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Two routes to enantiomerically pure 3-aminoinososе derivatives*

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ABSTRACT

Epoxidation with hydrogen peroxide/benzonitrile of (2*S*)-(2,4/3)-2,3,4-tribenzyloxycyclohex-5-enone ethylene acetal (**13**), obtained from methyl 2,3,4-tri-*O*-benzyl-6-deoxy-*α*-D-*xylo*-hex-5-enopyranoside (**9**), gave the (2,4/3,5,6)-5,6-anhydride **14** which, with sodium azide in 2-methoxyethanol, gave the (2,4,5/3,6)-5-azido-6-hydroxy derivative **15**. (2*S*)-(2,4/3)-2,3,4-Tribenzyloxy-6-phenylsulphonylcyclohex-5-enone ethylene acetal (**18**) was also prepared from **13** by reaction in sequence with *N*-chlorosuccinimide–thiophenol, *m*-chloroperbenzoic acid, and potassium *tert*-butoxide. Treatment of **18** with aqueous ammonia gave the inosamine derivative (2*S*)-2,4,5/3,6)-5-amino-2,3,4-tribenzyloxy-6-phenylsulphonylcyclohexanone ethylene acetal (**20**). Compounds **15** and **20** offer a novel access to 3-aminoinososе derivatives and suggest routes to enantiomerically pure compounds such as hydroxyvalidamine, validamine, and inosadiamines related to streptamine and deoxystreptamine.

INTRODUCTION

Aminocyclitols and diaminocyclitols play key roles in the functioning of many antibiotics of the aminoglycoside class[1], and some are components of important naturally occuring enzyme inhibitors[2].

Pseudo-sugars *i.e.*, monosaccharide analogues having the ring oxygen atom replaced by a methylene group, and thus cyclopentane or cyclohexane derivatives, are of appreciable biological significance because of the likelihood that they and their derivatives will perturb features of the enzymology of carbohydrate metabolism. We and others have reported the synthesis of pseudo-*α*-D-glucopyranose [3–5] (**1**), which can be expected to be derivatised to give compounds that will act as inhibitors of *α*-D-glucopyranosidase — an expectation borne out by the occurrence of valienamine (**2**) in the bacterial secondary metabolite acarbose[6] and related substances[2] which show inhibitory activity towards this enzyme. Valienamine also occurs together with validamine (**3**) in validamycin A[7], while validamycin B[8] and G[9] contain hydroxyvalidamine (**4**) and valiolamine (**5**), within their pseudo-trisaccharide structures. From these observations, it is apparent that the amino group is vital in the structures of this group of substances.

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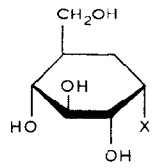
The aminoglycoside antibiotics contain members, for example, hygromycin A, which have aminocyclitol (inosamine) components, but, much more commonly, diaminocyclitols (inosadiamines) occur, and streptamine (**6**), and 2-deoxystreptamine (**7**) are key components of major groups of the family[1]. A further major group is based on fortamine B[1] (**8**), and, with the exception of the members of this category, all the compounds mentioned above have an amino group in the 1,3-relationship with either a carbon-bonded ring substituent or with a second amino group.



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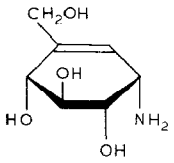
3 X = NH_2



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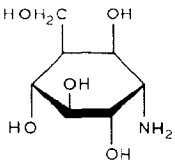

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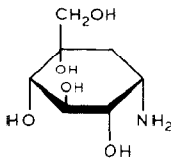

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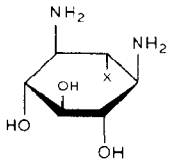

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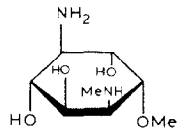

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Reactions of 6-deoxyhex-5-enopyranose derivatives with mercury(II) salts in aqueous media afford a simple way of producing 2-deoxyinosose derivatives[10], *e.g.*, the tri-*O*-benzyl compound **10** is readily available[2,11] from the alkene **9**, *i.e.*, 1,3-related hydroxyketones which can be considered as potential precursors of compounds of either the validamine (**2**–**5**) type or of insosadiamines (**6** and **7**) related to streptamine. Although these opportunities have not been fully exploited, several inosamine derivatives have been obtained by application of the reaction: 6-deoxyhex-5-enose compounds with nitrogen-bonded substituents at C-2[12–14] and C-3[15–17] have been employed, the carbonyl groups of such compounds as **10** have been aminated[11,18,19], and procedures have been reported for the potential preparation of 1,2-related inosadiamines therefrom[19]. One report has described an approach to 1,3-diaminocyclohexanes by a combination of these strategies; it involved carbocyclisation of a 3-azido-3,6-dideoxyhex-5-enopyranosyl compound and oximation of the resulting ketone[17].

Very few opportunities have been taken to introduce the amino function at the site of the hydroxy group of such cyclohexanones as **10**, but Sakairi and Kuzuhara[2] have shown the potential value of this approach in their synthesis of the acarbose-like α-D-gludosidase inhibitor amylostatin, in which they coupled an aminodisaccharide derivative with an allylic bromide analogue of valienamine, and these workers have also

prepared dihydroacarbose containing validamine by a reductive amination reaction applied to a carbocyclic ketone[20]. Our initial attempts to use the enones which are readily available by β-elimination reactions from the 2-deoxyinososes[10] and to add such nitrogen nucleophiles as azide to them in the Michael sense met with only modest success[21], and we therefore sought other routes to 3-amino-3-deoxyinososes. We now describe a high-yielding approach to such a compound and to a 2-deoxy analogue by an epoxide ring-opening procedure and by an addition to a vinyl sulphone, respectively.

RESULTS AND DISCUSSION

Treatment of the hydroxyketone **10**[2,11] with ethane-1,2-diol in the presence of sulphuric acid gave the spiro-acetal **11** in high yield and from it, by way of its trifluoromethanesulphonate (**12**), the alkene **13** was obtained — again in high yield — by base-catalysed elimination. Epoxidation of the alkene with hydrogen peroxide/benzonitrile[22] gave, in almost quantitative yield, one crystalline product (**14**) having a $J_{4,5}$ proton coupling-constant value of 0.5 Hz which is indicative of the *trans*-relationship between O-4 and the epoxide ring-oxygen atom[23]. Consistent with this finding is the expectation that, during oxidation, reaction would have occurred at the side of the alkene *trans* to O-4 and the axial oxygen atom of the spiro-acetal[24]. In related work, an enone closely related to compound **13** also gave an epoxide with the O-4, O-5 *trans*-relationship[25], and similar observations were made with closely related unsaturated pseudo-hexopyranose derivatives[26,27]

Opening of the epoxide ring of **14** by treatment with sodium azide in aqueous 2-methoxyethanol gave, after chromatography, a syrupy product that was shown by ^{13}C-n.m.r. spectroscopy to be a single compound. Its ^{1}H-n.m.r. spectrum was poorly resolved (Table I), but the signal for H-6 was clearly visible as a 3-Hz doublet which is comparable with the $J_{5,6}$ values of compounds having the 2,4,5/3,6 configuration discussed below. The 5-azido compound **15** is therefore assumed to have been formed, as expected, by *trans*-diaxial ring opening of the epoxide **14** in keeping with the selectivity of comparable reactions recorded for closely similar cyclitol epoxides which have been used in the synthesis of validamycin B and related compounds[8,27].

An alternative approach to 5-aminoinosose derivatives was sought by means of the vinyl sulphone approach[28,29]. Hence, the alkene **13** was treated with phenylsulphenyl chloride in dichloromethane[30], the crystalline adduct **16** was isolated in 78% yield, and, from it, the sulphone **17** was made by use of *m*-chloroperbenzoic acid. The ^{1}H-n.m.r. resonances of the ring protons of **17** were well resolved from those of the methylene protons of the acetal ring (Table I) and showed clearly that the ring retained the conformation with H-2, H-3, and H-4 axial ($J_{2,3}$ 9.4, $J_{3,4}$ 9.3 Hz), that H-5 was equatorial ($J_{4,5}$ 3.8 Hz), and, consequently, that the C-5 substituent was axial. That this was the chlorine atom was indicated by the formation of the alkenes **18** and **19** on treatment of the sulphone **17** with potassium *tert*-butoxide in tetrahydrofuran, the main product (**18**, 72% isolated) having the alkene group in conjugation with the sulphone group, and the minor (**19**) being formed by favourable 4,5-diaxial elimination of hydrogen chloride.

TABLE I

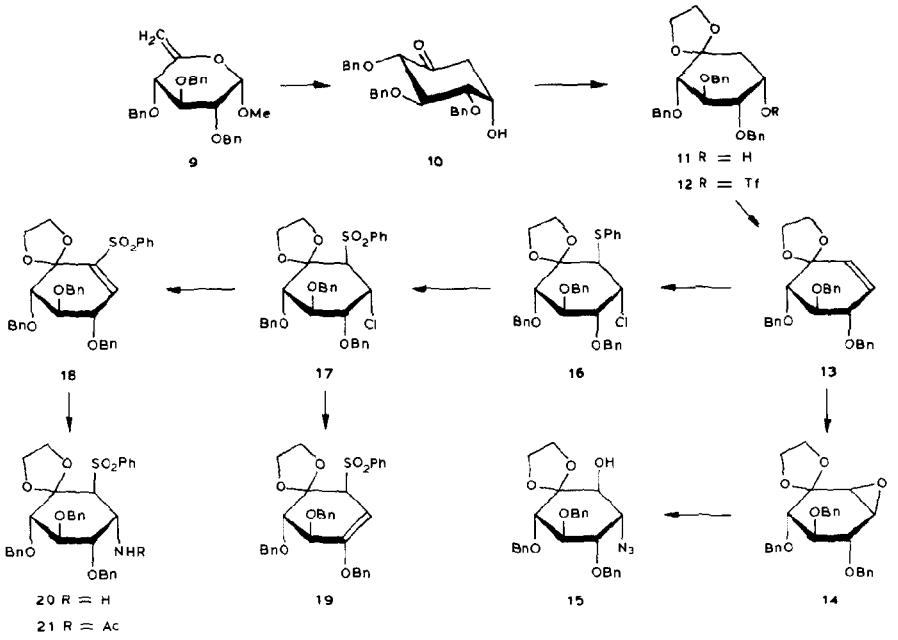
200-MHz ^{1}H-n.m.r. data for compounds **11**–**21** in $CDCl_3$

Compound	*Chemical shifts* (δ)						
	H-2	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*Others*[a]
11	3.52	4.1 ±0.2	3.43	4.1 ±0.2	1.72	2.02	CH_2CH_2 3.9–4.3
12	3.52	4.0 ±0.2	3.55	5.23	1.83	2.25	CH_2CH_2 3.9–4.1
13	3.68	4.1 ±0.2	4.1 ±0.2	5.82	5.56	-	CH_2-CH_2 3.9–4.2
14	3.67	3.90	3.80	3.12	3.25	-	CH_2CH_2 4.0–4.2
15		←———	3.8–4.1	———→	3.66	-	CH_2-CH_2 3.8–4.3
16	3.85	←———	3.9–4.3	———→	3.64	-	CH_2CH_2 3.9–4.3
17	4.32	4.05	4.15	5.31	3.75	-	CH_2CH_2 2.8, 3.6, 3.8, 4.1
18	3.52	4.1 ±0.1	4.26	7.16	-	-	CH_2-CH_2 3.8–4.2
19	4.32	4.48	-	4.8 ±0.1	3.98	-	CH_2CH_2 3.4, 3.8, 3.9, 4.1
20	4.47	←———	3.8–4.2	———→	3.60	-	CH_2CH_2 3.0, 3.7, 3.8, 4.0; NH_2, 1.80
21[b]	4.42	3.90	4.02	5.68	3.97	-	CH_2CH_2 4.6–4.9; NH, 7.03; CH_3, 1.93

Compound	*Coupling constants* (*Hz*)						
	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6}$	$J_{6,6'}$	$J_{4,6}$
11	9.6	9.6	3.3	3.2	3.3	14.8	0
12	9.7	8.9	3.2	2.7	3.5	15.6	0
13	10.6	7.8	2.2	10.2	-	-	2.0
14	10.2	7.5	0.5	3.7	-	-	0
15	-	-	-	3.0	-	-	0
16	9.4	-	-	2.6	-	-	0
17	9.4	9.3	3.8	1.7	-	-	0
18	10.3	7.8	2.5	-	-	-	-
19	8.2	-	-	5.7	-	-	-
20	9.4	-	4.3	1.6	-	-	0
21[b]	9.4	10.1	4.8	2.0	-	-	0

[a]All compounds gave resonances for aromatic protons within the range δ 7.3–7.5. The sulphones gave further resonances centred at δ 7.6 (3 H) and 7.95 (2 H). All gave $PhCH_2$ signals (6 H) at δ 4.6–4.9. [b]Measured in $(CD_3)_2CO$.

The sulphide **16** was apparently produced by electrophilic formation of the intermediate 2,4/3,5,6-episulphonium analogue of the epoxide **14** which, as is characteristic of the reaction, was attacked at C-5 by chloride to give the *trans*-diaxial product **16**.



Treatment of the main vinyl sulphone (**18**) with ammonium hydroxide in tetrahydrofuran gave, in keeping with reactions of such compounds[29], the low-melting amine **20**, which was isolated in 88% yield and gave a poorly resolved ^{1}H-n.m.r. spectrum. *N*-Acetylation, however, afforded a product (**21**) with a clearly resolved spectrum (Table I) from which it was apparent that H-2, H-3, and H-4 had remained axial ($J_{2,3}$ 9.4 Hz, $J_{3,4}$ 10.1 Hz), and that the nitrogen-containing substituent was also axial ($J_{4,5}$ 4.8 Hz). The evidence gained relating to the configuration at C-6 was the $J_{5,6}$ value of 2.0 Hz, indicating a diequatorial relationship between the protons, and the $J_{5,6}$ value for **19** which implies a quasi-equatorial H-5; thus, like compounds **15**, **16**, and **17**, the amidosulphone **21** has the 2,4,5/3,6 configuration which is in keeping with the *trans*-relationship in products of related additions to vinyl sulphones[28].

On the grounds that the azido-group of **15** could be reduced to the amino group and that the phenylsulphonyl substituent of **20** and **21** could be removed reductively[29,31,32], these developments suggest suitable new approaches to compounds related to streptamine and validamine.

The ^{13}C-n.m.r. chemical shifts for compounds **11**–**12** (Table II) were in keeping with their assigned structures.

TABLE II

^{13}C-N.m.r. chemical shifts for compounds **11**–**21** in $CDCl_3$

Compound	*Chemical shifts (δ)*[a]			
	C-1	*C-2,3,4*	*C-5*	*C-6*
11	107.9	72–78	62.1	37.7
12	108.3	72–78	79.2	35.8
13	107.4	73–76	128.6	129.4
14	108.4	72–76	53.9	56.5
15	109.4	72–76	60.8	76.1
16	109.9	72–76	59.0	55.9
17	108.3	72–76	52.1	71.6
18	107.5	72–76	141.4	-
19	107.8	70, 75, 159.1	87.8	68.8
20[b]	109.8	73–77	48.2	70.5
21[b]	109.6	72–77	44.3	68.7

[a]Appropriate resonances were observed for aryl carbon atoms and for benzyl methylene (δ 77–84) and dioxolane methylene (δ 65–69) carbon atoms. [b]Measured in CD_3CN.

EXPERIMENTAL

General procedures. — The ^{1}H- and ^{13}C-n.m.r. spectra were recorded for solutions in $CDCl_3$ (unless otherwise indicated) with Varian XL200 and FT80A spectrometers, respectively. Optical rotations were determined for 0.5–1% solutions in chloroform (unless otherwise indicated), using a 1-dm cell and a Perkin–Elmer 241 polarimeter.

(2S)-(2,4,5/3)-2,3,4-Tribenzyloxy-5-hydroxycyclohexanone ethylene acetal (**11**). — A mixture of the hydroxyketone **10**[2,11] (1.09 g), benzene (6 mL), 1,4-dioxane (4 mL), and ethane-1,2-diol (1.5 mL) containing conc. sulphuric acid (0.15 mL) was heated under reflux, using a Dean and Stark distillation head, for 3 h. After cooling of the solution, it was partitioned between dichloromethane and aqueous sodium hydrogen carbonate (5%), the organic phase was dried, and the solvent was removed to give a syrup which was purified on a column of silica gel, to give the acetal (1.09 g, 91%), m.p. 87–87.5° (from ethyl acetate–light petroleum), $[\alpha]_D$ −48.4°.

Anal. Calc. for $C_{29}H_{32}O_6$: C, 73.1; H, 6.8. Found: C, 72.8; H, 6.8.

(2S)-(2,4,5/3)-2,3,4-Tribenzyloxy-5-trifluoromethanesulphonyloxycyclohexanone ethylene acetal (**12**). — The alcohol (**11**, 1.3 g) in dichloromethane (80 mL) containing pyridine (3 mL) was treated with trifluoromethanesulphonic anhydride (0.65 mL, 1.5 mol. equiv.) in dichloromethane (10 mL). After 10 min at 20°, more dichloromethane (80mL) was added, and the solution was shaken successively with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, and then dried. The residual syrup (0.1 g) produced by removing the solvent from a portion of the solution was purified on a column of silica gel to give the triflate **12**, m.p. 99–100° (dec.) (from ethyl acetate–light petroleum), $[\alpha]_D$ −8.3°.

Anal. Calc. for $C_{30}H_{31}F_3O_8S$: C, 59.2; H, 5.1. Found: C, 59.1; H, 5.1.

(2S)-(*2,4/3*)-*2,3,4-Tribenzyloxycyclohex-5-enone ethylene acetal* (**13**). — The unpurified triflate **12** (1.5 g) in dichloromethane (80 mL) was treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (1.5 mL) for 16 h at 20°. Extraction of the solution with dilute hydrochloric acid and aqueous sodium hydrogen carbonate, drying, and removal of the solvent gave an oil which was purified on a column of silica gel to give the non-crystalline alkene **13** (1.1 g, 88% from the alcohol), $[\alpha]_D$ +10.1°.

Anal. Calc. for $C_{29}H_{30}O_5$: C, 76.0; H, 6.6. Found: C, 75.9; H, 6.4.

(2S)-(*2,4/3,5,6*)-*5,6-Anhydro-2,3,4-tribenzyloxy-5,6-dihydroxycyclohexanone ethylene acetal* (**14**). — To the alkene **13** (1.1 g) in methanol (50 mL) were added benzonitrile (3 mL), sodium hydrogen carbonate (0.3 g), and hydrogen peroxide (4.5 mL, 30%), and the mixture was stirred for 16 h at 20°. Partitioning between dichloromethane and water gave an organic phase which was dried, and the solvent was removed to give an oil which was purified on a column of silica gel to afford the epoxide **14** (1.08 g, 95%), m.p. 82–84°, $[\alpha]_D$ 0°.

Anal. Calc. for $C_{29}H_{30}O_6$: C, 73.4; H, 6.4. Found: C, 73.2; H, 6.4.

(2S)-(*2,4,5/3,6*)-*5-Azido-2,3,4-tribenzyloxy-6-hydroxycyclohexanone ethylene acetal* (**15**). — The epoxide **14** (0.17 g) and sodium azide (0.8 g) were stirred under reflux for 16 h in 2-methoxyethanol–water (6 mL, 10:1). Dichloromethane was added, the solution was extracted with water and dried, and the solvent was removed to give an oil which was purified on a column of silica gel to afford the syrupy azide **15** (0.16 g, 86%), $[\alpha]_D$ −25°.

Anal. Calc. for $C_{29}H_{31}N_3O_6 \cdot H_2O$: C, 65.0; H, 6.2; N, 7.8. Found: C, 65.5; H, 6.1; N, 7.3.

(2S)-(*2,4,5/3,6*)-*2,3,4-Tribenzyloxy-5-chloro-6-phenylthiocyclohexanone ethylene acetal* (**16**). — *N*-Chlorosuccinimide (1.36 g) was suspended in dichloromethane (25 mL), thiophenol (1.0 mL, 1.0 mol. equiv.) was added dropwise by syringe, and the orange-coloured solution and precipitated succinimide were stirred under nitrogen for 0.5 h. The supernatant solution (20 mL) was then added to the alkene **13** (1.4 g, 0.38 mol. equiv.) in dichloromethane 10 mL), and the orange-coloured solution was kept for 16 h at +5°. More dichloromethane was added, and the mixture was extracted with aqueous sodium hydrogen carbonate and water, and dried. Removal of the solvent and purification of the residue on a column of silica gel, with crystallisation from ethyl acetate — light petroleum, gave **16** (1.35 g, 73%), m.p. 109–111°, $[\alpha]_D$ −7.5°.

Anal. Calc. for $C_{35}H_{35}ClO_5S$: C, 69.7; H, 5.8; S, 5.3. Found: C, 69.6; H, 5.8; S, 5.3.

(2S)-(*2,4,5/3,6*)-*2,3,4-Tribenzyloxy-5-chloro-6-phenylsulphonylcyclohexanone ethylene acetal* (**17**). — m-Chloroperbenzoic acid (1.5 g, 70%) was added to a solution of the phenylthio-compound **16** (1.2 g, 0.33 mol. equiv.) in dichloromethane (60 mL), and the mixture was kept at 20° for 2.5 h. More dichloromethane was added, and the solution was washed with aqueous sodium hydrogen carbonate, aqueous sodium thiosulphate, and water, and then dried. Removal of the solvent gave a crystalline residue which, on recrystallisation from ethyl acetate–light petroleum, afforded the sulphone **17** (1.2 g, 95%), m.p. 152–154.5°, $[\alpha]_D$ −4.8°.

Anal. Calc. for $C_{35}H_{35}ClO_7S$: C, 66.2; H, 5.5; Cl, 5.6; S, 5.0. Found: C, 66.1; H, 5.3; Cl, 5.8; S, 5.1.

Treatment of the sulphone **17** *with potassium* tert-*butoxide.* — To a solution of **17** (0.84 g) in tetrahydrofuran (40 mL) was added potassium *tert*-butoxide (0.15 g, 1.0 mol. equiv.) in portions with stirring over 0.5 h. Dichloromethane was added, and the solution was extracted with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water. Drying and removal of the solvent gave an oily mixture of the isomeric alkenes **18** and **19**, which were separated on a column of silica gel.

(2*S*)-(2,4/3)-2,3,4-Tribenzyloxy-6-phenylsulphonylcyclohex-5-enone ethylene acetal (**18**; 0.57 g, 72%) had m.p. 133.5–134.5°, $[\alpha]_D$ +13.7°.

Anal. Calc. for $C_{35}H_{34}O_7S$: C, 70.2; H, 5.7; S, 5.4. Found: C, 69.8; H, 5.6; S, 5.5.

(2*S*)-(2/3,6)-2,3,4-Tribenzyloxy-6-phenylsulphonylcyclohex-4-enone ethylene acetal (**19**; 0.12 g, 15%) had $[\alpha]_D$ −13°.

Anal. Found: C, 69.6; H, 5.8; S, 5.1.

(2S)-(2,4,5/3,6)-5-Amino-2,3,4-Tribenzyloxy-6-phenylsulphonylcyclohexanone ethylene acetal (**20**). — The sulphonylalkene **18** (0.22 g) in tetrahydrofuran (2 mL) containing ammonium hydroxide (1.5 mL, sp. gr. 0.89) was left at 20° for 36 h. Evaporation of the volatiles and purification of the residue on a column of silica gel gave the amine **20** (0.20 g, 88%), m.p. 40–45° (sintering at 34–36°), $[\alpha]_D$ −19.5° (methanol).

Anal. Calc. for $C_{35}H_{37}NO_7S$: C, 68.3; H, 6.1; N, 2.3. Found: C, 68.2; H, 6.3; N, 2.1.

(2S)-(2,4,5/3,6)-5-Acetamido-2,3,4-tribenzyloxy-6-phenylsulphonylcyclohexanone ethylene acetal (**21**). — Treatment of the amine **20** (0.081 g) in pyridine (1 mL) with acetic anhydride (0.3 mL) for 15 h at 20°, followed by the usual isolation procedure and column chromatography, gave **21** (0.083 g, 98%) as a colourless syrup, $[\alpha]_D$ +28° (methanol).

Anal. Calc. for $C_{37}H_{39}O_8NS \cdot H_2O$: C, 65.8; H, 6.1; N, 2.1. Found: C, 66.1; H, 6.4; N, 2.0.

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