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Note

A new method for the preparation of acylated glycosylamines and their transformations into glycosyl isothiocyanates and *N,N'*-diglycosylthioureas*

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The glycosylthioureas are of interest because of their antifungal and antimicrobial properties[1], and as starting materials in the synthesis of *N*-nucleosides[2–5]. We have described[5–7] the preparation of acetylated glycosylthioureas from glycosyl isothiocyanates, and we now describe the preparation of acylated glycosylamines from the corresponding glycosylamines, using the method developed by Gómez-Sánchez[8] in the 2-amino-2-deoxy sugar series which provides a route easier than that *via* glycosyl azides[9–11]. Glycosylamines are valuable intermediates in the preparation of nucleosides and drugs[12–14]. We also report on the reaction of the acylated glycosylamines **6** and **7** with thiophosgene to yield the glycosyl isothiocyanates **9** and **10**, and their transformation into *N,N'*-diglycosylthioureas which are the by-products of several reactions from glycosyl isothiocyanates[15–17].

N-(2,2-Diethoxycarbonylvinyl)-β-D-gluco- (**1**) and -D-galacto-pyranosylamine (**2**) and the tetra-acetate **3** were prepared from β-D-gluco- and β-D-galacto-pyranosylamine by published methods[18]. The reaction of **3** with bromine in chloroform gave 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine hydrobromide (**5**), in good yield. Likewise, the syrupy product of benzoylation of **2** gave 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosylamine hydrobromide (**6**). The structures of **5** and **6** were demonstrated by elemental analyses and i.r. and ^{1}H-n.m.r. data. The coupling constants for **6** (see Table I) were in good agreement with those reported[5] for related β-D-galactopyranosyl derivatives. The β-D-glycopyranosyl structures are also evident from the ^{1}H-n.m.r. data for the free bases **7** and **8** (Table I). Com-

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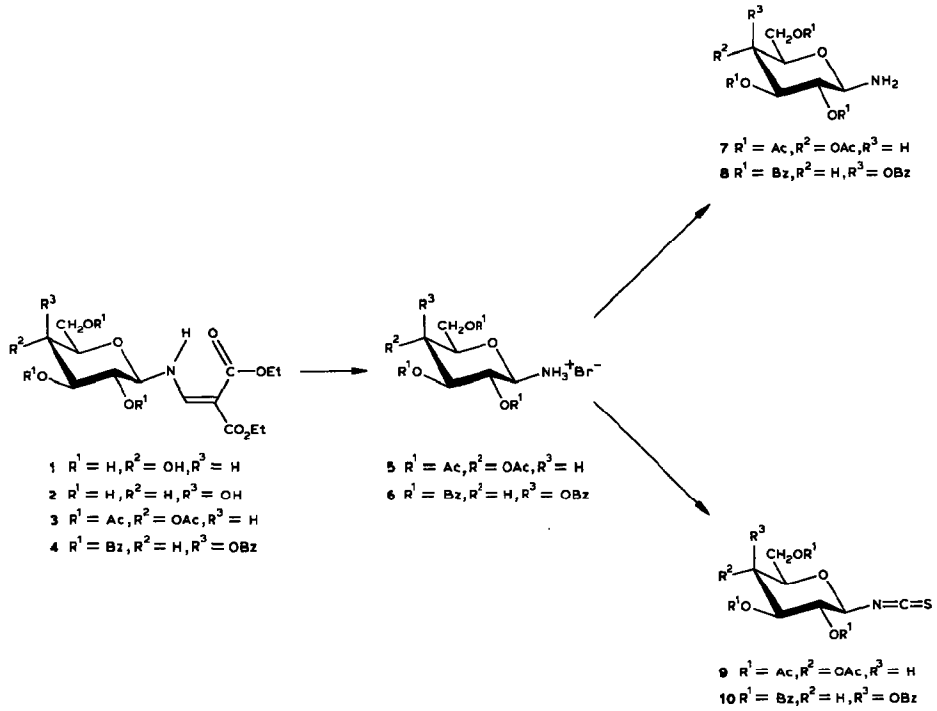
pound **7** had been obtained, but in a lower yield, by the glycosyl azide method[11]. Reaction of **5** and **6** with thiophosgene gave the 2,3,4,6-tetra-*O*-acyl-β-D-glycopyranosyl isothiocyanates **9** and **10**, respectively, the structures of which were demonstrated by elemental analyses and by ^{1}H- and ^{13}C-n.m.r. data (Tables I and III). Compound **9** had been prepared by reaction of tetra-*O*-acetyl-α-D-glucopyranosyl bromide with silver isothiocyanate[19] or potassium cyanate[20].



The reaction between acylated glycosylamines and acylated glycosyl isothiocyanates is a general method for preparing acylated *N,N'*-diglycosylthioureas hitherto known as by-products in some reactions of glycosyl isothiocyanates[15–17]. In this way, **11–13** were obtained and characterised by elemental analyses and spectral data (Tables II and III). The α-D-galactopyranose derivative **14** was obtained as a minor product in the preparation of **13**. The coupling constants of these products indicate that the preponderant conformation is $^4C_1$(D).

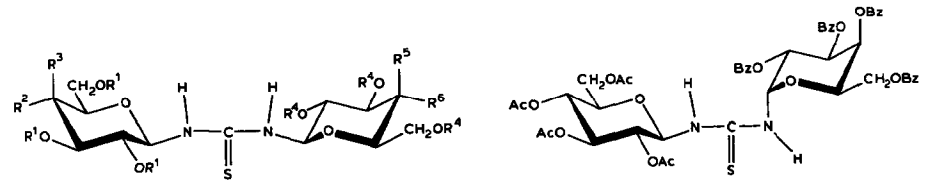


TABLE I

^{1}H-N.M.R. DATA FOR **5–10**

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*OAc*	*OBz*
5[a,d]	——— 5.63–4.80 (4 H) ———				——— 4.40–3.90 (3 H) ———			2.07 s (6 H) 2.03 s (3 H) 1.96 s (3 H)	
6[b,d]	5.46 d $J_{1,2}$ 8.7	6.09 dd $J_{2,3}$ 9.7	5.83 dd $J_{3,4}$ 2.7	6.04 d $J_{4,5}$ 0.0	4.73 dd $J_{5,6}$ 3.3 $J_{5,6'}$ 12.0	——— 4.51 ———			8.30–7.10 (20 H)
7[c,e]	4.28–4.11 $J_{1,2}$ 9.5	4.85 t $J_{2,3}$ 9.5	5.27 t $J_{3,4}$ 9.5	5.06 t $J_{4,5}$ 9.5	3.72 m $J_{5,6}$ 4.6 $J_{5,6'}$ 2.6	4.24 dd $J_{6,6'}$ 12.1	4.11 dd	2.10 s (3 H) 2.07 s (3 H) 2.03 s (3 H) 2.02 s (3 H)	
8[c,e]	4.54 d $J_{1,2}$ 8.3	5.63 dd $J_{2,3}$ 10.0	5.72 dd $J_{3,4}$ 3.1	6.02 d $J_{4,5}$ 0.0	4.49–4.30 $J_{5,6}$ 5.4	4.65 dd $J_{6,6'}$ 10.0	4.49–4.30		8.20–7.16 (20 H)
9[c,e]	5.04 d $J_{1,2}$ 8.3	——— 5.12–5.32 ———		$J_{4,5}$ 9.38	3.76 m $J_{5,6}$ 4.51 $J_{5,6'}$ 2.30	4.25 dd $J_{6,6'}$ 12.48	4.15 dd	2.11 s (6 H) 2.03 s (3 H) 2.02 s (3 H)	
10[c,e]	5.39 d $J_{1,2}$ 8.7	5.93 dd $J_{2,3}$ 10.7	5.63 dd $J_{3,4}$ 3.2	6.05 d $J_{4,5}$ 0.0	4.66 m	——— 4.46 m ———			8.16–7.20 (20 H)

[a]In $(CD_3)_2SO$. [b]In $CD_3C{\equiv}N$. [c]In $CDCl_3$. [d]At 90 MHz. [e]At 200 MHz.

TABLE II

^{1}H-N.M.R. DATA FOR **11–14** AT 200 MHz

Compound	D-*Glucopyranosyl group*						
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*
11[a]	5.68[b]	4.99 t $J_{2,1}$ 9.5 $J_{2,3}$ 9.5	5.35 t $J_{3,4}$ 9.5	5.06 t $J_{4,5}$ 9.5	3.90 m	4.32 dd $J_{5,6}$ 4.0 $J_{6,6'}$ 10.6	4.13 dd $J_{5,6'}$ 1.6
12[a]							
13[a]	[c]	5.10–4.90 $J_{2,3}$ 8.8	5.27 t $J_{3,4}$ 8.8	5.10–4.90	3.95–3.80 $J_{5,6}$ 4.4 $J_{5,6'}$ 2.2	4.27 dd $J_{6,6'}$ 12.7	4.13 dd
14[a]	5.80–6.20[b]	5.02 t $J_{2,1}$ 9.6 $J_{2,3}$ 9.6	5.38 t $J_{3,4}$ 9.6	5.09 t $J_{4,5}$ 9.6	3.85 m $J_{5,6}$ 4.2 $J_{5,6'}$ 2.0	4.32 dd $J_{6,6'}$ 12.5	4.07 dd

TABLE II *(continued)*

Compound	D-*Galactopyranosyl group*									
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*N-H*	*OAc*	*OBz*
11[a]								7.16 d $J_{1,NH}$ 7.8	2.10 s (6 H) 2.06 s (3 H) 2.04 s (3 H)	
12[a]	6.0–5.6[b] $J_{1,2}$ 9.3	5.66 dd $J_{2,3}$ 9.7	5.85 dd $J_{3,4}$ 2.9	6.07 d $J_{4,5}$ ~0	4.75–4.40					8.14–7.20 (40 H)
13[a]	[c]	5.64 t $J_{2,1}$ 9.9 $J_{2,3}$ 9.9	5.86 dd $J_{3,4}$ 3.3	6.05 d $J_{4,5}$ ~0	4.59				2.04 s (3 H) 2.02 s (6 H) 2.00 s (3 H)	8.20–7.20 (20 H)
14[a]	6.07 $J_{1,2}$ 2.2	5.85 dd $J_{2,3}$ 9.5	5.94 dd $J_{3,4}$ 1.6	6.07 $J_{4,5}$ ~0	4.64 m $J_{5,6}$ 5.3 $J_{5,6'}$ 7.9	4.84 dd $J_{6,6'}$ 10.4	4.44 dd		2.10 s (3 H) 2.04 s (3 H) 2.03 s (6 H)	8.16–7.26 (20 H)

[a]In $CDCl_3$. [b]Very broad peak. [c]Very broad peak indistinguishable from the base line.

TABLE III

^{13}C-N.M.R. DATA FOR **9–12** AT 20.15 MHz

Compound	*C-1*	*C-2*[a]	*C-3*[a]	*C-4*	*C-5*[a]	*C-6*	*C=S*
9	83.6	72.1	74.2	67.9	72.6	61.6	145.2
10	84.5	70.4	71.6	68.1	73.8	61.9	145.7
11	82.8	71.2	73.6	68.7	72.8	62.0	185.5
12	83.7	70.3	71.6	68.7	73.3	62.3	185.8

[a]Assignments may have to be interchanged.

EXPERIMENTAL

General methods. — Solutions were concentrated in vacuo at <40°. Melting points are uncorrected. Optical rotations were measured at 25 ±5°, using a 10-cm cell. T.l.c. was performed on silica gel GF_{254} (Merck) with chloroform–methanol (4:1) and benzene–ether (3:2 or 3:1), and detection with u.v. light or iodine vapor. Column chromatography was performed in the "flash" mode[21] with a benzene–ether gradient. Preparative t.l.c. was performed on silica gel (Merck PF_{254}) with benzene–ether (13:1). I.r. spectra were recorded for KBr discs. ^{1}H-N.m.r. spectra were recorded with Perkin–Elmer R-32 (90 MHz) and Varian XL-200 (200 MHz, F.t.) spectrometers. Assignments were confirmed by decoupling experiments. ^{13}C-N.m.r. spectra were recorded with a Bruker WP-80-SY spectrometer (20.15 MHz).

N-*(2,2-Diethoxycarbonylvinyl)-β-*D-*glucopyranosylamine* (**1**). — (*a*) Prepared by the literature method[18] from D-glucopyranosylamine (33 g, 184.2 mmol) and diethyl ethoxymethylenemalonate (49.5 mL, 247.4 mmol) in 1:1 ethanol–methanol (600 mL), **1** (86%) had m.p. 171–172° $[\alpha]_D$ +27° (*c* 0.5, methanol); lit.[18] m.p. 167–169°, $[\alpha]_{546}$ +30° (methanol).

(*b*) Dry ammonia gas was bubbled through a suspension of D-glucose (5 g, 27.7 mmol) in methanol (25 mL) at 0° until dissolution occurred. The mixture was kept at 0° for 3 days and then at room temperature for 2 days. Methanol (125 mL) was added followed, after aeration to remove most of the ammonia, by diethyl ethoxymethylenemalonate (15 mL, 74.9 mmol). The mixture was kept at room temperature for 24 h, then concentrated to a quarter of its volume, and stored at ~5° to give **1** (3.5 g, 36%), m.p. 171–172°, $[\alpha]_D$ +26° (*c* 0.5, methanol).

*2,3,4,6-Tetra-*O*-acetyl-β-*D*-glucopyranosylamine hydrobromide* (**5**). — To a solution of 2,3,4,6-tetra-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-β-D-glucopyranosylamine[18] (**3**; 30 g, 58.0 mmol) in chloroform (90 mL) was added gradually a solution of bromine (9.6 g, 60.1 mmol) in chloroform (240 mL) and water (1.0 mL, 55.6 mmol). The mixture was kept for 2 days at room temperature, and the product was collected, washed with chloroform (20 g, 81%), and recrystallised from ethanol to give **5**, m.p. >155° (dec.), $[\alpha]_D$ +59°, $[\alpha]_{578}$ +59°, $[\alpha]_{546}$ +67°, $[\alpha]_{436}$ +111°,

$[\alpha]_{365}$ +116° (*c* 0.5, water); ν_{max} 3140–2730 (NH_3^+), 1755, 1728 (C=O, acetyl), 1590, 1550 cm^{-1} (NH_3^+).

Anal. Calc. for $C_{14}H_{22}BrNO_9$: C, 39.26; H, 5.18; N, 3.27. Found: C, 39.30; H, 5.44; N, 3.04.

2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosylamine hydrobromide (**6**). — To a stirred solution of *N*-(2,2-diethoxycarbonylvinyl)-β-D-galactopyranosylamine[18] (**2**; 3.0 g, 8.6 mmol) in pyridine (7.5 mL) at 0° was added gradually benzoyl chloride (7.5 mL). After 24 h at room temperature, the mixture was poured into ice–water (500 mL) and extracted with chloroform (4 × 150 mL), and the combined extracts were washed with M sulfuric acid, saturated aqueous sodium hydrogencarbonate, and water, dried ($MgSO_4$), and concentrated. The syrupy residue was gradually treated with a 4% solution of bromine in chloroform (36 mL, 9.0 mmol) and water (0.15 mL, 8.6 mmol). The mixture was kept for 48 h at room temperature and concentrated to ~20 mL, and hexane was added to incipient opalescence. The crystals (5.6 g, 96%) were triturated with ice–water and recrystallised from chloroform–hexane to give **6**, m.p. 133–135°, $[\alpha]_D$ +116°, $[\alpha]_{578}$ +121°, $[\alpha]_{546}$ +140°, $[\alpha]_{436}$ +260°, $[\alpha]_{365}$ +471° (*c* 0.5, chloroform); ν_{max} 3100–2700 (NH_3^+), 1730 (C=O, benzoyl), 1600 cm^{-1} (C=C, aromatic).

Anal. Calc. for $C_{34}H_{30}BrNO_9$: C, 60.36; H, 4.47. N, 2.07. Found: C, 60.62; H, 4.55. N, 1.92.

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosylamine (**7**). — To a suspension of **5** (10.0 g, 23.35 mmol) in chloroform (200 mL) was added a solution of sodium carbonate (2.48 g, 23.35 mmol) and sodium hydrogencarbonate (1.96 g, 23.35 mmol) in water (40 mL), and the mixture was stirred vigorously for 10 h. The organic layer was separated, the aqueous layer was extracted with chloroform (3 × 50 mL), the combined chloroformic solutions were dried ($MgSO_4$) and concentrated to dryness, and the residual white powder was crystallised from ethanol to give **7** (6.7 g, 83%), m.p. 122–124°, $[\alpha]_D$ +18°, $[\alpha]_{578}$ +18°, $[\alpha]_{546}$ +20°, $[\alpha]_{436}$ +30°, $[\alpha]_{365}$ +39° (*c* 0.5, chloroform); ν_{max} 3405, 3315 (NH_2), 1758, 1738 cm^{-1} (C=O, acetates); lit.[11] m.p. 126°, $[\alpha]_D$ +11° (*c* 0.5, methanol).

Anal. Calc. for $C_{14}H_{21}NO_9$: C, 48.41; H, 6.10; N, 4.03. Found: C, 48.43; H, 6.33; N, 4.15.

2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosylamine (**8**). — To a solution of **6** (0.40 g, 0.6 mmol) in chloroform (15 mL) was added a solution of sodium carbonate (0.1 g, 0.9 mmol) and sodium hydrogencarbonate (0.1 g, 1.2 mmol) in water (3 mL), and the mixture was treated as described for the preparation of **7**. The resulting white powder was triturated with ice–water to give **8** (0.30 g, 85%), m.p. 74–76°, $[\alpha]_D$ +114°, $[\alpha]_{578}$ +121°, $[\alpha]_{546}$ +138°, $[\alpha]_{436}$ +257°, $[\alpha]_{365}$ +452° (*c* 0.5, chloroform); ν_{max} 3060, 2962 (NH_2), 1730 (C=O, benzoyl), 1600, 1584 cm^{-1} (C=C, aromatic).

Anal. Calc. for $C_{34}H_{29}NO_9 \cdot 0.5\ H_2O$: C, 67.43; H, 4.99; N, 2.31. Found: C, 67.46; H, 4.91; N, 2.23.

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl isothiocyanate (**9**). — To a

heterogeneous mixture of **5** (10 g, 23.3 mmol) in chloroform (100 mL) and calcium carbonate (7.0 g, 70.1 mmol) in water (35 mL) was added thiophosgene (4.0 mL, 35.1 mmol). The mixture was stirred vigorously for 48 h and then filtered, the organic layer was separated, washed with water, dried ($CaCl_2$), and concentrated to a small volume, and light petroleum was added to incipient opalescence to give **9** (4.9 g, 54%), m.p. 108–110°, $[\alpha]_D$ +4°, $[\alpha]_{578}$ +3°, $[\alpha]_{546}$ +2°, $[\alpha]_{436}$ +4°, $[\alpha]_{365}$ +25° (*c* 0.5, chloroform); ν_{max} 2110, (NCS) and 1748 cm^{-1} (C=O, acetyl); lit.[19] m.p. 114°, $[\alpha]_D$ +5.66° (acetylene tetrachloride).

Anal. Calc. for $C_{15}H_{19}NO_9S$: C, 46.27; H, 4.92; N, 3.60; S, 8.23. Found: C, 46.33; H, 5.05; N, 3.48; S, 7.97.

*2,3,4,6-Tetra-*O*-benzoyl-β-*D*-galactopyranosyl isothiocyanate* (**10**). — To a heterogeneous mixture of **6** (10.0 g, 14.8 mmol) in chloroform (100 mL) and calcium carbonate (4.4 g, 44.3 mmol) in water (35 mL) was added thiophosgene (2.5 mL, 22.2 mmol), and the mixture was stirred vigorously for 48 h and then filtered. The organic layer was separated, washed with water, dried ($CaCl_2$), and concentrated to dryness. The residue was extracted with warm light petroleum (3 × 50 mL), and acetone was repeatedly evaporated from the residue which was then poured into ice–water to give **10** (9.2 g, 97%), which was used without purification for the preparation of **12**.

A sample of **10**, purified by preparative t.l.c., had m.p. 68–71°, $[\alpha]_D$ +137°, $[\alpha]_{578}$ +141°, $[\alpha]_{546}$ +163°, $[\alpha]_{436}$ +299°, $[\alpha]_{365}$ +522° (*c* 0.5, chloroform); ν_{max} 2020 (NCS), 1735 (C=O, benzoyl), 1605, 1588 cm^{-1} (C=C, aromatic).

Anal. Calc. for $C_{35}H_{27}NO_9S$: C, 65.93; H, 4.27; N, 2.20; S, 5.03. Found: C, 66.16; H, 4.27; N, 2.19; S, 5.40.

N,N′-*Bis-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)thiourea* (**11**). — To a solution of **9** (0.40 g, 1.03 mmol) in pyridine (5 mL) was added **5** (0.44 g, 1.03 mmol), the mixture was kept at room temperature for 48 h and then poured into ice–water (100 mL), and the crude product (0.65 g, 86%) was recrystallised from ethanol to give **11**, m.p. 205–206°, $[\alpha]_D$ +5°, $[\alpha]_{578}$ +8°, $[\alpha]_{546}$ +11°, $[\alpha]_{436}$ +42°, $[\alpha]_{365}$ +223° (*c* 0.5, chloroform); ν_{max} 3470, 3320 (NH), 1740 (C=O, acetyl), 1520 (NH); lit.[16] m.p. 220–221°, $[\alpha]_D$ +8° (*c* 0.5, chloroform).

Anal. Calc. for $C_{29}H_{40}N_2O_{18}S$: C, 47.28; H, 5.47; N, 3.80; S, 4.35. Found: C, 47.14; H, 5.61; N, 3.73; S, 4.61.

N,N′-*Bis-(2,3,4,6-tetra-*O*-benzoyl-β-*D*-galactopyranosyl)thiourea* (**12**). — To a solution of **10** (0.40 g, 0.63 mmol) in pyridine (5 mL) was added **6** (0.42 g, 0.63 mmol). The mixture was processed as described for the preparation of **11**, to give an amorphous solid that was crystallised from ethanol and recrystallised from ether–ethanol (5:1) after treatment with charcoal to give **12** (0.4 g, 51%), m.p. 152–155°, $[\alpha]_D$ +116°, $[\alpha]_{578}$ +123°, $[\alpha]_{546}$ +143°, $[\alpha]_{436}$ +294°, $[\alpha]_{365}$ +668° (*c* 0.5, chloroform); ν_{max} 3340, 3220 (NH), 1730 (C=O, benzoyl), 1600, 1584 (C=C, aromatic), 1540 cm^{-1} (NH).

Anal. Calc. for $C_{69}H_{56}N_2O_{18}S \cdot C_2H_5OH$: C, 66.39; H, 4.86; N, 2.21; S, 2.53. Found: C, 66.12; H, 4.67; N, 2.22; S, 2.87.

N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-N'-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)thiourea (**13**) *and N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-N'-(2,3,4,6-tetra-O-benzoyl-α-D-galactopyranosyl)thiourea* (**14**). — To a solution of **9** (0.4 g, 1.03 mmol) in pyridine (5 mL) was added **6** (0.69 g, 1.03 mmol). The reaction was processed as described for the preparation of **11**. Column chromatography of the products gave **13** (0.60 g, 59%), R_F 0.37 (benzene–ether, 3:1), m.p. 116–119°, $[\alpha]_D$ +88°, $[\alpha]_{578}$ +93°, $[\alpha]_{546}$ +108°, $[\alpha]_{436}$ +226°, $[\alpha]_{365}$ +545° (*c* 0.5, chloroform); ν_{max} 3350 (NH), 1730 (C=O, ester), 1600, 1583 (C=C, aromatic), 1530 cm^{-1} (NH).

Anal. Calc. for $C_{49}H_{48}N_2O_{18}S$: C, 59.75; H, 4.91; N, 2.84; S, 3.25. Found: C, 59.78; H, 5.15; N, 2.73; S, 3.55.

The fraction of R_F 0.23 contained **14** (0.05 g, 5%), m.p. 113–115°, $[\alpha]_D$ +59°, $[\alpha]_{578}$ +63°, $[\alpha]_{546}$ +70°, $[\alpha]_{436}$ +126°, $[\alpha]_{365}$ +171.5° (*c* 0.33, chloroform); ν_{max} 3350 (NH), 1730 (C=O, ester), 1600, 1582 (C=C, aromatic), 1530 cm^{-1} (NH).

Anal. Found: C, 59.67; H, 4.91; N, 2.70; S, 2.92.

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