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PREPARATION AND PROPERTIES OF SOME PHOTOLABILE SUGAR DERIVATIVES FOR AFFINITY LABELLING

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ABSTRACT

Sugar derivatives carrying various photolabile groups at various positions have been synthesised, namely, 4-azido-4-deoxy-D-galactose, 4-azi-4-deoxy-D-*xylo*-hexopyranose (**4**), 3,7-anhydro-2-azi-1,2-dideoxy-D-*glycero*-L-*manno*-octitol (**6**), and 3-azi-1-methoxybutyl β-D-glucopyranoside (**8**), and 4-(2-diazo-3,3,3-trifluoropropionyl)-D-glucose. They were tested for their applicability in the photoaffinity labelling of sugar-binding proteins, and the best results with regard to wavelength of irradiation and rate of photolytic decay were obtained with the diazirino derivatives **4, 6,** and **8**.

INTRODUCTION

Protein–sugar interactions play an essential role in many biological processes such as the attachment of substrates to enzymes, sugar transport through membranes and in body fluids, recognition phenomena on cell surfaces, *etc.* These interactions are mainly non-covalent, and a dissociation–association equilibrium exists between the receptor–ligand complex and the free components. Even where association is strongly favoured, isolation and chemical identification of the complex is not normally possible.

One way to stabilise the complex for identification is by the formation of a covalent bond between receptor and ligand by affinity labelling[1]. The ligand is chemically modified so that it reacts with its receptor either spontaneously or after activation at the binding site, which is conveniently carried out by photolysis, *i.e.*, photo-affinity labelling[2]. Substituents introduced into ligands for such labelling are generally azide[3], diazo[4], and diazirino groups[5] which lose nitrogen on irradiation, leaving either a nitrene or a carbene either of which can undergo insertion reactions, thereby forming covalent links between ligand and receptor. The wavelength of light used for irradiation and the rate of photolysis under given conditions can differ greatly depending on the kind of chromophore. For some purposes, especially if the protein structure must be kept intact, the limitations are strict. For example, light of a wavelength below 300 nm, needed to decompose certain groups

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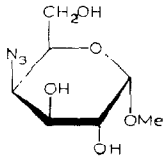
at a reasonable rate, can severely damage proteins. Even stricter limitations on the choice of photolabile substituents are imposed through the specificity of the receptor. Excessive change of the ligand structure can reduce the specific binding to the receptor protein and lead to non-specific, mainly hydrophobic, attachment to foreign proteins[6].

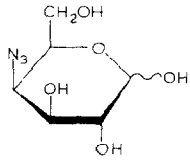
Most sugar derivatives so far known as potential reagents for photo-affinity labelling carry groups, for instance aromatic azides[7], which alter the bulk and polarity of the ligand so drastically that their application may give misleading results. For this reason, we sought photolabile sugar derivatives which resemble natural ligands as much as possible. Six sugar derivatives have been synthesised differing in the kind of photolabile substituent and in the linkage between the substituent and the ligand.

RESULTS AND DISCUSSION

Aliphatic azido derivatives of sugars have λ_{max} 280–290 nm, and therefore u.v. light <300 nm is required for photolysis and this may severely damage the receptor on prolonged irradiation. The azido group, however, is normally easily introduced into, and does not alter, the conformation of sugars. Methyl 4-azido-4-deoxy-α-D-galactopyranoside (**1**) was synthesised from methyl 2,3,6-tri-*O*-acetyl-4-*O*-methanesulfonyl-α-D-glucopyranoside[8] by treatment with sodium azide in hot methyl sulfoxide followed by deacetylation. Acid hydrolysis then gave 4-azido-4-deoxy-D-galactose (**2**).



1



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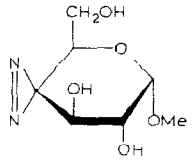

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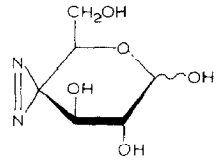


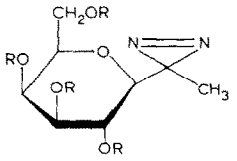
4

Unlike the azido group, the diazirine group is photolysed by u.v. light >300 nm (λ_{max} 320–360 nm), but is much more difficult to introduce into a monosaccharide. The first sugar derivative of this kind, methyl 4-azi-4-deoxy-α-D-*xylo*-hexopyranoside (**3**) was synthesised as follows. Treatment of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[9] with methyl sulfoxide–dicyclohexylcarbodiimide–phosphoric acid gave the 4-keto derivative which was subjected in sequence to catalytic debenzylation, trimethylsilylation, ammonia–hydroxylamine *O*-sulfonic acid, and iodine–triethylamine. Trimethylsilylation of **3** and treatment of the product with iodotrimethylsilane then gave 4-azi-4-deoxy-D-*xylo*-hexopyranose (**4**).

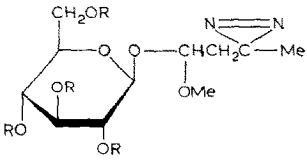
Some *C*-glycosides compete with the corresponding sugars for receptor binding-sites[10]. 4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1-deoxy-D-*glycero*-L-*manno*-oct-2-ulose[11] was therefore an ideal starting point for the preparation of 4,5,6,8-tetra-*O*-

acetyl-3,7-anhydro-2-azi-1,2-dideoxy-D-*glycero*-L-*manno*-octitol (**5**). Saponification then gave crystalline 3,7-anhydro-2-azi-1,2-dideoxy-D-*glycero*-L-*manno*-octitol (**6**) by reaction in sequence with ammonia–hydroxylamine *O*-sulfonic acid, iodine–trimethylamine, and acetic anhydride.

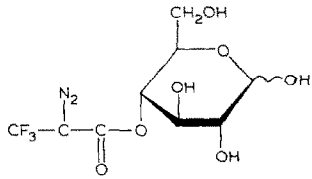
Attachment of photolabile groups directly to the carbon skeleton of a sugar is often difficult experimentally. For some purposes, it may be sufficient to introduce the group through conventional acylation, alkylation, or acetalation with an appropriate photolabile reagent. A new class of sugar derivative, mixed acetal glycosides[12,13], can be prepared with any kind of glyconic moiety. According to a method by Tietze and Fischer[13], the aglycon, which may carry various functional groups, is introduced by transacetalation. The compounds sterically resemble fragments of oligosaccharides and might be expected to associate well with corresponding receptors.



5 R = Ac
6 R = H



7 R = Ac
8 R = H



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Photolabile 3-azi-1-methoxybutyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**7**) was prepared from 2,3,4,6-tetra-*O*-acetyl-1-*O*-trimethylsilyl-β-D-glucose[14] and 3-azibutyraldehyde dimethyl acetal[15] by trimethylsilyl triflate-catalysed transacetalation. Deacetalation of **7** gave crystalline 3-azi-1-methoxybutyl β-D-glucopyranoside (**8**).

2-Diazo-3,3,3-trifluoropropionyl chloride[16], which has been used to introduce a photolabile group into hydroxy fatty acids[4], was employed to synthesise 4-(2-diazo-3,3,3-trifluoropropionyl)-D-glucose (**9**) from 2,3:5,6-di-*O*-isopropylidene-D-glucose dimethyl acetal[17] followed by acid-catalysed cleavage of the acetal groups.

The foregoing products were tested for affinity for the transport proteins of human erythrocytes and rat adipocytes[18]. For the promising substrates, the half lives ($t_{1/2}$) of decomposition on irradiation were determined (Table I, Fig. 1). From

TABLE I

IRRADIATION OF PHOTOLABILE SUGAR DERIVATIVES

Compounds	ε_λ		$t_{1/2}$ *(min)*	*Irradiation lamp*
2	ε_{286}	2	28.5	RPR 3000 (λ_{max} 300 nm)
3	ε_{334}	92	6.1	RPR 3500 (λ_{max} 350 nm)
4	ε_{331}	81	7.35	RPR 3500
6	ε_{334}	62	5.45	RPR 3500
8	ε_{344}	90	5.45	RPR 3500
9	ε_{244}	717	275	RPR 3000

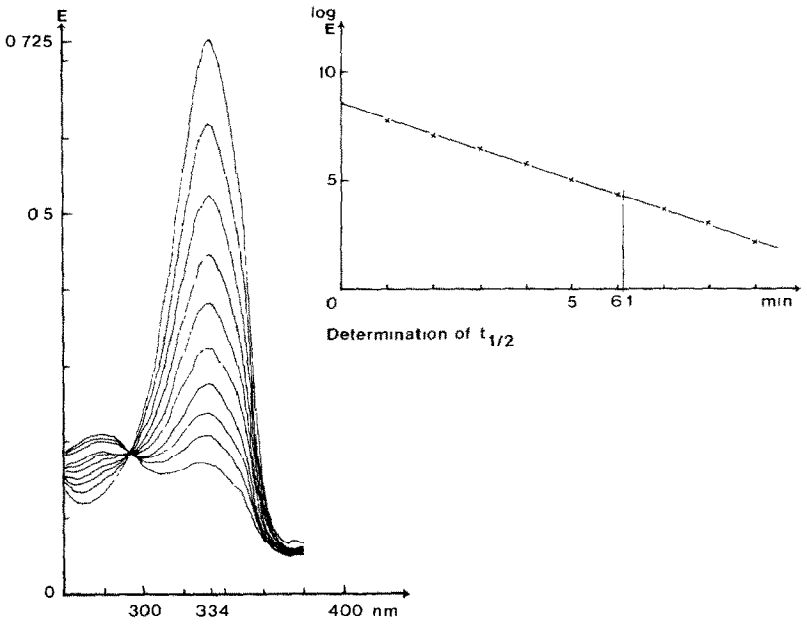

Fig. 1. U.v. spectra of solutions of compound **3** in methanol (7.8mM) irradiated at different times (0, 1, 2, 3, 4, 5, 6, 7, and 9 min). Insert: determination of the half life of **3** in methanol (7.8mM), irradiated at 350 nm, by measuring the extinction at the same wavelength.

the results, it is clear that the diazirine derivatives are the preferable photolabile compounds.

EXPERIMENTAL

General methods. — All reactions were monitored by t.l.c. on silica gel 60 F_{254} (Merck), using the solvents indicated. Flash column chromatography[19] was performed on silica gel (230–400 mesh, Merck). Optical rotations were measured with a Perkin–Elmer 141 polarimeter. ^{1}H-N.m.r. spectra were recorded with a Bruker WM 250 (250 MHz) spectrometer for solutions in $CDCl_3$ (internal Me_4Si) or D_2O (internal 2,2,3,3-tetradeuterio-4,4-dimethyl-4-silapentanoate). Elemental analyses were performed using a Perkin–Elmer 240 analyser. Photolyses were carried out in a Rayonet RPR 100 reactor equipped with 16 RPR 3000 Å or 16 RPR 3500 Å lamps and monitored using a Perkin–Elmer 555 u.v. spectrometer or a Bruker FT JFS 113 i.r. spectrophotometer. Light petroleum refers to the fraction b.p. 60–70°.

*Methyl 4-azido-4-deoxy-α-*D*-galactopyranoside* (**1**). — A solution of methyl 2,3,6-tri-*O*-acetyl-4-*O*-methanesulfonyl-α-D-glucopyranoside[8] (5 g, 12.5 mmol) and sodium azide (7.5 g, 115 mmol) in dry methyl sulfoxide (25 mL) was stirred for 150 h at 80°. Acetone (400 mL) was then added and inorganic material was removed. The filtrate was concentrated *in vacuo* to yield a residue, a solution of which in

TABLE II

^{1}H-NMR DATA[a] (250 MHz)

Proton	**1**	**2**	**3**	**4α**	**4β**	**5**	**6**	**7**[b]	**8**	**9**
Chemical shifts (δ)										
H-1	3.53–3.94 m	4.39 d, 5.45 d	4.99 d	5.40 d	4 02 d	1 09 s	1.12 s	5 18 d, 5.23 d	4 55 d, 4.64 d	4.67 d_{ax}, 5.26 d_{eq}
H-2	3.53–3.94 m	3.50–4.04 m	3.87 dd	3.85 dd	3 51 dd	—	—	5.02 dd, 5.05 dd	3 21–3.45 m	3.29–4.09 m
H-3	3.53–3.94 m	3.50–4.04 m	4.16 d	4.18 d	3 01 d	2 68 d	2 99 d	4 74 dd	3 21–3.45 m	3.29–4.09 m
H-4	3 53–3 94 m	3.31 dd	—	—	—	5 27 dd	3.34 dd	4.06 dd	3.21–3 45 m	3.29–4.09 m
H-5	3 53–3 94 m	3 50–4.04 m	4.25 dd	4.41 dd	4.07 dd	4.93 dd	3.57 dd	3.69 ddd	3 68 ddd	3 29–4.09 m
H-6	3 53–3 94 m	3.50–4.04 m	3.12 dd	3.11 dd	2.96 dd	5.39 dd	3.90 dd	4 22 dd	3.84 dd	3 29–4 09
H-6*	3.53–3 94 m	3.50–4.04 m	2 93 dd	3 07 dd	2.93 dd	—	—	4 14 dd	3 38 dd	3 29–4.09 m
H-7	—	—	—	—	—	3.82 ddd	3.60 ddd	—	—	—
H-8	—	—	—	—	—	4.16 dd	3 74 dd	—	—	—
H-8*	—	—	—	—	—	4.11 dd	3 69 dd	—	—	—
H-1'[c]	—	—	—	—	—	—	—	4 55 dd, 4 77 dd	4 64 dd, 4 93 dd	—
H-2',H-2'*	—	—	—	—	—	—	—	1 52–1 76 m	1 57–1 88 m	—
H-4'	—	—	—	—	—	—	—	1 03 s, 1.06 s	1.70 s	—
MeO	3.21 s	—	3.44 s	—	—	—	—	—	—	—
MeO-1'	—	—	—	—	—	—	—	3.32 s, 3 38 s	3.42 s, 3.48 s	—
Ac⁻	—	—	—	—	—	1.96–2.21 s	—	1.99–2.10 s	—	—

			3	**4α**	**4β**	**5**	**6**	**7**	**8**	**9**
$J_{H,H}$ *(Hz)*										
1,2			3 75	3.75	9.30	—	—	9.30	7 95	3 75, 8.25
2,3			11 7	10.35	8.25	—	—	8.1	—	—
3,4			—	—	—	10.3	11.2	12.0	—	—
4,5			—	—	—	10 3	11 1	10.2	12.0	—
5,6			4.1	3 75	3 75	3.15	3 0	5.25	4.8	—
5,6*			5.1	5.25	5.25	—	—	2 25	3 3	—
6,6*			12.0	12.75	12.8	—	—	12 0	12.4	—
6,7			—	—	—	1.35	1.0	—	—	—
7,8			—	—	—	6.3	7 8	—	—	—
7,8*			—	—	—	6.3	4 5	—	—	—
8,8*	—	—	—	—	—	11 5	12.0	—		
1',2'			—	—	—	—	—	4.8	4.5	—
1',2'*			—	—	—	—	—	6.4	7.3	—

[a]$CDCl_3$ for **6** and **7**, D_2O for the other compounds [b]The ratio of (*R*)- and (*S*)-forms at the aglyconic acetal carbon for **7** and **8** was 19:15. It is assumed that the major component is (*R*). [c]H-1', *etc.* refer to aglycon atoms

ether (300 mL) was washed with water (3 × 75 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The resulting syrup was purified by column chromatography (1:3 ethyl acetate–light petroleum) to give syrupy methyl 2,3,6-tri-*O*-acetyl-4-azido-4-deoxy-α-D-galactopyranoside, which was deacetylated to give **1**. Crystallisation from ethanol gave material (1.75 g, 64%) having m.p. 153°, $[\alpha]_{589}^{23}$ +40.5° (*c* 1, methanol). For the ^{1}H-n.m.r. data, see Table II.

Anal. Calc. for $C_7H_{13}N_3O_5$: C, 38.36; H, 5.98; N, 19.17. Found: C, 38.62; H, 5.70; N, 19.37.

4-Azido-4-deoxy-D-galactose (**2**). — A solution of **1** (1 g, 4.5 mmol) in water (10 mL) was boiled under reflux in the presence of Amberlite IR-120 (H^+) resin (5 mL) for 70 h, filtered, clarified with charcoal (1 g), and concentrated to dryness *in vacuo*. The syrup was purified by column chromatography (12:2:1 ethyl acetate–methanol–water), and crystallised from methanol–toluene–acetone to give **2** (540 mg, 55%), m.p. 147–150° (dec.), $[\alpha]_{589}^{23}$ −30° (*c* 1, methanol). For the ^{1}H-n.m.r. data, see Table II.

Anal. Calc. for $C_6H_{11}N_3O_5 \cdot 0.5\ H_2O$*: C, 33.64; H, 5.65; N, 19.62. Found: C, 33.64; H, 5.64; N, 19.91.

Photolysis of **2** (12.2mM in methanol) was performed using RPR 3000 lamps (emission maximum 300 nm). The decrease in the i.r. absorption of the azide group at 1900–2500 cm^{-1} was recorded after irradiation for 0, 5, 10, 15, 25, and 35 min. Log E · 10^2 at 2110 cm^{-1} was plotted against irradiation (min). The half life ($t_{1/2}$) of the azide group was determined to be 28.5 min.

Methyl 4-azi-4-deoxy-α-D-xylo-hexopyranoside (**3**). — Methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[9] (10 g, 21.5 mmol) was oxidised (methyl sulfoxide–dicyclohexylcarbodiimide–orthophosphoric acid)[20,21] to give, after purification by column chromatography (1:3 ethyl acetate–light petroleum), unstable methyl 2,3,6-tri-*O*-benzyl-α-D-*xylo*-hexopyranosid-4-ulose (8.6 g, 86%), which was immediately dissolved in methanol (100 mL) and hydrogenated in the presence of 10% Pd/C (1 g). The resulting methyl α-D-*xylo*-hexopyranosid-4-ulose (3.4 g, 95%) was trimethylsilylated[22] to yield syrupy methyl 2,3,6-tri-*O*-trimethylsilyl-α-D-*xylo*-hexopyranosid-4-ulose (6.7 g, 93%). Dry ammonia was passed for 2 h through a solution of the foregoing compound in dry methanol (60 mL) at −20°. A solution of hydroxylamine *O*-sulfonic acid (1.85 g, 16 mmol) in dry methanol (40 mL) was then added dropwise, and the suspension was stirred vigorously at −20° for 3 h and then at room temperature overnight. The ammonium sulfate was removed, the filtrate was concentrated *in vacuo*, and to a solution of the residue in dry methanol (50 mL) containing triethylamine (5 mL) at 0° was added iodine portionwise until the red colour persisted. The solution was then concentrated *in vacuo* and the product (R_F 0.46, 17:2:1 ethyl acetate–methanol–water) was purified by repeated column chromatography (30:2:1 ethyl acetate–methanol–water) to give **3** (350 mg,

*The water of crystallisation was determined from the difference in weight before and after drying *in vacuo* (P_2O_5) at 80°.

10%), which crystallised from ethanol–light petroleum, and had m.p. 115° (dec.), $[\alpha]_{589}^{25}$ +122° (*c* 0.18, methanol). For the ^{1}H-n.m.r. data, see Table II.

Anal. Calc. for $C_7H_{12}N_2O_5$: C, 41.18; H, 5.92; N, 13.72. Found: C, 40.80; H, 5.82; N, 14.02.

Photolysis of **3** (7.8mM in methanol) was performed using RPR 3500 lamps (emission maximum 350 nm). The decrease in the u.v. absorption of the diazirine group at 400–280 nm was recorded after irradiation for 0, 1, 2, 3, 4, 5, 6, 7, and 9 min. Log E · 10 at 334 nm (ε_{334} 92) was plotted against irradiation (min). The half life ($t_{1/2}$) of the compound was determined to be 6.1 min.

4-Azi-4-deoxy-D-xylo-*hexopyranose* (**4**). — Compound **3** (100 mg, 0.49 mmol) was trimethylsilylated[22] to give syrupy methyl 4-azi-4-deoxy-2,3,6-tri-*O*-trimethylsilyl-α-D-*xylo*-hexopyranoside (200 mg, 97%), a solution of which in dry carbon tetrachloride (5 mL) was treated under nitrogen with freshly distilled iodotrimethylsilane[23] (1 mL). The reaction was monitored by t.l.c. (17:2:1 ethyl acetate–methanol–water) of hydrolysed samples of the reaction mixture. When the reaction was complete (3–5 h), the solution was washed thoroughly with ice–water (3 × 10 mL), and the combined aqueous layers were passed through a column of Amberlite CG-400 (AcO^-) resin (100 mL) and concentrated to dryness *in vacuo*. Purification of the residue by column chromatography (30:2:1 ethyl acetate–methanol–water) gave **4** which crystallised from ethanol–light petroleum (60 mg, 66%), and had m.p. 123° (dec.), $[\alpha]_{589}^{25}$ −152° (*c* 0.14, methanol). For the ^{1}H-n.m.r. data, see Table II.

Anal. Calc. for $C_6H_{10}N_2O_5$: C, 37.89; H, 5.30; N, 14.73. Found: C, 37.94; H, 5.27; N, 14.91.

Photolysis of **4** (7.18mM in methanol) was performed as described for **3**. The half life ($t_{1/2}$) of **4** at 331 nm (ε_{331} 81) was 7.35 min.

4,5,6,8-Tetra-O-*acetyl-3,7-anhydro-2-azi-1,2-dideoxy*-D-glycero-L-manno-*octitol* (**5**). — A solution of 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1-deoxy-D-*glycero*-L-*manno*-oct-2-ulose[11] (2 g, 5.3 mmol) in dry methanol (100 mL) was treated with ammonia, hydroxylamine *O*-sulfonic acid (1 g, 8.8 mmol), triethylamine (5 mL), and iodine as described for **3**. The product was purified first by column chromatography (17:2:1 ethyl acetate–methanol–water, R_F 0.20), and then by reacetylation with acetic anhydride (4 mL) and pyridine (30 mL), to yield **5** (700 mg, 34%), m.p. 124°, $[\alpha]_{589}^{25}$ +5° (*c* 0.26, methanol). For the ^{1}H-N.m.r. data, see Table II.

Anal. Calc. for $C_{16}H_{22}N_2O_9$: C, 49.74; H, 5.74; N, 7.25. Found: C, 49.88; H, 5.79; N, 7.32.

3,7-Anhydro-2-azi-1,2-dideoxy-D-glycero-L-manno-*octitol* (**6**). — Compound **5** (700 mg, 1.8 mmol) was deacetylated (Zemplén) and the product was recrystallised from ethanol to yield **6** (285 mg, 72%), m.p. 135° (dec.), $[\alpha]_{589}^{25}$ +96° (*c* 0.28, methanol). For the ^{1}H-n.m.r. data, see Table II.

Anal. Calc. for $C_8H_{14}N_2O_5$: C, 44.03; H, 6.46; N, 12.82. Found: C, 43.76; H, 6.58; N, 12.44.

Photolysis of **6** (7.3mM in methanol) was performed as described for **3**. The

half life ($t_{1/2}$) of **6** at 334 nm (ε_{334} 62) was 5.45 min.

3-Azi-1-methoxybutyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**7**). — A solution of 2,3,4,6-tetra-*O*-acetyl-1-*O*-trimethylsilyl-β-D-glucose[14] (1.47 g, 3.5 mmol) and 3-azibutyraldehyde dimethyl acetal[15] in dry methylene chloride (25 mL) was treated at −80° with trimethylsilyl triflate (2 mL, 0.1M in CH_2Cl_2) for 48 h. Triethylamine (2 mL) was then added, and the mixture was allowed to attain room temperature, washed with saturated aqueous sodium hydrogencarbonate (2 × 25 mL) and saturated aqueous sodium chloride (2 × 50 mL), dried (Na_2CO_3, Na_2SO_4), and concentrated *in vacuo*. The residue was purified by column chromatography (1:1 ethyl acetate–light petroleum, R_F 0.39) to give **7** (350 mg, 22%), m.p. 73°, $[\alpha]_{589}^{25}$ −46° (*c* 0.16, methanol). For the ^{1}H-n.m.r. data, see Table II.

Anal. Calc. for $C_{19}H_{28}N_2O_{11}$: C, 49.55; H, 6.13; N, 6.08. Found: C, 49.66; H, 6.07; N, 6.33.

3-Azi-1-methoxybutyl β-D-glucopyranoside (**8**). — Compound **7** (300 mg, 0.65 mmol) was deacetylated (Zemplén) and the product was crystallised from ethanol–light petroleum to give **8** (175 mg, 91%), m.p. 141°, $[\alpha]_{589}^{25}$ −45° (*c* 0.41, methanol). For the ^{1}H-n.m.r. data, see Table II.

Anal. Calc. for $C_{11}H_{20}N_2O_7$: C, 45.20; H, 6.89; N, 9.58. Found: C, 45.24; H, 6.92; N, 9.76.

Photolysis of **8** (9.9mM in methanol) was performed as described for **3**. The half life ($t_{1/2}$) of **8** at 344 nm (ε_{334} 90) was 5.45 min.

4-(2-Diazo-3,3,3-trifluoropropionyl)-D-glucose (**9**). — A solution of 2,3:5,6-di-*O*-isopropylidene-D-glucose dimethyl acetal[17] (3 g, 10 mmol) in dry pyridine (20 mL) at 0° was stirred with 2-diazotrifluoropropionyl chloride (3.4 g, 20 mmol) for 60 h at room temperature. The mixture was then poured into ice–water (300 mL) and extracted with methylene chloride (3 × 100 mL), and the combined extracts were washed with aqueous sodium hydrogencarbonate (5%, 100 mL) and water (2 × 100 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The dark syrupy residue was purified by column chromatography (1:4 ethyl acetate–light petroleum) and then suspended together with Amberlite IR-120 (H^+) resin (10 mL) in water (20 mL). The suspension was shaken vigorously at 50° for 48 h, filtered, and concentrated *in vacuo*. The resulting syrup was purified by column chromatography (27:2:1 ethyl acetate–methanol–water) to give **9** (500 mg, 16%) which, after crystallisation from ethanol–light petroleum, had m.p. 161°, $[\alpha]_{589}^{25}$ +125° (*c* 0.24, methanol). For the ^{1}H-n.m.r. data, see Table II.

Anal. Calc. for $C_9H_{11}F_3N_2O_7$: C, 34.20; H, 3.51; N, 8.86. Found: C, 34.34; H, 3.46; N, 9.33.

Photolysis of **9** (2.8mM in methanol) was performed as described for **3**, except that RPR 3000 lamps were used. The half life ($t_{1/2}$) of **9** at 244 nm (ε_{244} 717) was 275 min.

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