,4-positions of the OAc groups for **13** are supported by shifts of ~1.6 p.p.m. in the signals for H-3 and H-4 relative to those for **14**. The $J_{H\text{-}4,OH}$ values (**14α**, 2.0 Hz; **14β**, 2.8 Hz) are smaller than those reported for D-glucose[16] and 2-acetamido-2-deoxy-D-glucose[17] in $(CD_3)_2SO$, and accord[18] with a *gauche* relationship of H-4,OH. The values of $J_{5,6}$ and $J_{5,6'}$ for **14** indicate[19,20] the participation of

gt and gg rotamers about the C-5–C-6 bond, whereas **11** in the solid state[21] or in solution[15] in D_2O exists exclusively as the gt conformer. The chemical shifts of the signals for H-6 and H-6′ do not accord with the *syn*-upfield rule[19]. A smaller proportion of the *trans* H-N–C-H form[17] was found for **14** ($J_{H\text{-}2,NH}$ 7.6, 7.7 Hz) than for its di-*O*-acetyl derivative **13** ($J_{H\text{-}2,NH}$ 9.5 Hz).

The ^{1}H-n.m.r. spectra for **13** and **14** showed that, at equilibrium in $(CD_3)_2SO$, the α,β-ratio of the pyranose forms was 73:27 and 77:23, respectively; furanose forms were not detected. Similar α,β-ratios have been reported for 2-acetamido-2-deoxy-D-glucopyranose[22,23] and for **11** and **12**[15].

Oxidation of the disulphide **6** with hydrogen peroxide in acetic acid, performed in the presence of sodium acetate in order to avoid hydrolysis of the amido group, gave **15**. The sulphonates **14–16** were prepared by *N*-acylation of the sulphonic acid **11** with acyl chlorides in acetone–water containing sodium hydrogencarbonate. The overall yields of **14–16** were similar by the three methods studied.

EXPERIMENTAL

General. — Melting points are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. I.r. spectra (KBr) were recorded with a Perkin–Elmer spectrophotometer. ^{1}H-N.m.r. spectra were recorded with a Varian XL-200 spectrometer at 20°. Assignments were confirmed by H/D exchange and spin-decoupling experiments. T.l.c. was performed on Silica Gel HF_{254} (Merck) with *A*, dichloromethane–methanol (20:1); and *B*, dichloromethane–methanol (10:1); and detection with iodine vapour or by charring with sulphuric acid. P.c. (horizontal) was performed at 20° on Whatman No. 1 paper with *C*, 1-butanol–pyridine–water (1:1:1). Alkaline silver nitrate and ninhydrin were used for detection.

*1,3,4-Tri-*O*-acetyl-6-*S*-acetyl-2-deoxy-2-octanamido-6-thio-α-*D*-glucopyranose* (**3**). — Compound **1**[13] (0.10 g, 0.2 mmol) was treated conventionally with acetic anhydride and pyridine, and a solution of the syrupy product (0.10 g, 85%; 0.17 mmol) and potassium thiolacetate (0.02 g, 0.17 mmol) in butanone (3 mL) was boiled for 6 h under reflux and then filtered. Insoluble material was washed with acetone, the combined filtrate and washings were concentrated to dryness, and a solution of the residue in chloroform was washed with water, dried ($MgSO_4$), and concentrated. The residue was crystallised from ethanol–water to give **3** (0.08 g, 80%), m.p. 119–120°, $[\alpha]_D^{20}$ +67°, $[\alpha]_{546}^{20}$ +79° (*c* 1, pyridine), R_F 0.73 (solvent *A*); ν_{max} 1740 (C=O ester), 1685 (C=O thioester), 1610 (Amide I), 1520 (Amide II), and 1220 cm^{-1} (C–O ester). The ^{1}H-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{22}H_{35}NO_9S$: C, 53.97; H, 7.20; N, 2.86; S, 6.53. Found: C, 54.01; H, 7.23; N, 2.83; S, 6.80.

*1,3,4-Tri-*O*-acetyl-6-*S*-acetyl-2-deoxy-2-dodecanamido-6-thio-α-*D*-glucopyranose* (**4**). — Compound **2**[13] (1 g, 1.9 mmol) was treated as described above for **3**. The product was crystallised from methanol–water to give **4** (0.45 g, 40%), m.p.

85–86°, $[\alpha]_D^{28}$ +68°, $[\alpha]_{546}^{28}$ +80° (*c* 1, chloroform), R_F 0.80 (solvent *A*); ν_{max} 1740 (C=O ester), 1685 (C=O thioester), 1655 (Amide I), 1530 (Amide II), and 1225 cm^{-1} (C–O ester).

Anal. Calc. for $C_{26}H_{43}NO_9S$: C, 57.22; H, 7.94; N, 2.56; S, 5.87. Found: C, 57.27; H, 7.95; N, 2.76; S, 6.04.

*6,6'-Dithiobis(2,6-dideoxy-2-octanamido-*D*-glucopyranose)* (**5**). — A solution of **3** (0.24 g, 0.5 mmol) in methanol (4 mL) containing sodium methoxide (2 mmol) was kept for 45 min at room temperature, then decationised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The residue was crystallised from methanol–water to give **5** (0.07 g, 84%), m.p. 202–203°, $[\alpha]_D^{30}$ +128° (*c* 0.6, methanol), R_F 0.17 (solvent *B*); ν_{max} 3400–3330 (OH, NH), 1620 (Amide I), and 1535 cm^{-1} (Amide II).

Anal. Calc. for $C_{14}H_{26}NO_5S$: C, 52.47; H, 8.17; N, 4.37; S, 10.00. Found: C, 52.47; H, 8.42; N, 4.15; S, 10.38.

Conventional treatment of **5** (0.02 g, 0.06 mmol) with acetic anhydride and pyridine gave the hexa-acetate (0.018 g, 65%), m.p. 180–182° (from methanol–water), R_F 0.65 (solvent *A*).

Anal. Calc. for $C_{20}H_{32}NO_8S$: C, 53.79; H, 7.22; N, 3.13. Found: C, 53.70; H, 7.51; N, 3.17.

*6,6'-Dithiobis(2,6-dideoxy-2-dodecanamido-*D*-glucopyranose)* (**6**). — Compound **4** (0.3 g, 0.56 mmol) was treated with sodium methoxide (2.2 mmol) in methanol (4 mL), as described for **3**. Column chromatography (silica gel; dichloromethane–methanol, 10:1) of the product gave **6** (0.03 g, 30%), m.p. 175–176°, $[\alpha]_D^{30}$ +83° (*c* 0.5, methanol), R_F 0.24 (solvent *B*); ν_{max} 3350 (OH, NH), 1640 (Amide I), and 1535 cm^{-1} (Amide II).

Anal. Calc. for $C_{18}H_{34}NO_5S$: C, 57.41; H, 9.10; N, 3.72; S, 8.51. Found: C, 56.87; H, 9.27; N, 3.66; S, 8.17.

*1,3,4-Tri-*O*-acetyl-6-*S*-acetyl-2-amino-2-deoxy-6-thio-β-*D*-glucopyranose*[14] (**7**). — A solution of 1,3,4-tri-*O*-acetyl-6-*S*-acetyl-2-amino-2-deoxy-6-thio-β-D-glucopyranose hydrochloride[24] (1.4 g, 3.5 mmol) and sodium acetate (0.6 g, 7 mmol) in water (3 mL) was stirred for 2 h and then extracted with chloroform (3 × 5 mL). The combined extracts were washed with aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), and concentrated. The residue was crystallised from methanol to give **7** (0.87 g, 72%), m.p. 150–151°, $[\alpha]_D^{30}$ +21° (*c* 1, dichloromethane), R_F 0.50 (solvent *A*); ν_{max} 3360, 3280 (NH), 1740 (C=O ester), 1685 (C=O thioester), 1590 (NH), and 1220 cm^{-1} (C–O ester).

Anal. Calc. for $C_{14}H_{21}NO_8S$: C, 46.27; H, 5.82; N, 3.85; S, 8.82. Found: C, 46.27; H, 5.90; N, 3.79; S, 8.61.

*1,3,4-Tri-*O*-acetyl-6-*S*-acetyl-2-deoxy-2-octanamido-6-thio-β-*D*-glucopyranose* (**9**). — To a solution of **7** (0.5 g, 1.3 mmol) in pyridine (0.12 mL) at 0° was added a solution of octanoyl chloride (0.24 mL, 1.3 mmol) in chloroform (5 mL). The mixture was stirred for 1 h at room temperature, then washed with 0.05M sulphuric acid, aqueous sodium hydrogencarbonate, and water, dried ($MgSO_4$), and concen-

trated. The residue was crystallised from ethanol–water to give **9** (0.26 g, 40%), m.p. 135–137°, $[\alpha]_D^{28}$ +10°, $[\alpha]_{546}^{28}$ +12° (*c* 1, chloroform), R_F 0.11 (solvent *A*); ν_{max} 1745 (C=O ester), 1690 (C=O thioester), 1665 (Amide I), 1520 (Amide II), and 1220 cm^{-1} (C–O ester).

Anal. Calc. for $C_{22}H_{35}NO_9S$: C, 53.97; H, 7.20; N, 2.86; S, 6.54. Found: C, 54.08; H, 7.27; N, 2.94; S, 6.65.

*1,3,4-Tri-*O*-acetyl-6-*S*-acetyl-2-deoxy-2-dodecanamido-6-thio-β-*D*-glucopyranose* (**10**). — Compound **7** (0.5 g, 1.3 mmol) was treated with dodecanoyl chloride (0.33 mL, 1.3 mmol) as described for the preparation of **9**. The product was crystallised from ethanol–water to give **10** (0.4 g, 57%), m.p. 132–134°, $[\alpha]_D^{28}$ +7°, $[\alpha]_{546}^{28}$ +10°, R_F 0.70 (solvent *A*); ν_{max} 1745 (C=O ester), 1685 (C=O thioester), 1655 (Amide I), 1515 (Amide II), and 1220 cm^{-1} (C–O ester). The ^{1}H-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{26}H_{34}NO_9S$: C, 57.22; H, 7.94; N, 2.56; S, 5.87. Found: C, 57.45; H, 8.00; N, 2.72; S, 6.02.

*Sodium 3,4-di-*O*-acetyl-2,6-dideoxy-2-octanamido-*D*-glucopyranose-6-sulphonate* (**13**). — To a solution of **3** (0.25 g, 0.5 mmol) and sodium acetate (0.08 g, 1 mmol) in acetic acid (2 mL) was added aqueous 30% hydrogen peroxide (0.47 mL, 4.6 mmol). The solution was kept for 1 h at 80°, then cooled to room temperature, and concentrated (0.5 mmHg). The residue was crystallised from water to give **13** (0.1 g, 41%), m.p. 255° (dec.), $[\alpha]_D^{28}$ +12→+40° (*c* 0.66, methyl sulphoxide), R_F 0.84 (solvent *C*); ν_{max} 1745 (C=O ester), 1655 (Amide I), 1540 (Amide II), 1220 (C–O ester and SO_3^-), 1180 cm^{-1} (SO_3^-). The ^{1}H-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{18}H_{30}NNaO_{10}S$: C, 45.46; H, 6.36; N, 2.94; S, 6.74. Found: C, 45.00; H, 6.39; N, 2.87; S, 6.34.

*Sodium 2,6-dideoxy-2-octanamido-*D*-glucopyranose-6-sulphonate* (**14**). — To a solution of **13** (0.12 g, 0.2 mmol) in methanol (4 mL) was added a solution of sodium methoxide (0.4 mmol) in methanol (2.5 mL). After storage for 1 h at room temperature, the solution was neutralised with acetic acid and concentrated to dryness. The residue was crystallised from ethanol–water (1:1) to give **14** (0.025 g, 27%), m.p. 220° (dec.) $[\alpha]_D^{28}$ +42→+36° (*c* 1, water), R_F 0.75 (solvent *C*); ν_{max} 1630 (Amide I), 1540 (Amide II), 1200 and 1170 cm^{-1} (SO_3^-). The ^{1}H-n.m.r. data are shown in Tables I and II.

Anal. Calc. for $C_{14}H_{26}NNaO_8S$: C, 42.95; H, 6.69; N, 3.57; S, 8.19. Found: C, 42.57; H, 7.01; N, 3.40; S, 7.83.

Compound **14** was also obtained by treating a solution of **11** (0.2 g, 0.8 mmol) and sodium hydrogencarbonate (0.15 g, 1.7 mmol) in water–acetone (7 mL, 4:3) at 0° with octanoyl chloride (0.14 mL, 0.8 mmol). After stirring for 1 h, more sodium hydrogencarbonate (0.07 g, 0.8 mmol) and octanoyl chloride (0.14 mL, 0.8 mmol) were added, and the stirring was continued overnight at room temperature. The mixture was concentrated to half volume, diluted with water (10 mL), washed with ether (3 × 10 mL), and filtered. Insoluble material was washed with water, and the

combined filtrate and washings were concentrated to half volume and cooled to give **14** (0.1 g, 28%).

*Sodium 2,6-dideoxy-2-dodecanamido-*D*-glucopyranose-6-sulphonate* (**15**). — To a solution of **6** (0.2 g, 0.53 mmol) and sodium acetate (0.09 g, 1.1 mmol) in acetic acid (5 mL) was added aqueous 30% hydrogen peroxide (0.48 mL, 4.7 mmol). The solution was kept for 1 h at 80°, then cooled, and concentrated (1 mmHg). Crystallisation of the residue from water gave **15** (0.075 g, 32%), m.p. 210° (dec.), $[\alpha]_D^{28}$ +40→+30° (*c* 1, water), R_F 0.80 (solvent *C*); ν_{max} 1640 (Amide I), 1540 (Amide II), 1200 and 1160 cm^{-1} (SO_3^-).

Anal. Calc. for $C_{18}H_{34}NNaO_8S \cdot H_2O$: C, 46.44; H, 7.79; N, 3.00; S, 6.88. Found: C, 46.34; H, 7.52; N, 2.93; S, 7.32.

Compound **15** (0.17 g, 40%) was also prepared by treating **11** (0.23 g, 0.94 mmol) with dodecanoyl chloride (0.23 mL, 0.94 mmol), as described for the preparation of **14** from **11**.

*Sodium 2,6-dideoxy-2-hexadecanamido-*D*-glucopyranose-6-sulphonate* (**16**). — A solution of **11** (0.23 g, 0.94 mmol) and sodium hydrogencarbonate (0.24 g, 2.8 mmol) in water–acetone (7 mL, 4:3) at 0° was treated with hexadecanoyl chloride (0.6 mL, 1.8 mmol), as described for the preparation of **14**. The product (0.08 g, 17%) was recrystallised from water to give **16**, m.p. 205° (dec.), $[\alpha]_D^{28}$ +50→+38° (*c* 0.34, water), R_F 0.84 (solvent *C*); ν_{max} 1640 (Amide I), 1540 (Amide II), 1200 and 1165 cm^{-1} (SO_3^-).

Anal. Calc. for $C_{22}H_{42}NNaO_8S \cdot 0.5\ H_2O$: C, 51.54; H, 8.45; N, 2.73; S, 6.25. Found: C, 51.17; H, 8.84; N, 2.45; S, 6.29.

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