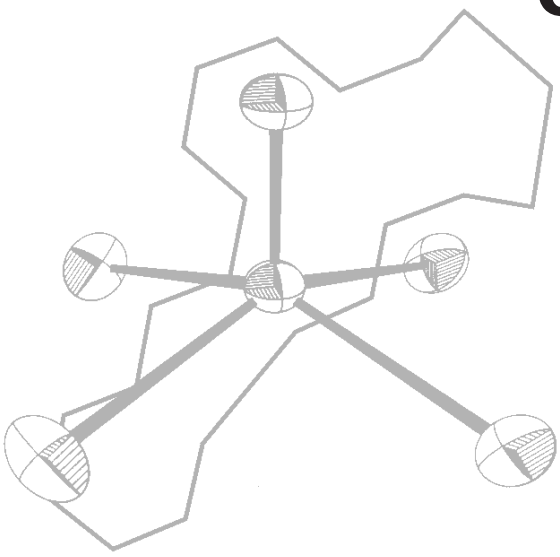
CSIRO PUBLISHING

Australian Journal of Chemistry



Volume 52, 1999

A journal for the publication of original research
in all branches of chemistry and chemical technology

www.publish.csiro.au/journals/ajc

All enquiries and manuscripts should be directed to
The Managing Editor
Australian Journal of Chemistry
CSIRO PUBLISHING
PO Box 1139 (150 Oxford St)
Collingwood Telephone: 61 3 9662 7630
Vic. 3066 Facsimile: 61 3 9662 7611
Australia Email: john.zdysiewicz@publish.csiro.au

Published by **CSIRO** PUBLISHING
for CSIRO Australia and
the Australian Academy of Science

Aust. J. Chem., 1999, **52**, 885–894

β-Acarbose. VII*
Approaches Towards the Synthesis of Some *N*-Linked Carba-Oligosaccharides

Robert V. Stick,[A,B] *D. Matthew G. Tilbrook*[A] *and Spencer J. Williams*[A]

[A] Department of Chemistry, The University of Western Australia, Nedlands, W.A. 6907.
[B] Author to whom correspondence should be addressed.

3,4-Anhydro-1,6-dideoxy-1,6-episeleno-β-D-glucose was treated with cyclohexylamine to afford an amino diol which was subsequently converted into a cyclic carbamate, a compound shown to be a moderately successful glycosyl donor. Treatment of the same 3,4-anhydro sugar and the 1,6-epithio analogue with a 1-epivalienamine derivative afforded the corresponding secondary amines which were converted into the analogous cyclic carbamates. The epithio analogue was unsuccessful as a glycosyl donor, failing to glycosylate a carbohydrate alcohol. On the other hand, the episeleno compound appeared to function as a glycosyl donor but decomposition of the product occurred under the conditions necessary for its isolation.

Beginning in the early 1970s, a novel group of secondary metabolites with inhibitory activity towards α-glucosidases was isolated from culture broths of organisms of the order *Actinomycetales*. Many organisms were investigated, including representatives of the family Actinoplanacae which encompasses the genera *Actinoplanes*, *Ampullariella* and *Streptosporangium*.[2]

A prime result of this screening was the identification of a carba-tetrasaccharide, acarbose (1) (BAY g 5421) which was shown to exhibit pronounced and potent inhibitory activity against intestinal α-sucrase and also to inhibit starch digestion *in vivo*.[3,4] Since its discovery, acarbose has been the subject of prolific investigations which have culminated in its approval for clinical usage in the management of non-insulin dependent diabetes mellitus. In addition, acarbose has found application in the treatment of insulin dependent (type I) diabetes, particularly in combination with insulin. Marketed under a variety of names including Prandase, Precose and Glucobay by Bayer in a number of countries, acarbose has been shown to control effectively the metabolism of complex carbohydrates and thence the production of D-glucose.[5]

For some time now, we have had an interest in this area as it seemed that the β-linked diastereoisomer of acarbose, namely β-acarbose (2), could be an inhibitor of β-glucan hydrolases.[6] More recently, we have improved on our original concept and decided to prepare the β-anomer of the methyl glycoside of β-acarbose, namely methyl β-acarboside (3), it being more substrate-like.

Our approach to methyl β-acarboside (3) centred on the 1,6-dideoxy-1,6-epithio- and -1,6-episeleno sugars (4) and (5), molecules beautifully arranged for the introduction of an amine (C 4), formation of a glycosidic linkage (C 1) and deoxygenation (C 6) (Scheme 1). This paper describes efforts towards this end which, ultimately, were unsuccessful.

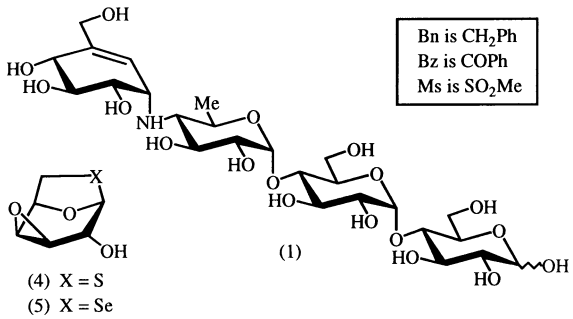
Ring-opening reactions with the amine (6) on the two epoxides (4) and (5) were seen as key steps in the synthesis of methyl β-acarboside (3). Initially, we chose cyclohexylamine as a more accessible amine for the development of the methodology necessary for the approach towards the carba-tetrasaccharide (3). Previously described formative experiments have shown that the epoxide (4) reacts in the desired fashion with cyclohexylamine or sodium azide, affording the diaxially-opened amine (7) and azide (8), respectively, in moderate yields.[7,8] These model studies on the epoxide (4) were to be extended to include the seleno sugar (5). Furthermore, these studies were to investigate the manipulation of an amine such as (7) into a glycosyl donor which would provide the desired β-selectivity in the glycosylation step.

Our initial efforts were directed towards an improvement in the synthesis of the epoxide (4) and the preparation of the epoxide (5) and the approach followed the published sequence starting with D-glucose.[7] Treatment of 1,2,3-tri-*O*-acetyl-D-glucopyranose with methanesulfonyl chloride in pyridine gave the dimesylates (9a,b) which were converted, upon prolonged treatment with hydrogen bromide in acetic acid, into the very stable, crystalline bromide (10). Treatment of (10) with benzyltriethylammonium tetrathiomolybdate provided the 1,6-epithio mesylate (11).[7] Alternatively, treatment of the bromide (10) with a solution of sodium hydrogen selenide in ethanol was equally successful, affording the 1,6-episeleno mesylate (12).[9]

The conversion of the two mesylates (11) and (12) into the epoxides (4) and (5) was next addressed. The procedure described previously used sodium methoxide to remove the

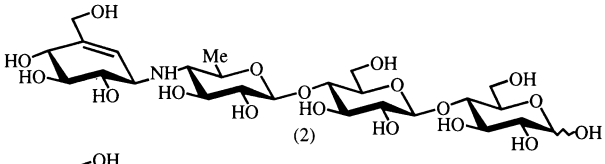
*Part VI, *Aust. J. Chem.*, 1997, **50**, 225.[1]

Manuscript received 10 March 1999 10.1071/CH99030 0004-9425/99/090885

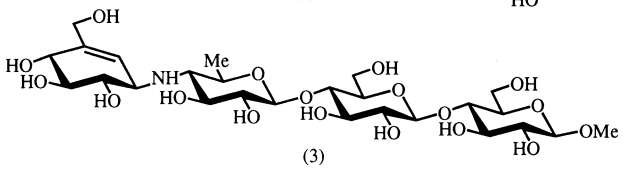


(1)

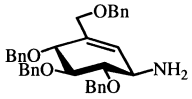
(4) X = S
(5) X = Se



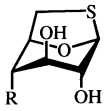
(2)



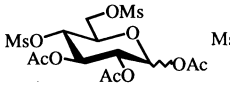
(3)



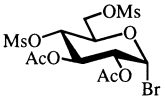
(6)



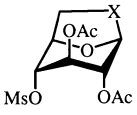
(7) R = $C_6H_{11}NH$
(8) R = N_3



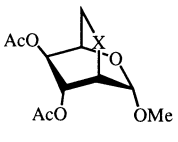
(9a,b)



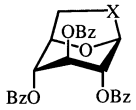
(10)



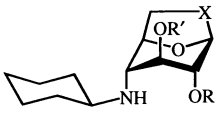
(11) X = S
(12) X = Se



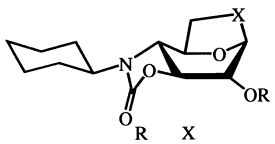
(13) X = Se
(14) X = O



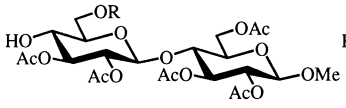
(15) X = Se
(16) X = S



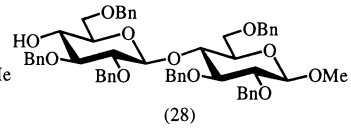
	R	R′	X
(17)	H	H	Se
(18)	Bn	H	O
(23)	CO_2Et	H	Se
(24)	CO_2Et	CO_2Et	Se
(26)	Bz	H	Se



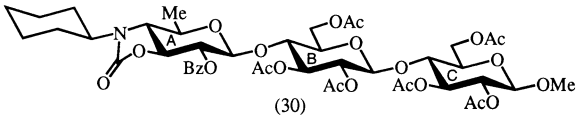
	R	X
(19)	Bn	O
(20)	COCl	Se
(21)	H	Se
(22)	CO_2Et	Se
(25)	Bz	Se



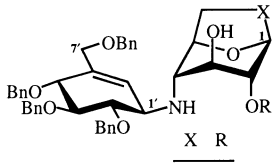
(27) R = Ac
(29) R = H



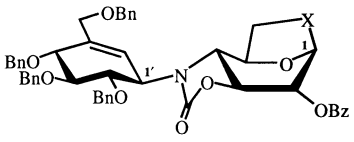
(28)



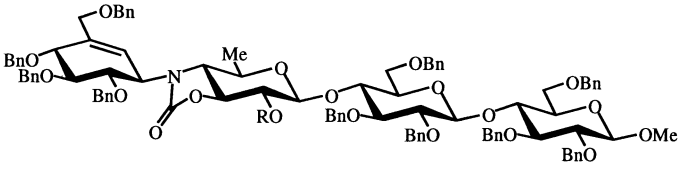
(30)



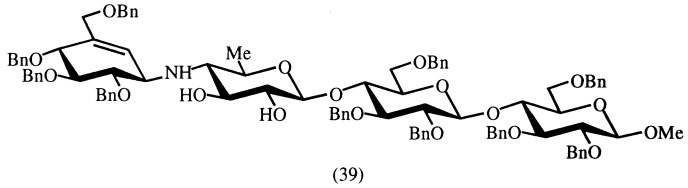
	X	R
(31)	S	H
(32)	S	Bz
(33)	Se	Bz
(34)	Se	H



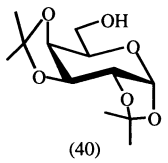
(35) X = S
(36) X = Se



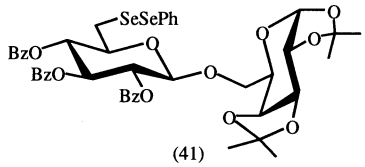
(37) R = Bz
(38) R = H



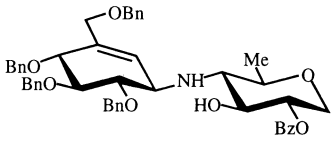
(39)



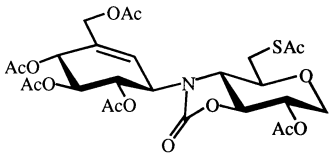
(40)



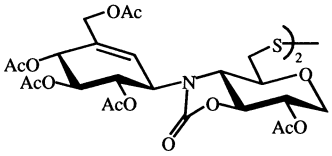
(41)



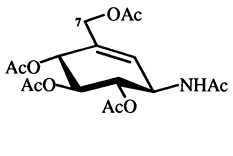
(42)



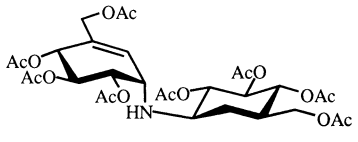
(43)



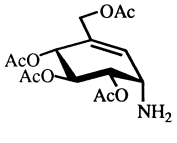
(44)



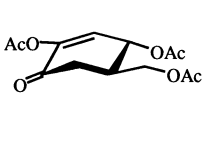
(45)



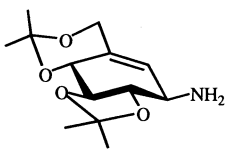
(46)



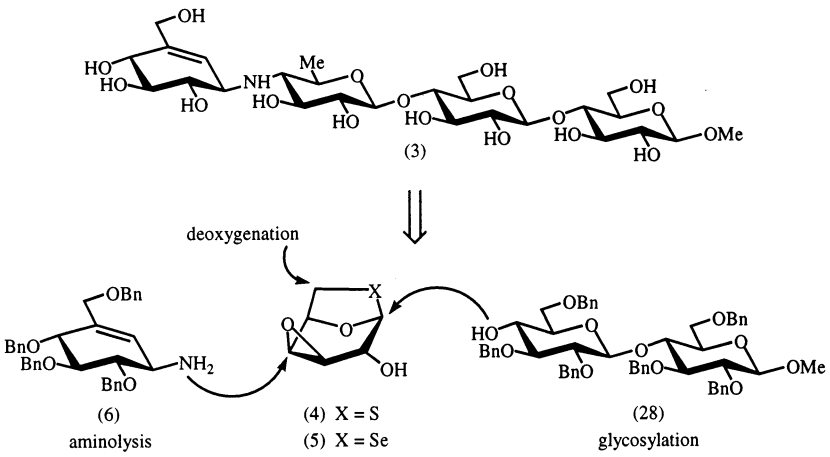
(47)



(48)



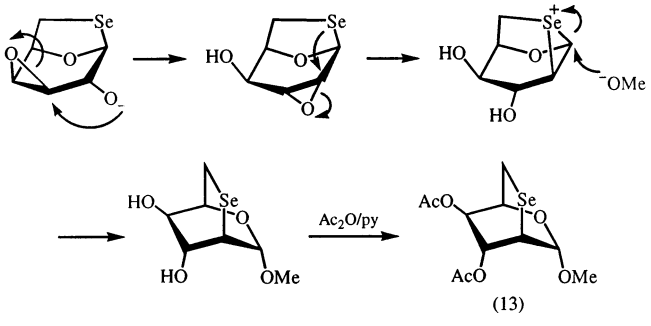
(49)



Scheme 1

acetyl groups and to form directly the 3,4-anhydro ring; neutralization with acid resin followed by crystallization provided (4).[7] Although effective on a small scale, this procedure proved unsatisfactory upon scale-up owing to the formation of copious amounts of a fine precipitate (sodium mesylate). A better procedure involved the removal of the bulk of the solvent and extraction of the residue with ethyl acetate—this gave a good recovery of the epoxides (4) and (5) which were then easily purified by flash chromatography.

There always existed the possibility that the epoxides (4) and (5) would undergo a Payne rearrangement upon prolonged treatment with base.[10] Indeed, when the mesylate (12) was treated with a large excess of sodium methoxide in methanol, t.l.c. analysis indicated the gradual conversion of the initially formed epoxide (5) into another product. Acetylation of the reaction mixture, after removal of the solvent, then provided a compound with an intriguing ^{1}H n.m.r. spectrum. A signal at δ 3.40 was indicative of a methyl glycoside, although the relatively small magnitude of the observed coupling constants for most resonances still indicated the presence of an anhydro ring. The problem was eventually resolved in favour of the 2,6-episeleno-D-*ido* sugar (13); further confirmation was provided by a comparison with the known 2,6-anhydro-D-*ido* sugar (14).[11] A rationalization for this transformation is presented in Scheme 2.



Scheme 2

The choice of epoxide, either (4) or (5), for the aminolysis reaction now became the next issue. Given the relatively greater reactivity of the 1,6-episeleno sugar (15) as a glycosyl donor, and the easier deoxygenation of the resultant product to afford a 6-deoxy glycoside when compared to the epithio sugar (16), it was decided to concentrate efforts in the model series on the 1,6-episeleno epoxide (5).[12] Treatment of the episeleno sugar (5) with a fivefold excess of cyclohexylamine in butanol afforded the crystalline amino diol (17), in excellent yield.

The presence of unprotected amino and hydroxy groups in (17) was the source of concern for the planned glycosylation step. Triphosgene has been used previously to execute the protection of the vicinal amino alcohol (18) as the carbamate (19).[13,14] Here, the matter was complicated by the presence of another hydroxy group at C 2. Upon treatment of the amino diol (17) with triphosgene, material was formed with variable chromatographic properties, believed to be the chloroformate (20) and products derived from its degradation. Upon treatment of this material with sodium methoxide in methanol, the chromatographic properties improved and resulted in the eventual isolation of the carbamate (21), although in a less than satisfactory yield (49%). The identity of the carbamate (21) was confirmed, in part, by the large magnitude for $J_{3,4}$, namely 12.5 Hz, indicative of an enforced *trans*-diaxial arrangement of H 3 and H 4, typical of a *trans*-fused oxazolone ring.[13]

As a result of the low yield for the production of (21), attention was directed away from the use of triphosgene to form the desired oxazolone. McAuliffe and coworkers have shown that, depending on the conditions, either a cyclic carbamate or an *O*-ethyl carbamate may be formed upon treatment of the amino alcohol (18) with ethyl chloroformate.[13] In the event, prolonged treatment of the amino diol (17) with ethyl chloroformate and triethylamine in dichloromethane gave a mixture of the carbamate (22) and the amino alcohol (23). The formation of these two products can be rationalized on the basis of two competing pathways for the reaction: either the C 2 hydroxyl of (17) may react first, providing the amino alcohol (23) and reducing the reactivity of the amine

and remaining hydroxy group, or reaction at the C 3 hydroxyl would lead, first, to the carbamate (21) which can react, subsequently, with a further equivalent of ethyl chloroformate to give (22). The lack of reaction at nitrogen was to be expected for such a hindered system.[13]

Under more forcing conditions, with 4-(dimethylamino)-pyridine as a catalyst, the treatment of the amino diol (17) with ethyl chloroformate provided an inseparable mixture of what appeared to be the carbamate (22) and the dicarbonate (24). The reluctance of the dicarbonate (24) to cyclize to the carbamate (22) is surprising; upon reflux overnight in tetrahydrofuran, the composition of the mixture of carbamate (22) and dicarbonate (24) appeared unchanged.

Although a moderate yield of the carbamate (22) was achieved with ethyl chloroformate and elaboration of (22) into the putative donor (25) was an option, it was decided on the basis of the above result to attempt the direct, selective functionalization of (17) at O 2. Accordingly, the amino diol (17) was treated with benzoyl chloride at low temperature to give an excellent yield of the monobenzoate (26), a significant result. Subsequent treatment of the amino alcohol (26) with triphosgene cleanly furnished the putative donor (25) in an almost quantitative yield.

Two possible alcohols for the glycosylation reaction were now identified, namely (27) and (28). Of these, the alcohol (27) was likely to cause fewer problems in the final (deprotection) steps of the synthesis; treatment of the diol (29) with *N*-acetylimidazole in dry dichloroethane at 80° for 3 days provided the alcohol (27) in 51% yield.

Now, treatment of a solution of the donor (25) and the alcohol (27) with a solution of *N*-iodosuccinimide/trifluoromethanesulfonic acid and, after consumption of the donor (t.l.c.), with tributylstannane, gave the trisaccharide (30) as a crystalline product, albeit in a poor yield of just 10%, along with other, unidentified side-products. Nevertheless, given the presumed low reactivity of the acetylated alcohol (27), this result was certainly encouraging and the knowledge gained in the model studies was placed directly into practice on the actual sequence towards methyl β-acarboside (3).

Tetra-*O*-benzyl-1-epivalienamine (6) was readily available through the excellent procedure of Nicotra and coworkers[15] and the subsequent modifications introduced by McAuliffe and Stick.[16] In order to exploit fully any successes which may arise from the work planned, it was decided to include both epoxides, namely (4) and (5), in the upcoming investigations. With access to suitable quantities of the amine (6), the coupling of this compound to the epoxides (4) and (5) became the next goal.

In contrast to the earlier work, purification of the product of aminolysis of the 1,6-epithio epoxide (4) with the 1-epivalienamine (6) was not possible by crystallization.[17] The reaction produced a very dark, thick liquid and, although t.l.c. indicated the formation of a new product, presumably (31), in addition to the presence of excess epoxide, complete purification was not possible; ultimately, the partially purified material was treated directly with benzoyl chloride at –40° and the reaction mixture allowed to warm. Encouragingly, a new compound was formed with a much lower polarity and this was readily purified, furnishing the amino alcohol (32). A similar, two-step treatment of the 1,6-episeleno epoxide (5) also provided the analogous amino alcohol (33) via the diol (34).

The conversion of the monobenzoates (32) and (33) into the cyclic carbamates (35) and (36), respectively, was readily accomplished upon treatment with triphosgene at low temperature. The ^{1}H n.m.r. spectra of both of these cyclic carbamates differed from that of the model carbamate (25) in that the signal for H 1′ was not readily apparent. For compound (33), the signal for H 1′ was eventually located as a complex multiplet in the range δ 4.49–4.64, whereas for (32) the signal for H 1′ could not be located. Similarly, the signal for C 1′ in both compounds showed significant line broadening, resulting in a very slow acquisition of the ^{13}C n.m.r. spectra. Effects such as these have been noted in similar systems[17,18] and ascribed to hindered rotation around a carbon–nitrogen bond, resulting in diastereoisomeric conformations.[18]

With both glycosyl donors in hand, the more reactive alcohol (28) was readily prepared. Treatment of a mixture of the donor (36) and the alcohol (28) with *N*-iodosuccinimide/TfOH resulted in the rapid consumption of the donor (36) (t.l.c. analysis). Workup of the mixture and the subsequent treatment of the residue with tributylstannane resulted in the eventual isolation of an oil.[19] T.l.c. and ^{1}H n.m.r. analysis at this stage, however, indicated that this oil was composed of a number of compounds. Flash chromatography resolved the mixture into a major fraction, the ^{1}H n.m.r. spectrum of which indicated that it was itself composed of a number of products, each of which showed characteristic spectroscopic features suggesting the presence of products of glycosylation and of 6-deoxy sugar residues. The variety of spectroscopically similar products resulting from the glycosylation reaction led to the conclusion that some degree of benzyl ether cleavage had occurred. Indeed, treatment of the mixture obtained from one such glycosylation attempt with acetic anhydride and pyridine resulted in the conversion into a number of unidentified compounds which appeared to have incorporated acetyl groups (^{1}H n.m.r. spectroscopy).

In one instance, the oil isolated from a glycosylation attempt was treated with sodium methoxide to remove the benzoyl group from the presumed product (37), to aid in its isolation. Following flash chromatography, a poor mass return of an inseparable mixture of at least four compounds was evident, with each component exhibiting some spectroscopic characteristics expected for the product (38) and also showing the absence of the benzoyl protecting group. Alternatively, a portion of the same oil was treated with sodium hydroxide in a mixture of pyridine and water at 95° for 4 h, conditions which should effectively remove both the carbamoyl and benzoyl functions.[1,13,17] Again, a poor mass return was evident and, although only two compounds were present in the isolated mixture, each possessing spectroscopic characteristics expected for the amino diol (39), both this and the above route appeared unrewarding.

It was believed that the decomposition of material in the glycosylation reaction performed with the donor (36) may have arisen from a detrimental degradation of an intermedi-

ate selenenyl triflate or selenenic acid present after the quenching of the glycosylation reaction. As a result, an alternative promoter for the glycosylation reaction was sought which would not result in the formation of such a potentially reactive intermediate. It was anticipated that the use of phenylselenenyl triflate as a promoter would ideally result in the formation of a mixed diselenide as the product.[20,21] Exploratory experiments with the model donor (15) and alcohol (40) were inconclusive as to the benefits of such a promoter—whilst glycosylation was apparent, the mass return was poor and the complete purification of the mixed diselenide (41) was not achieved.

Under the impression that degradation of the product was the result of the acid-promoted loss of benzyl ethers, the replacement of the benzyl ethers of (36) with a less labile protecting group was attempted. Of particular concern were the benzyl ethers at the allylic positions of (36)—earlier work had shown that such benzyl ethers are labile in acetolysis reactions performed with an analogous 1,6-anhydro sugar.[17]

Recently, a number of Lewis-acid promoted reactions have been used to remove benzyl ethers, with varying degrees of efficiency. Olah and coworkers have reported the use of trimethylsilyl iodide, generated *in situ*, as a mild but effective reagent for the removal of benzyl ethers.[22] Anhydrous iron(III) chloride in dichloromethane has been used to good effect for the debenzylation of some quite complex carbohydrates.[23] Similarly, trimethylsilyl triflate in acetic anhydride is established as a powerful reagent for the acetolysis of benzyl ethers.[24] Quite recently, iodine in acetic anhydride has been shown to possess a remarkable ability to cleave benzyl ethers.[25] The application of each of these procedures to the modification of the donor (36) was unsuccessful, in some cases no reaction was evident and in others incomplete removal of the benzyl ethers appeared to have occurred. In at least one of these procedures, there was concern that allylic cleavage may have been favoured over the desired benzylic cleavage.

The use of base-promoted procedures for the removal of benzyl ethers has been the subject of fewer studies but has shown good promise. A procedure modified from that of Feutrill and Mirrington, using lithium ethanethiolate in hot dimethylformamide to effect a nucleophilic displacement of the benzyl ethers of (36), was attempted but resulted in extensive degradation and afforded an intractable, black oil.[26]

As an aside, the amino alcohol (33) was treated with tributylstannane and α,α′-azobisisobutyronitrile in toluene at reflux, conditions which were hoped to remove the selenium atom. Disappointingly, instead of the predicted reduction to furnish (42), a compound of unidentified composition was formed; however, it was clear that the 1,6-episeleno ring remained intact, on the basis of a singlet being present at δ 5.81 in the ^{1}H n.m.r. spectrum.

Being mindful of the important reactivity differences between 1,6-epithio and 1,6-episeleno sugars firmly established in preliminary work and having some concern as to the potential for degradation arising from decomposition of an intermediate selenenic acid, we now hoped that the glycosylation reaction using the 1,6-epithio donor (35) would bring relief to the above unsuccessful glycosylation.[27]

A solution of the donor (35) and the alcohol (28) in a mixture of 1,2-dichloroethane and diethyl ether was treated with *N*-iodosuccinimide/TfOH as outlined previously. However, despite the addition of extra triflic acid and warming of the reaction mixture to room temperature, after 1 h no reaction was evident by t.l.c. With the additional triflic acid present, decomposition of the donor and alcohol occurred at an appreciable rate and the reaction was necessarily abandoned. The reaction was repeated on another occasion with no obvious differences. Triethylsilyl triflate has been suggested as an alternative to triflic acid as an efficient reagent in combination with *N*-iodosuccinimide for the activation of n-pentenyl glycosides without concomitant degradation of acid-sensitive donors or alcohols.[28] However, repetition of the above reaction with triethylsilyl triflate in place of triflic acid led to no obvious differences in the outcome of the reaction. The lack of reaction was a significant setback, but it was not entirely unexpected. The relative reactivities of 1,6-epithio and 1,6-episeleno donors previously demonstrated have shown the donor (16) to be the poorest of all those examined and, given a presumed low reactivity of the disaccharide alcohol (28) and of the donor (35) (resulting from the presence of the oxazolone ring), even the powerful promoter system *N*-iodosuccinimide/TfOH failed to activate the compound towards glycosylation.[27] It may also be possible that the addition of iodonium ions to the electron-rich alkene in (35) caused a significant reduction in the concentration of such ions available for promotion of the glycosylation reaction.[29]

With the availability of methods for the modification of the protecting groups of the donors (35) and (36) into different forms rapidly running short, methods for their reductive removal were sought. Unsurprisingly, an attempt at hydrogenolysis of the benzyl ethers of (35) using palladium on charcoal failed, chalcogens being widely recognized as potent catalyst poisons.

More reasonably, reduction using lithium in liquid ammonia appeared an attractive option. Accordingly, the carbamate (35) was debenzoylated and then treated with lithium metal in a mixture of liquid ammonia and tetrahydrofuran, the solvent removed and the residue treated with acetic anhydride and pyridine. Upon workup, a very low mass return of a product of intermediate polarity was isolated—spectroscopic analysis suggested that the product was in fact a mixture of the thioacetate (43) and the disulfide (44).

A much more polar compound was also isolated. ^{1}H n.m.r. spectroscopy showed this compound to be homogenous and it was readily identified as the acetamide (45), further confirmation being provided by a comparison of the ^{1}H n.m.r. spectrum with that of the racemate prepared by Ogawa and coworkers.[30] The degradation resulting in cleavage of the C 4–N bond of (35) appears to be a result of the 1,6-epithio bridge, a closely related oxygen-containing analogue being immune to such a degradation upon treatment with Na/NH_3. The degradation may result from the formation of an anomeric anion or radical, which then undergoes a fragmentation, ultimately cleaving the C 4–N bond.

The fragmentation of carba-sugars, with a similar result, has been observed by others. Ogawa and coworkers have

reported that the treatment of *per*-acetylvalidoxylamine A (46) with *N*-bromosuccinimide in aqueous *N,N*-dimethylformamide affords, among other products, tetra-*O*-acetylvalienamine (47) and the cyclohexenone (48).[31] Whilst the rationalization for such a degradation undoubtedly differs from that proposed above, the products demonstrate the lability of the C 4–N bond under suitable conditions.

The failure of the donors (35) and (36) to glycosylate the alcohol (28) and provide a novel route to the target compound, methyl β-acarboside (3), represented a major blow to our synthetic plan. One option now was to investigate another synthesis of epivalienamine in a differently protected form, perhaps as the di-*O*-isopropylidene acetal (49). Whilst this was an option which may have borne fruit, an alternative synthesis of methyl β-acarboside (3) was envisioned by way of the alkylation of the same tetra-*O*-benzyl-1-epivalienamine (6) with a suitably protected triflate. These investigations form the basis of the next paper.

Experimental

General experimental procedures have been given previously.[16]

1,2,3-Tri-O-*acetyl-4,6-di*-O-*methylsulfonyl*-D-*glucose (9a,b)*

1,2,3-Tri-*O*-acetyl-4,6-*O*-benzylidene-D-glucose[7] (20.0 g,50.8 mmol) and palladium on carbon (10%, 0.4 g) was suspended in a mixture of EtOAc (300 ml) and MeOH (50 ml) containing two drops of AcCl and the mixture was treated with hydrogen (6 h). The mixture was filtered and the solvent evaporated to afford a colourless foam. This foam was dissolved in pyridine (100 ml) and the solution treated with MsCl (15.8 ml, 23.3 g, 203 mmol) at 0° for 30 min, then room temperature for 2 h. The mixture was poured into an ice/water slurry (500 ml) which was stirred vigorously for 10 min and then allowed to stand (10 min). The supernatant was decanted and the doughy residue was washed with water and crystallized from EtOH to afford a white powder. The aqueous supernatant deposited crystals overnight and these were filtered off and washed with EtOH and combined with the first crop to afford the dimesylate (9a,b) as a white powder (16.5 g, 71%). The ^{1}H n.m.r. spectrum agreed with that reported in the literature.[7]

2,3-Di-O-*acetyl-4,6-di*-O-*methylsulfonyl*-α-D-*glucosyl Bromide (10)*

A suspension of the triacetate (9a,b) (10.0 g, 21.6 mmol) in dry AcOH (30 ml) and HBr in AcOH (30%, 10 ml, 50 mmol) was stirred at room temperature for 2 days. The solution was subjected to the usual workup (CH_2Cl_2, excluding the acid wash) and the crystalline residue was dissolved in EtOAc; crystallization ensued upon the addition of petrol to give the bromide (10) as chunky crystals (8.06 g, 77%), m.p. 143–145° (EtOAc/petrol), $[\alpha]_D$ +172.6° (Found: C, 30.0; H, 4.2. Calc. for $C_{12}H_{19}BrO_{11}S_2$: C, 29.8; H, 4.0%). ^{1}H n.m.r. (500 MHz) δ 2.09, 2.10, 2s, 6H, Ac; 3.09, 3.09, 2s, 6H, Ms; 4.36, ddd, $J_{4,5}$ 10.1, $J_{5,6}$ 2.1, 3.5 Hz, H 5; 4.42, dd, $J_{6,6}$ 11.6 Hz, H 6; 4.48, dd, H 6; 4.81, dd, $J_{1,2}$ 4.1, $J_{2,3}$ 10.0 Hz, H 2; 4.85, dd, $J_{3,4}$ 9.3 Hz, H 4; 5.63, dd, H 3; 6.59, d, H 1. ^{13}C n.m.r. (125.8 MHz) δ 20.52, 20.74, 2C, CO**Me**; 37.73, 38.67, 2C, Ms; 65.41, C 6; 69.01, 70.29, 71.41, 71.62, C 2,3,4,5; 85.53, C 1; 169.58, 169.85, 2C, CO.

2,3-Di-O-*acetyl-1,6-dideoxy-1,6-episeleno-4*-O-*methylsulfonyl*-β-D-*glucose (12)*

A mixture of sodium borohydride (47 mg, 1.2 mmol) and selenium (79 mg, 1.0 mmol) in EtOH (5 ml) was stirred under nitrogen until all of the selenium had dissolved and a clear solution had formed. The bromide (10) (320 mg, 0.66 mmol) was added, along with dry dimethylformamide (5 ml). The mixture was left to stir overnight and then the mixture was poured into water and extracted with EtOAc. The combined extracts were washed successively with water and brine, then dried and the solvent evaporated to give a pale yellow oil which crystallized. Flash chromatography (30–40% EtOAc/petrol) gave the *mesylate* (12) as a pale yellow oil (197 mg, 76%). This oil crystallized to give fine, white needles, m.p. 143–145° (EtOH), $[\alpha]_D$ –68.4° (Found: C, 34.1; H, 4.5. $C_{11}H_{16}O_8SSe$ requires C, 34.1; H, 4.2%). ^{1}H n.m.r. (300 MHz) δ 2.06, 2.07, 2s, 6H, Ac; 3.05, s, Ms; 3.10, dd, $J_{5,6}$ 5.9, $J_{6,6}$ 9.9 Hz, H 6; 3.31, br d, H 6; 4.54, dd, $J_{3,4}$ 7.0, $J_{4,5}$ 2.3 Hz, H 4; 4.86, br d, $J_{2,3}$ 4.9 Hz, H 2; 5.04, br dd, H 5; 5.12, dd, H 3; 5.72, br s, H 1. ^{13}C n.m.r. (75.5 MHz) δ 20.81, 2C, CO**Me**; 31.81, C 6; 38.34, Ms; 68.95, 76.65, 77.20, 78.21, 81.91, C1,2,3,4,5; 169.51, 170.11, 2 C, CO.

3,4-Anhydro-1,6-dideoxy-1,6-epithio-β-D-*galactose (4)*

A suspension of the mesylate (11)[7] (12.2 g, 36.0 mmol) in dry MeOH (50 ml) was treated with sodium metal (998 mg, 43.4 mmol) at 0° for 16 h. The solvent was evaporated from the resultant suspension and the residue was suspended in EtOAc and filtered off, with repeated washing of the filter cake with additional EtOAc. The solvent was evaporated from the filtrate and the residue purified by flash chromatography (60% EtOAc/petrol) to give the epoxide (4) as a pale yellow, crystalline solid (5.11 g, 89%). The ^{1}H n.m.r. spectrum agreed with that reported in the literature.[7]

3,4-Anhydro-1,6-dideoxy-1,6-episeleno-β-D-*galactose (5)*

The 1,6-episeleno mesylate (12) (5.32 g) was treated in the same manner as for the 1,6-epithio mesylate (11) to give the *epoxide* (5) as a white, crystalline solid (2.35 g, 83%), m.p. 117–119°, $[\alpha]_D$ –71.0° (Found: C, 35.0; H, 3.8. $C_6H_8O_3Se$ requires C, 34.8; H, 3.9%). ^{1}H n.m.r. (500 MHz) δ 2.72–2.77, m, OH; 3.12, dd, $J_{5,6}$ 6.6, $J_{6,6}$ 8.6 Hz, H 6; 3.18, br d, $J_{3,4}$ 3.5 Hz, H 3; 3.31, d, H 6; 3.53, dd, $J_{4,5}$ 5.3 Hz, H 4; 4.08, br d, $J_{2,OH}$ 6.3 Hz, H 2; 5.15, dd, H 5; 5.65, br s, H 1. ^{13}C n.m.r. (125.8 MHz) δ 29.93, C 6; 50.64, 53.67, C 3,4; 67.57, 76.36, 77.02, C 1,2,5.

Methyl 3,4-Di-O-*acetyl-2,6-dideoxy-2,6-episeleno*-α-D-*idoside (13)*

The mesylate (12) (341 mg, 0.872 mmol) was suspended in dry MeOH (5 ml) and a solution of NaOMe (1.0 ml of 0.93 M in MeOH, 0.93 mmol) was added at room temperature under nitrogen. The mixture became clear and turned light orange after 1 min. After 24 h, more NaOMe (7 ml of 0.93 M in MeOH, 6.5 mmol) was added and the solution left for another 24 h. T.l.c. at this stage indicated the presence of one major compound, so the solvent was evaporated and the residue was treated with pyridine (8 ml) and Ac_2O (4 ml) at 0° for 1 h. The solvent was evaporated and the residue subjected to a normal workup (EtOAc). The residue was purified by flash chromatography (25% EtOAc/petrol) to give the *methyl* D-*idoside* (13) as a clear oil (64 mg, 23%), $[\alpha]_D$ +44.4° (Found: C, 40.9; H, 5.0. $C_{11}H_{16}O_6Se$ requires C, 40.9; H, 5.0%). ^{1}H n.m.r. (500 MHz) δ 2.05, 2.07, 2s, OAc; 2.88, ddd, $J_{4,6}$ 1.0, $J_{5,6}$ 4.0, $J_{6,6}$ 10.8 Hz, H 6; 2.91, dd, $J_{5,6}$ 2.0 Hz, H6; 3.09, dd, $J_{1,2}$ 2.1, $J_{2,3}$ 1.9 Hz, H 2; 3.40, s, OMe; 4.46, ddd, $J_{4,5}$ 4.2 Hz, H 5; 5.12, dd, $J_{1,3}$ 0.92 Hz, H 1; 5.33, ddd, $J_{3,4}$ 5.1 Hz, H 4; 5.42, ddd, H 3. ^{13}C n.m.r. (125.8 MHz) δ 15.53, C 6; 20.87, 21.08, 2C, COMe; 29.31, C 2; 55.26, OMe; 66.26, 72.15, 75.14, C 3,4,5; 100.54, C 1; 169.71, 170.54, 2C, CO.

4-Cyclohexylamino-1,6-episeleno-1,4,6-trideoxy-β-D-*glucose (17)*

A solution of the epoxide (5) (694 mg, 3.56 mmol) and cyclohexylamine (1.66 g, 1.9 ml, 16.8 mmol) in BuOH (5 ml) was heated (100°) under nitrogen for 16 h. The solvent was evaporated with the aid of toluene. The crystalline residue so obtained was purified by flash chromatography (60% EtOAc/petrol, then 10% EtOH/1% Et_2NH/EtOAc) to give the *amine* (17) as a pale brown, crystalline solid (904 mg, 87%) which crystallized as pale yellow needles, m.p. 163–164° (CH_2Cl_2/Pr^i_2O), $[\alpha]_D$ –39.0° (Found: C, 47.1; H, 7.0. $C_{12}H_{21}NO_3Se$ requires C, 47.1; H, 6.9%). ^{1}H n.m.r. (500 MHz) δ 0.90–1.30, 1.56–2.03, 2m, 10H, cyclohexyl CH_2; 2.54, tt, *J* 3.6, 10.5 Hz, cyclohexyl CH; 2.88, d, $J_{3,4}$ 1.8 Hz, H 4; 3.26, dd, $J_{5,6}$ 7.6, $J_{6,6}$ 9.6 Hz, H 6; 3.37, br d, H 6; 3.68, br s, H 2; 3.76, d, H 3; 4.80, br d, $J_{5,6}$ 7.5 Hz, H 5; 5.90, br s, H 1. ^{13}C n.m.r. (125.8 MHz) δ 25.02, 25.10, 25.79, 30.45, 33.52, 34.11, 6C, C 6, cyclohexyl CH_2; 53.82, cyclohexyl CH; 57.74, C 4; 70.28, 72.16, 80.41, 81.07, C 1,2,3,5.

3,4-O,N-*Carbonyl-4-cyclohexylamino-1,6-episeleno-1,4,6-trideoxy*-β-D-*glucose (21)*

Triphosgene (149 mg, 540 μmol) was added to a solution of the amine (17) (153 mg, 500 μmol) and pyridine (480 μl) in CH_2Cl_2 (10 ml) at –78°. The mixture was allowed to warm to room temperature, then water (0.5 ml) was added and the mixture stirred for a further 10 min. The reaction mixture was subjected to the usual workup (CH_2Cl_2) and the residue dissolved in MeOH (5 ml). The solution was treated with a small piece of sodium. After 30 min, t.l.c. indicated a homogenous product, so the solution was neutralized with resin (Dowex-50, H^+) and the solvent evaporated. Flash chromatography of the residue (30–40% EtOAc/petrol) gave the *carbamate* (21) as a clear oil (82 mg, 49%) which crystallized as needles, m.p. 194–195° (EtOH), $[\alpha]_D$ –35° (Found: C, 47.0; H, 5.6. $C_{13}H_{19}NO_4Se$ requires C, 47.0; H, 5.8%). ν_{max} (NaCl) 1736 cm^{-1}. ^1H n.m.r. (500 MHz) δ 1.05–1.43, 1.67–2.02, 2m, 10H, cyclohexyl CH_2; 3.16–3.22, m, 2H, H 6; 3.61–3.67, m, cyclohexyl CH; 3.66, dd, $J_{3,4}$ 12.5, $J_{4,5}$ 4.7 Hz, H 4; 3.98, dd, $J_{2,3}$ 8.6 Hz, H 3; 4.18, d, H 2; 5.04, dd, $J_{5,6}$ 1.6, 3.4 Hz, H5; 5.75, s, H 1. ^{13}C n.m.r. (125.8 MHz) δ 25.47, 25.93, 29.72, 32.67, 35.86, 6C, C 6, cyclohexyl CH_2; 55.36, cyclohexyl CH; 58.73, C 4; 76.47, 77.07, 79.68, 81.42, C 1,2,3,5; 159.28, CO.

3,4-O,N-*Carbonyl-4-cyclohexylamino-1,6-episeleno-2*-O-*ethoxycarbonyl-1,4,6-trideoxy*-β-D-*glucose (22) and 4-Cyclohexylamino-2*-O-*ethoxycarbonyl-1,6-episeleno-1,4,6-trideoxy*-β-D-*glucose (23)*

Ethyl chloroformate (143 μl, 1.50 mmol) was added to a solution of the amino diol (17) (153 mg, 500 μmol) and Et_3N (420 μl, 3.0 mmol) in dry CH_2Cl_2 (10 ml) at –30° under N_2. The solution was allowed to warm to room temperature and was left for 8 h. More ethyl chloroformate (50 μl, 0.17 mmol) was added and the solution was left overnight. Water (0.5 ml) was added to the solution and the mixture was stirred for 10 min, before being subjected to the usual workup (CH_2Cl_2). The residue was purified by flash chromatography (20–50% EtOAc/petrol) to give firstly the *oxazolone* (22) as a clear oil (117 mg, 59%), $[\alpha]_D$ –31.1° (Found: C, 47.4; H, 5.8. $C_{16}H_{23}NO_6Se$ requires C, 47.5; H, 5.7%). ^1H n.m.r. (500 MHz) δ 1.05–1.42, 1.67–2.02, 2m, 10H, cyclohexyl CH_2; 1.32, t, *J* 7.1 Hz, CH_3; 3.18, m, 2H, H 6; 3.62–3.68, m, cyclohexyl CH; 3.73, dd, $J_{3,4}$ 12.6, $J_{4,5}$ 4.7 Hz, H 4; 4.11, dd, $J_{2,3}$ 9.0 Hz, H 3; 4.18–4.26, m, C**H**$_2$CH$_3$; 4.96, d, H 2; 5.02, ddd, $J_{5,6}$ 2.5, 2.5 Hz, H 5; 5.77, s, H 1. ^{13}C n.m.r. (125.8 MHz) δ 14.10, CH_3; 25.42, 25.91, 29.65, 32.61, 35.84, 6C, C 6, cyclohexyl CH_2; 55.40, cyclohexyl CH; 58.55, C 4; 64.86, **C**H$_2$CH$_3$; 72.38, 77.99, 79.98, 81.00, C 1,2,3,5; 154.18, OC=O; 158.36, NC=O.

Next to elute was the *amino alcohol* (23) as needles (45 mg, 24%), m.p. 76–80°, $[\alpha]_D$ –37.6° (Found: C, 48.0; H, 7.0. $C_{15}H_{25}NO_5Se$ requires C, 47.6; H, 6.7%). ^1H n.m.r. (500 MHz) δ 1.02–1.28, 1.57–1.88, 2m, 10H, cyclohexyl CH_2; 1.31, t, *J* 7.1 Hz, CH_3; 2.55, tt, *J* 3.7, 10.3 Hz, cyclohexyl CH; 2.72, dd, $J_{3,4}$ 6.4, $J_{4,5}$ 2.6 Hz, H 4; 3.15–3.20, m, 2H, H 6; 3.63, br t, H 3; 4.21, q, C**H**$_2$CH$_3$; 4.72, br d, $J_{2,3}$ 4.6 Hz, H 2; 4.83, dt, $J_{5,6}$ 2.5, 4.4 Hz, H 5; 5.85, s, H 1. ^{13}C n.m.r. (125.8 MHz) δ 14.15, CH_3; 24.75, 24.84, 25.91, 33.11, 33.23, 34.30, 6C, C 6, cyclohexyl CH_2; 53.70, cyclohexyl CH; 57.60, C 4; 64.46, **C**H$_2$CH$_3$; 68.60, 77.53, 81.68, 83.71, C 1,2,3,5; 154.52, CO.

3,4-O,N-*Carbonyl-4-cyclohexylamino-1,6-episeleno-2*-O-*ethoxycarbonyl-1,4,6-trideoxy*-β-D-*glucose (22) and 4-Cyclohexylamino-2,3-di*-O-*ethoxycarbonyl-1,6-episeleno-1,4,6-trideoxy*-β-D-*glucose (24)*

Ethyl chloroformate (278 μl, 2.92 mmol) was added to an ice-cold solution of the amine (17) (149 mg, 487 μmol), Et_3N (400 μl, 2.9 mmol) and 4-(dimethylamino)pyridine (60 mg, 0.5 mmol) in dry CH_2Cl_2 (5 ml) under N_2. The solution was allowed to warm to room temperature and was left for 3 h. The solution was quenched by the addition of water (1 ml) and the mixture was stirred for 5 min, before being subjected to the usual workup (CH_2Cl_2). The residue was purified by flash chromatography (15–50% EtOAc/ petrol) to give a clear oil (163 mg) that appeared to be a mixture of two compounds, the oxazolone (22) and the dicarbonate (24), in a ratio of 3 : 2, respectively, as determined by ^1H n.m.r. spectroscopy and by a comparison with the spectra recorded above. Partial ^1H n.m.r. (500 MHz) for (24): δ 2.48–2.58, m, cyclohexyl CH; 2.69–2.71, m, H 4; 5.82, br s, H 1. Partial ^{13}C n.m.r. (125.8 MHz) for (24): δ 14.14, CH_3; 24.39, 24.61, 30.79, 33.39, 33.47, 6C, C 6, cyclohexyl CH_2; 53.27, cyclohexyl CH; 55.01, C 4; 64.30, 64.42, **C**H$_2$CH$_3$; 72.67, 76.25, 76.89, 82.40, C 1,2,3,4,5; 153.94, 154.26, 2C, CO.

Attempted Formation of the Carbamate (22)

A solution of a mixture of the oxazolone (22) and the dicarbonate (24) (50 mg, 3 : 2) in dry tetrahydrofuran was heated at reflux under N_2 overnight. The solvent was evaporated to afford an oil (49 mg). The composition of the material was shown by ^1H n.m.r. (300 MHz) to be essentially unchanged from that of the starting mixture.

2-O-*Benzoyl-4-cyclohexylamino-1,6-episeleno-1,4,6-trideoxy*-β-D-*glucose (26)*

Benzoyl chloride (320 μl, 2.8 mmol) was added slowly to a stirred suspension of the amine (17) (610 mg, 2.0 mmol), 4-(dimethylamino)pyridine (24 mg, 0.20 mmol) and Et_3N (840 μl, 6.0 mmol) in dry CH_2Cl_2 (20 ml) at –50° under N_2. The solution was allowed to warm to –20° over the space of 1 h, at which stage t.l.c. indicated almost complete consumption of the starting material. MeOH (1 ml) was added and the solution was left to warm to room temperature. The solution was then diluted with CH_2Cl_2 and washed with water, then dried and the solvent evaporated. The residue was purified by flash chromatography (30–50% EtOAc/petrol plus 1% Et_3N) to give the *benzoate* (26) as an off-white solid (690 mg, 84%) that crystallized as white needles, m.p. 136–137° (CH_2Cl_2/Pr$^i_2$O), $[\alpha]_D$ +10.7° (Found: C, 55.9; H, 6.2. $C_{19}H_{25}NO_4Se$ requires C, 55.7; H, 5.9%). ^1H n.m.r. (500 MHz) δ 1.07–1.33, 1.55–1.90, 2m, 10H, cyclohexyl CH_2; 2.63, tt, *J* 3.7, 10.1 Hz, cyclohexyl CH; 2.83, dd, $J_{3,4}$ 2.4, $J_{4,5}$ 5.2 Hz, H 4; 3.25, dd, $J_{5,6}$ 6.1, $J_{6,6}$ 9.3 Hz, H 6; 3.29, dd, $J_{5,6}$ 1.1 Hz, H 6; 3.82, m, H 3; 4.94, br d, H 5; 5.11, d, $J_{2,3}$ 3.5 Hz, H 2; 5.96, br s, H 1; 7.43–7.47, 7.57–7.61, 8.03–8.06, 3m, Ph. ^{13}C n.m.r. (125.8 MHz) δ 24.68, 24.75, 25.99, 32.64, 33.45, 34.05, 6C, C 6, cyclohexyl CH_2; 53.47, cyclohexyl CH; 57.58, C 4; 68.89, 77.64, 77.81, 83.37, C 1,2,3,5; 128.45–129.77, 133.44, Ph; 165.80, CO.

2-O-*Benzoyl-3,4*-O,N-*carbonyl-4-cyclohexylamino-1,6-episeleno-1,4,6-trideoxy*-β-D-*glucose (25)*

Triphosgene (148 mg, 500 μmol) was added to a solution of the benzoate (26) (409 mg, 1.00 mmol) and pyridine (242 μl, 3.00 mmol) in dry CH_2Cl_2 (10 ml) at –78° under N_2. The solution was allowed to warm to room temperature over 1 h, then water (0.5 ml) was added and the solution stirred (1 min). The mixture was subjected to the usual workup (CH_2Cl_2) and the residue was purified by flash chromatography (10–30% EtOAc/petrol) to give the *carbamate* (25) as a white, crystalline solid (414 mg, 95%) that crystallized as white, lustrous, long plates, m.p. 164–165° (EtOAc/petrol), $[\alpha]_D$ +25.4° (Found: C, 55.1; H, 5.3. $C_{20}H_{23}NO_5Se$ requires C, 55.1; H, 5.3%). ν_{max} (KBr) 1751, 1711 cm^{-1}. ^1H n.m.r. (500 MHz) δ 1.06–1.16, 1.30–1.47, 1.67–2.06, 3m, 10H, cyclohexyl CH_2; 3.22–3.27, m, 2H, H 6; 3.65–3.73, m, cyclohexyl CH; 3.82, dd, $J_{3,4}$ 12.5, $J_{4,5}$ 4.7 Hz, H 4; 4.32, dd, $J_{2,3}$ 9.2 Hz, H 3; 5.08–5.12, m, H 5; 5.25, d, H 2; 5.83, s, H 1; 7.42–7.48, 7.56–7.65, 8.04–8.08, 3m, Ph. ^{13}C n.m.r. δ 25.43, 25.90, 29.68, 32.65, 35.76, 6C, C 6, cyclohexyl CH_2; 55.42, cyclohexyl CH; 58.84, C 4; 72.42, 78.41, 78.91, 79.88, C 1,2,3,5; 128.37–129.85, 133.68, Ph; 158.52, NCO; 165.91, **C**OPh.

Methyl 2,3,6-Tri-O-*acetyl-4*-O-*(2,3,6-tri*-O-*acetyl*-β-D-*glucopyranosyl)*-β-D-*glucoside (27)*

AcCl (110 μl, 1.5 mmol) was added slowly to an ice-cold solution of imidazole (200 mg, 3.0 mmol) in dry 1,2-dichloroethane (10 ml) under N_2. The mixture was filtered after 1 min and a portion of the filtrate (9.0 ml of 0.15 M, 13 mmol) was added to the diol (29)[32] (762 mg, 1.34 mmol) and the solution was heated in a sealed ampoule at 80° for 3 days. The mixture was cooled to room temperature and subjected to the usual workup (CH_2Cl_2) to give a clear oil which was purified by flash chromatography (50–60% EtOAc/petrol) to give the *alcohol* (27)

as a clear syrup (412 mg, 51%), $[\alpha]_D$ –44.7° (Found: C, 49.4; H, 6.0. $C_{25}H_{36}O_{17}$ requires C, 49.3; H, 6.0%). ^{1}H n.m.r. (500 MHz) δ 2.02, 2.02, 2.03, 2.04, 2.11, 2.12, 6s, 18H, Ac; 3.22, d, $J_{4',OH}$ 4.5 Hz, OH; 3.43–3.46, m, H 5′; 3.46, s, OMe; 3.50, ddd, $J_{3',4'}$ 9.8, $J_{4',5'}$ 9.8 Hz, H 4′; 3.57, ddd, $J_{4,5}$ 9.9, $J_{5,6}$ 2.1, 5.0 Hz, H 5; 3.77, dd, $J_{3,4}$ 9.4 Hz, H 4; 4.09, dd, $J_{6,6}$ 12.0 Hz, H 6; 4.20, dd, $J_{5',6'}$ 2.0, $J_{6',6'}$ 12.5 Hz, H 6′; 4.36, d, $J_{1,2}$ 7.9 Hz, H 1; 4.47, d, $J_{1',2'}$ 7.9 Hz, H 1′; 4.51, dd, H 6; 4.57, dd, H 6′; 4.83, dd, $J_{2',3'}$ 9.4 Hz, H 2′; 4.87, dd, $J_{2,3}$ 9.6 Hz, H 2; 4.98, dd, H 3′; 5.16, dd, H 3. ^{13}C n.m.r. (125.8 MHz) δ 20.53, 20.55, 20.70, 20.74, 20.75, 20.82, 6C, CO**Me**; 56.98, OMe; 61.80, C 6; 62.55, C 6′; 68.11, C 4′; 71.48, C 2,2′; 72.56, 72.64, C 3,5; 74.23, C 5′; 75.06, C 3′; 76.44, C 4; 100.86, C 1′; 101.36, C 1; 169.26, 169.69, 169.88, 170.34, 171.07, 171.85, 6C, CO.

Methyl O-*(2*-O-*Benzoyl-3,4*-O,N-*carbonyl-4-cyclohexylamino-4,6-dideoxy*-β-D-*glucosyl)-(1→4)*-O-*(2,3,6-tri*-O-*acetyl*-β-D-*glucosyl)-(1→4)-2,3,6-tri*-O-*acetyl*-β-D-*glucoside (30)*

A solution of *N*-iodosuccinimide (145 mg, 645 μmol) and TfOH (15 μl) in dry 1,2-dichloroethane/Et_2O (1 : 1, 4 ml) at 0° under N_2 was added to a solution of the donor (25) (241 mg, 553 μmol) and alcohol (27) (281 mg, 461 μmol) in dry 1,2-dichloroethane (3 ml) at 0° under N_2. The mixture was left to stand for 1 h, then was quenched by the addition of saturated aqueous sodium bicarbonate solution (1 ml) and aqueous sodium thiosulfate solution (0.5 M, 1 ml). The organic phase was separated, dried and evaporated to give a residue which was dissolved in toluene (3 ml) and treated with Bu_3SnH (0.4 ml) and α,α′-azobisisobutyronitrile (1 mg) at reflux under N_2 for 30 min. The solvent was evaporated and the residue was dissolved in MeCN. The MeCN solution was washed repeatedly with petrol (5 times) and the solvent was evaporated. The residue was subjected to flash chromatography (60% EtOAc/petrol) to give a semicrystalline residue (120 mg) which was purified by crystallization to give the *trisaccharide* (30) as plates (45 mg, 10%), m.p. 151–153° (CH_2Cl_2/EtOH), $[\alpha]_D$ –28.7° (Found: C, 55.8; H, 6.3. $C_{45}H_{59}NO_{22}$ requires C, 55.9; H, 6.2%). ν_{max} (KBr) 1755 cm^{-1}. ^{1}H n.m.r. (500 MHz) δ 1.10–1.29, 1.61–1.88, 2m, 10H, cyclohexyl CH_2; 1.50, d, $J_{5,6}$ 6.2 Hz, 3H, H 6^A; 1.93, 1.98, 2.00, 2.01, 2.02, 2.10, 6s, Ac; 3.19–3.27, m, cyclohexyl CH; 3.42, dd, $J_{3,4}$ 11.7, $J_{4,5}$ 8.9 Hz, H 4^A; 3.45, s, OMe; 3.51, ddd, $J_{4,5}$ 9.8, $J_{5,6}$ 2.3, 4.6 Hz, H 5^C; 3.56, ddd, $J_{4,5}$ 9.8, $J_{5,6}$ 2.0, 4.8 Hz, H 5^B; 3.71, dd, $J_{3,4}$ 9.6 Hz, H 4^B; 3.82, dq, H 5^A; 3.84, dd, $J_{3,4}$ 9.5 Hz, H 4^C; 4.06, dd, $J_{6,6}$ 12.0 Hz, H 6^B; 4.09, dd, $J_{2,3}$ 10.2 Hz, H 3^A; 4.24, dd, $J_{6,6}$ 12.3 Hz, H 6^C; 4.30, dd, H 6^C; 4.35, d, $J_{1,2}$ 7.9 Hz, H 1^B; 4.46, d, $J_{1,2}$ 7.9 Hz, H 1^C; 4.52, dd, H 6^B; 4.73, d, $J_{1,2}$ 4.9 Hz, H 1^A; 4.79, dd, $J_{2,3}$ 9.4 Hz, H 2^C; 4.84, dd, $J_{2,3}$ 9.6 Hz, H 2^B; 5.11, dd, H 3^C; 5.13, dd, H 3^B; 5.20, dd, H 2^A; 7.44–7.50, 7.56–7.61, 8.02–8.05, 3m, Ph. ^{13}C n.m.r. (125.8 MHz) δ 20.50, 20.58, 20.69, 20.85, 20.92, 6C, CO**Me**; 21.44, C 6^A; 25.10, 25.74, 26.17, 29.72, 5C, cyclohexyl CH_2; 55.78, cyclohexyl CH; 56.96, OMe; 61.70, C 4^A; 61.74, C 6^B; 62.23, C 6^C; 71.49, C 2^B; 71.99, C 2^C; 72.38, C 3^B; 72.57, 72.62, C 5^B,5^C; 73.74, 73.78, C 2^A,3^C; 73.96, C 5^A; 75.94, C 4^C; 76.39, C4^B; 76.47, C3^A; 100.32, C 1^C; 101.35, C 1^B; 102.65, C1^A; 128.55, 128.60, 129.95, 133.71, Ph; 157.45, NCO; 164.88, **C**OPh; 169.45, 169.60, 169.78, 170.32, 170.39, 6C, **C**OMe.

2-O-*Benzoyl-1,6-epithio-4-[(1* R,*4* R,*5* S,*6* S*)-4,5,6-tribenzyloxy-3-(benzyloxymethyl)cyclohex-2-enyl]amino-1,4,6-trideoxy*-β-D-*glucose (32)*

(A) A solution of tetra-*O*-benzyl-1-epivalienamine (6)[15] (2.74 g, 5.11 mmol) and the epoxide (4) (1.64 g, 10.2 mmol) in BuOH (8 ml) was heated at 100° for 2.5 days. The solvent was evaporated with the aid of toluene and the residue purified by flash chromatography (50–10% petrol/$CHCl_3$ plus 1% Et_3N) to give the impure amino diol (31) as a black oil (2.69 g).

(B) Benzoyl chloride (530 μl) was added to a solution of some of the above amino diol (31) (1.96 g), pyridine (690 μl) and 4-(dimethylamino)pyridine (35 mg) in CH_2Cl_2 (50 ml) at –30°. The solution was allowed to warm to 0°, at which stage t.l.c. indicated the presence of unreacted starting material. The solution was cooled again (–20°) and more benzoyl chloride (100 μl) was added. The solution was allowed to warm to 0°, whereupon t.l.c indicated the absence of the starting material. EtOH (1 ml) was added and the solution was stirred for 5 min. The solution was diluted with CH_2Cl_2 and washed with water, then dried and the solvent evaporated. The dark brown residue was purified by flash chromatography (50–75% $CHCl_3$/petrol plus 1% Et_3N) to afford a solid residue which was crystallized to yield the *amino alcohol* (32) as pale brown needles (891 mg, 30% over the two steps), m.p. 139–140° (CH_2Cl_2/Pr^i_2O), $[\alpha]_D$ –56.6° (Found: C, 72.0; H, 6.3. $C_{48}H_{49}NO_8S$ requires C, 72.1; H, 6.2%). ^{1}H n.m.r. (500 MHz) δ 2.82, dd, $J_{3,4}$ 4.6, $J_{4,5}$ 1.7 Hz, H 4; 2.99, d, $J_{6,6}$ 9.8 Hz, H 6; 3.07, dd, $J_{5,6}$ 6.3 Hz, H 6; 3.40, d, $J_{3,OH}$ 6.4 Hz, OH; 3.46, $J_{1',6'}$ 9.2 Hz, H 1′; 3.54, $J_{5',6'}$ 9.9 Hz, H 6′; 3.72–3.76, m, H 3; 3.77, br d, $J_{7',7'}$ 11.9 Hz, H 7′; 3.89, dd, $J_{4',5'}$ 7.7 Hz, H 5′; 4.19, br d, H 7′; 4.35, br d, H 4′; 4.42–5.03, m, 8H, C**H**$_2$Ph; 4.80–4.83, m, H 5; 4.96–4.98, m, H 2; 5.59, br s, H 2′; 5.61, br s, H 1; 7.25–7.38, 7.50–7.55, 8.01–8.04, 3m, Ph. ^{13}C n.m.r. (125.8 MHz) δ 36.08, C 6; 57.11, C 1′; 58.99, C 4; 70.09, C 7′; 70.16, C 3; 72.44, 74.60, 75.24, 75.41, 4C, CH_2Ph; 77.25, C 2; 80.07, C 4′; 80.96, C 5; 82.05, C 1; 83.37, C 6′; 85.00, C 5′; 127.64, C 2′; 127.66–138.36, C 3′, Ph; 165.75, CO.

2-O-*Benzoyl-3,4*-O,N-*carbonyl-1,6-epithio-4-[(1* R,*4* R,*5* S,*6* S*)-4,5,6-tribenzyloxy-3-(benzyloxymethyl)cyclohex-2-enyl]amino-1,4,6-trideoxy*-β-D-*glucose (35)*

Triphosgene (213 mg, 0.717 mmol) was added to a solution of the amino alcohol (32) (1.15 mg, 1.44 mmol) and pyridine (350 μl, 4.3 mmol) in dry CH_2Cl_2 (20 ml) at –78° under N_2. The mixture was allowed to warm to 0°, water (0.5 ml) was added and the mixture was stirred for 10 min. The mixture was diluted with CH_2Cl_2 and then washed with water. The organic layer was dried and the solvent evaporated to leave an oil which was purified by flash chromatography (10–30% EtOAc/petrol) to afford the *carbamate* (35) as a colourless foam (895 mg, 75%), $[\alpha]_D$ –70.2° (Found: C, 71.1; H, 5.7. $C_{49}H_{47}NO_9S$ requires C, 71.2; H, 5.7%). ν_{max} (NaCl) 1769, 1721 cm^{-1}. ^{1}H n.m.r. (500 MHz) δ 2.74, d, $J_{6,6}$ 9.4 Hz, H 6; 2.92, dd, $J_{5,6}$ 4.1 Hz, H 6; 3.25–3.35, m, H 4; 3.90–3.96, m, H 5′,6′; 3.95, br d, $J_{7',7'}$ 12.5 Hz, H 7′; 4.13, br t, $J_{2,3} \approx J_{3,4}$ 9.3 Hz, H 3; 4.19, br d, H 7′; 4.30–4.35, m, H 4′; 4.46–5.01, m, 8H, C**H**$_2$Ph; 4.90, br d, H 2; 5.02, t, $J_{4,5} \approx J_{5,6}$ 4.1 Hz, H 5; 5.40, s, H 1; 5.67, br s, H 2′; 7.25–7.53, 7.61–7.66, 8.09–8.13, 3m, Ph. The signal for H 1′ could not be located. ^{13}C n.m.r. (125.8 MHz) δ 39.35, C 6; 57.06, C 1′; 58.47, C 4; 69.36, C 7′; 72.29, 74.58, 74.81, 75.26, 4C, **C**H_2Ph; 73.10, C 3; 77.58, C 5; 77.83, C 2; 79.03, C 4′; 84.01, C 1; 77.25, 84.22, C 5′,6′; 123.04, C 2′; 127–138.97, C 3′, Ph; 157.67, NCO; 165.74, **C**OPh. High-resolution mass spectrum (f.a.b.) *m/z* 826.3059 [$C_{49}H_{48}NO_9S$ $(M+H)^{+\bullet}$ requires 826.3050].

2-O-*Benzoyl-1,6-episeleno-4-[(1* R,*4* R,*5* S,*6* S*)-4,5,6-tribenzyloxy-3-(benzyloxymethyl)cyclohex-2-enyl]amino-1,4,6-trideoxy*-β-D-*glucose (33)*

(A) A solution of tetra-*O*-benzyl-1-epivalienamine (6)[15] (6.17 g, 11.5 mmol) and the epoxide (5) (4.77 g, 23.0 mmol) in BuOH (25 ml) was heated at 100° for 2.5 days. The solvent was evaporated and the residue purified by flash chromatography (20–10% petrol/$CHCl_3$ plus 1% Et_3N) to give the impure amino diol (34) as a black oil (5.00 g).

(B) A solution of some of the above amino diol (34) (1.98 g), pyridine (1.11 ml) and 4-(dimethylamino)pyridine (32 mg) in CH_2Cl_2 (40 ml) was treated with benzoyl chloride (430 μl, –40 to –5°). At this stage t.l.c. indicated the presence of unreacted starting material. The solution was treated with more benzoyl chloride (100 μl, –30 to –5°), whereupon t.l.c indicated the absence of the starting material. The reaction mixture was quenched and subjected to a workup as for (31) above. The dark brown residue after workup was purified by flash chromatography (25–40% $CHCl_3$/petrol plus 1% Et_3N) to afford the *amino alcohol* (33) as a light brown oil (1.58 g, 41% over the two steps). Crystallization of a portion of this oil yielded a microcrystalline powder, m.p. 123–129° (CH_2Cl_2/Pr^i_2O), $[\alpha]_D$ –69.3° (Found: C, 68.0; H, 5.8. $C_{48}H_{49}NO_8Se$ requires C, 68.1; H, 5.8%). ^{1}H n.m.r. (500 MHz) δ 2.79, dd, $J_{3,4}$ 2.6, $J_{4,5}$ 6.5 Hz, H 4; 3.07, d, $J_{6,6}$ 9.2 Hz, H 6; 3.13, dd, $J_{5,6}$ 5.9 Hz, H 6; 3.45, br d, $J_{1',6'}$ 8.5 Hz, H 1′; 3.52, dd, $J_{5',6'}$ 9.9 Hz, H 6′; 3.65, br m, H 3; 3.81, br d, $J_{7',7'}$ 11.8 Hz, H 7′; 3.90, dd, $J_{4',5'}$ 7.7 Hz, H 5′; 4.20, br d, H 7′; 4.35, br d, H 4′; 4.43–5.02, m, 8H, C**H**$_2$Ph; 4.86–4.88, m, H 5; 5.08, dd, $J_{1,2}$ 0.8, $J_{2,3}$ 4.6 Hz, H 2; 5.62, br s, H 2′; 5.92, s, H 1; 7.26–7.43, 7.53–7.57, 8.03–8.06, 3m, Ph. ^{13}C n.m.r.

(125.8 MHz) δ 33.44, C 6; 57.03, C 1′; 59.14, C 4; 69.91, C 3; 70.14, C 7′; 72.53, 74.62, 75.26, 75.37, 4C, **C**H_2Ph; 77.95, C 1; 79.33, C 2; 80.04, C 4′; 82.83, C 6′; 82.96, C 5; 84.98, C 5′; 126.17, C 2′; 127.68–129.77, 133.39, 138.20, 138.36, C 3′, Ph; 166.06, CO.

2-O-*Benzoyl-3,4*-O,N-*carbonyl-1,6-episeleno-4-[(1* R,*4* R,*5* S,*6* S)*-4,5,6-tribenzyloxy-3-(benzyloxymethyl)-cyclohex-2-enyl]amino-1,4,6-trideoxy*-β-D-*glucose (36)*

The amino alcohol (33) (847 mg) was treated in the same manner as for the amino alcohol (32) to give, after flash chromatography (5–30% EtOAc/petrol), the *carbamate* (36) as a clear glass (726 mg, 83%), $[\alpha]_D$ –65.4° (Found: C, 67.2; H, 5.5. $C_{49}H_{47}NO_9Se$ requires C, 67.4; H, 5.4%). ν_{max} (NaCl) 1770, 1719 cm^{-1}. ^{1}H n.m.r. (500 MHz) δ 2.97, d, $J_{6,6}$ 9.1 Hz, H 6; 3.05, dd, $J_{5,6}$ 4.3 Hz, H 6; 3.90–4.00, m, H 5′,6′; 3.98, br d, $J_{7',7'}$ 12.6 Hz, H 7′; 4.11, br t, $J_{2,3} \approx J_{3,4}$ 10.3 Hz, H 3; 4.18, br d, H 7′; 4.31–4.35, m, H 4′; 4.33, m, H 4; 4.46–4.98, m, 8H, C**H**$_2$Ph; 4.49–4.64, m, H 1′; 5.04, t, $J_{4,5}$ 4.3 Hz, H 5; 5.04–5.08, m, H 2; 5.66, br s, H 2′; 5.76, s, H 1; 7.26–7.65, 8.08–8.11, 2m, Ph. ^{13}C n.m.r. (125.8 MHz) δ 35.89, C 6; 57.21, 59.17, C 4,1′; 69.37, C 7′; 72.28, 74.87, 75.30, 4C, **C**H_2Ph; 72.88, C 3; 77.56, 84.28, C 5′,6′; 122.81, C 2′; 127.60–129.88, 133.72, 137.74–139.04, Ph; 157.65, NCO; 165.87, **C**OPh.

Attempted Glycosylation of the Alcohol (28) with the Carbamate (36)

A solution of *N*-iodosuccinimide (105 mg, 468 μmol) and TfOH (20 μl) in dry Et_2O/1,2-dichloroethane (1 : 1, 4 ml) at 0° was added to a solution of the carbamate (36) (350 mg, 400 μmol) and the alcohol (28) (300 mg, 334 μmol) in dry 1,2-dichloroethane (3 ml) at 0°. The solution immediately went dark brown and was left at room temperature for 20 min. The solution was then quenched with saturated aqueous $NaHCO_3$ (1 ml) and aqueous $Na_2S_2O_3$ (0.5 M, 2 ml), the organic layer was separated, dried and the solvent evaporated. The crude residue was dissolved in dry toluene (5 ml) and treated with Bu_3SnH (800 μl, 3.0 mmol) and α,α′-azobisisobutyronitrile (1 mg) at reflux for 2 h. The solvent was evaporated and the residue partitioned between MeCN and petrol. The MeCN layer was separated and evaporated and the residue subjected to flash chromatography (7–9% EtOAc/petrol). The residue after flash chromatography was taken up in pyridine/acetic anhydride (1 : 1, 2 ml) and left to stand for 2 h. The solvent was evaporated to give an oil which was purified by flash chromatography (7–9% EtOAc/petrol) to give a clear oil (96 mg). Partial ^{1}H n.m.r. (500 MHz): δ 5.41, 5.48, 5.52, 5.54, 4 br s. Partial ^{13}C n.m.r. (125.8 MHz): δ 18.77, 19.03, 19.23, 20.48, 20.55, 21.41, 22.08, Me; 100.11, 100.63, 102.14, 102.25, 104.55, 104.58, 100.92, 101.38, CH.

Attempted Glycosylation of (40) with (15) Using Phenylselenenyl Triflate

(A) A mixture of powdered 4 Å molecular sieves (0.5 g) and silver triflate (77 mg, 0.30 mmol) in dry 1,2-dichloroethane (3 ml) was stirred at 0° under N_2 for 10 min. Phenylselenenyl chloride (58 mg, 0.30 mmol) was added and the mixture was stirred for a further 5 min.

(B) A solution of the tribenzoate (15) (129 mg, 0.24 mmol) and the alcohol (40) (52 mg, 0.20 mmol) in dry 1,2-dichloroethane (3 ml) at 0° was added to the solution generated in (A) under N_2. Stirring was continued for 5 min, at which stage t.l.c. indicated that no tribenzoate remained. Saturated $NaHCO_3$ solution (1 ml) was added and the mixture was stirred for 30 min. The mixture was filtered through Celite (EtOAc) and the organic phase was washed with water, then dried and the solvent evaporated. The residue was purified by flash chromatography to afford a yellow oil (84 mg), shown to contain two spectroscopically similar products. Partial ^{1}H n.m.r. (200 MHz): δ 1.20, 1.28, 1.43, 3s, 12H, Me; 4.88, d, $J_{1,2}$ 8.2 Hz, H 1; 4.94, d, $J_{1,2}$ 8.2 Hz, H 1.

Attempted Glycosylation of the Alcohol (28) with the Carbamate (35)

A solution of *N*-iodosuccinimide (63 mg, 280 μmol) and TfOH (10 μl) in dry Et_2O/1,2-dichloroethane (1 : 1, 4 ml) at 0° was added to a solution of the carbamate (35) (198 mg, 240 μmol) and the alcohol (28) (179 mg, 200 μmol) in dry 1,2-dichloroethane (3 ml) at 0°. T.l.c. indicated no change after 5 min, so additional TfOH (10 μl) was added and the solution left at room temperature for 1 h. After this time, substantial degradation had occurred to give poorly defined material (t.l.c.), in addition to some residual starting materials. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 ml) and aqueous $Na_2S_2O_3$ (0.5 M, 1 ml), the organic layer was separated, dried and the solvent evaporated. The residue was subjected to flash chromatography, resulting in the recovery of some starting material (^{1}H n.m.r.).

Attempts at Protecting Group Manipulation of the 1,6-Episeleno Carbamate (36)

(A) Trimethylsilyl chloride (17 μl, 137 μmol) was added to a solution of sodium iodide (21 mg, 137 μmol) and the carbamate (36) (20 mg, 23 μmol) in dry MeCN (1.5 ml) and the resultant solution was stirred for 2 h at room temperature under N_2, then heated under reflux for 5 h. T.l.c. indicated that a complex mixture containing a considerable amount of starting material was present and the reaction was abandoned.

(B) A mixture of anhydrous $FeCl_3$ (59 mg, 370 μmol) and the carbamate (36) (20 mg, 23 μmol) in dry CH_2Cl_2 was stirred at 0° for 1 h and then at room temperature for 2 h whilst under N_2. Water (0.1 ml) was added and the mixture was stirred for 5 min. Pyridine (3 ml), acetic anhydride (2 ml) and 4-(dimethylamino)pyridine (2 mg) were added and the mixture was stirred for 10 min. The reaction mixture was subjected to the usual workup (EtOAc) to afford a light orange residue, shown to consist of a complex mixture of products (t.l.c.).

(C) Trimethylsilyl triflate (80 μl) was added to a solution of the carbamate (36) (21 mg) in acetic anhydride (1 ml) and the reaction mixture allowed to stand at 15° for 5 h. Aqueous sodium carbonate (2 M, 1 ml) was added to the reaction mixture, followed by the usual workup (EtOAc). Flash chromatography of the residue after evaporation of the solvent afforded a major fraction (10 mg) which was shown to be a complex mixture (^{1}H n.m.r.).

(D) The carbamate (36) (40 mg) was dissolved in acetic anhydride (1 ml) and iodine (20 mg) was added. The reaction mixture was allowed to stand overnight under N_2. MeOH (1 ml) was added and the mixture was allowed to stand at room temperature for 10 min. Workup (EtOAc) afforded a light brown oil which was shown to be a complex mixture (^{1}H n.m.r.).

(E) Butyllithium (860 μl of 1.4 M in pentane, 1.2 mmol) was added slowly to a solution of ethanethiol (88 μl, 1.2 mmol) in tetrahydrofuran (1 ml) at room temperature. A white precipitate formed and the solvent was evaporated under a stream of N_2. The off-white solid was dissolved in dry dimethylformamide (1 ml) and the carbamate (36) (44 mg, 50 μmol) was added. The solution was heated at 100° for 2 h, then the solution was cooled and subjected to a workup (EtOAc) to provide a black oil. T.l.c. showed this oil to contain u.v.-active material.

Treatment of the 1,6-Episeleno Monobenzoate (33) with Tributylstannane

A solution of the monobenzoate (33) (64 mg, 74 μmol), tributylstannane (120 μl, 450 μmol) and α,α′-azobisisobutyronitrile in toluene (3 ml) was heated at reflux for 30 min under N_2. More tributylstannane (50 μl, 160 μmol) was added and the solution was heated under reflux for 30 min and then additional tributylstannane (50 μl, 160 μmol) was added and reflux continued (30 min). The solvent was evaporated and the residue was partitioned between MeCN and petrol. The MeCN layer was evaporated to give a residue which was purified by flash chromatography (10–30% EtOAc/petrol plus 1% Et_3N) to afford a clear oil (11 mg). Partial ^{1}H n.m.r. (200 MHz): δ 5.64, br s, 1H; 5.81, s, 1H.

Treatment of the Carbamate (35) with Sodium Metal in Liquid Ammonia: N-*[(1* R,*4* R,*5* S,*6* S)*-4,5,6-Triacetoxy-3-(acetoxymethyl)cyclohex-2-enyl]acetamide (45)*

A small piece of sodium metal was added to a solution of the carbamate (35) (100 mg, 121 μmol) in dry tetrahydrofuran/MeOH (4 ml, 1 : 1) and the mixture allowed to stand for 1 h. The solvent was evaporated and the residue was dried under high vacuum for 2 h. Lithium metal (50 mg, 8 mmol) was dissolved in NH_3 (25 ml) at –78° and a solution of the above residue in dry tetrahydrofuran (4 ml) was added dropwise to the ammoniacal solution. The blue mixture was stirred at –78° for 2 h, then NH_4Cl (100 mg) was added and the ammonia allowed to

evaporate. The residue was treated with pyridine (4 ml), Ac_2O (4 ml) and 4-(dimethylamino)pyridine (50 mg) overnight at room temperature. The solvent was evaporated and the residue was partitioned between water and EtOAc. The organic layer was separated and washed with water and brine and then dried. The solvent was evaporated and the residue purified by flash chromatography (40–100% EtOAc/petrol) to afford, first, a mixture of the thioacetate (43) and the disulfide (44) as an oil (13 mg). Partial ^{1}H n.m.r. (200 MHz): δ 2.35, s, SAc; 2.80–2.96, m, CH_2S; 3.31, dd, $J_{1,1}$ 12.3, $J_{1,2}$ 8.6 Hz, H 1; 4.24, dd, $J_{1,2}$ 5.8 Hz, H 1; 5.93, br s, H 2′.

Next to elute was the amide (45) as a pale yellow oil (24 mg, 51%) which crystallized as shards, m.p. 137–140° (EtOH/Pr^i_2O), $[\alpha]_D$ –108.9°. ^{1}H n.m.r. (500 MHz) δ 1.96, s, NH**Ac**; 2.02, 2.05, 2.05, 2.05, 4s, 12H, OAc; 4.37, br d, $J_{7,7}$ 13.0 Hz, H 7; 4.66, br d, H 7; 4.85, br t, $J_{1,6} \approx J_{1,NH}$ 8.1 Hz, H 1; 5.10, dd, $J_{5,6}$ 10.8 Hz, H 6; 5.36, dd, $J_{4,5}$ 8.1 Hz, H 5; 5.71–5.78, m, H 2,4, NH. ^{13}C n.m.r. (125.8 MHz) δ 20.60, 20.62, 20.69, 20.72, 4C, OCO**Me**; 23.21, NHCO**Me**; 50.40, C 1; 62.66, C 7; 70.25, 71.23, 72.14, C 4,5,6; 128.60, C 2; 132.20, C 3; 169.79, 169.96, 170.16, 170.37, 4C, OC=O; 171.23, NHC=O.

References

[1] McAuliffe, J. C., and Stick, R. V., *Aust. J. Chem.*, 1997, **50**, 225.
[2] Truscheit, E., Frommer, W., Junge, B., Müller, L., Schmidt, D. D., and Wingender, W., *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 744.
[3] Schmidt, D. D., Frommer, W., Junge, B., Müller, L., Wingender, W., Truscheit, E., and Schäfer, D., *Naturwissenschaften*, 1977, **64**, 535.
[4] Puls, W., Keup, U., Krause, H. P., Thomas, G., and Hoffmeister, F., *Naturwissenschaften*, 1977, **64**, 536.
[5] McAuliffe, J., and Hindsgaul, O., *Chem. Ind.*, 1997, 170.
[6] Stick, R. V., *Top. Curr. Chem.*, 1997, **187**, 187.
[7] Driguez, H., McAuliffe, J. C., Stick, R. V., Tilbrook, D. M. G., and Williams, S. J., *Aust. J. Chem.*, 1996, **49**, 343.
[8] Fürst, A., and Plattner, Pl. A., *Helv. Chim. Acta*, 1949, **32**, 275.
[9] Klayman, D. L., and Griffin, T. S., *J. Am. Chem. Soc.*, 1973, **95**, 197.
[10] Payne, G. B., *J. Org. Chem.*, 1962, **27**, 3819.
[11] Köll, P., Tayman, F. S., and Heyns, K., *Chem. Ber.*, 1979, **112**, 2305.
[12] Stick, R. V., Tilbrook, D. M. G., and Williams, S. J., *Tetrahedron Lett.*, 1997, **38**, 2741.
[13] McAuliffe, J. C., Skelton, B. W., Stick, R. V., and White, A. H., *Aust. J. Chem.*, 1997, **50**, 209.
[14] Bracher, F., and Litz, T., *J. Prakt. Chem.*, 1995, **337**, 516.
[15] Nicotra, F., Panza, L., Ronchetti, F., and Russo, G., *Gazz. Chim. Ital.*, 1989, **119**, 577.
[16] McAuliffe, J. C., and Stick, R. V., *Aust. J. Chem.*, 1997, **50**, 193.
[17] McAuliffe, J. C., and Stick, R. V., *Aust. J. Chem.*, 1997, **50**, 219.
[18] Knapp, S., Naughton, A. B. J., and Dhar, T. G. M., *Tetrahedron Lett.*, 1992, **33**, 1025.
[19] Stick, R. V., Tilbrook, D. M. G., and Williams, S. J., *Aust. J. Chem.*, 1999, **52**, 895.
[20] Ito, Y., and Ogawa, T., *Tetrahedron Lett.*, 1988, **29**, 1061.
[21] Ito, Y., Ogawa, T., Numata, M., and Sugimoto, M., *Carbohydr. Res.*, 1990, **202**, 165.
[22] Olah, G. A., Narang, S. C., Gupta, B. G. B., and Malhotra, R., *J. Org. Chem.*, 1979, **44**, 1247.
[23] Debenham, J. S., Rodebaugh, R., and Fraser-Reid, B., *J. Org. Chem.*, 1997, **62**, 4591.
[24] Alzeer, J., and Vasella, A., *Helv. Chim. Acta*, 1995, **78**, 177.
[25] Kartha, K. P. R., and Field, R. A., *Tetrahedron*, 1997, **53**, 11753.
[26] Feutrill, G. I., and Mirrington, R. N., *Aust. J. Chem.*, 1972, **25**, 1719.
[27] Stick, R. V., Tilbrook, D. M. G., and Williams, S. J., *Aust. J. Chem.*, 1997, **50**, 237.
[28] Fraser-Reid, B., Udodong, U. E., Wu, Z., Ottosson, H., Merritt, J. R., Rao, C. S., Roberts, C., and Madsen, R., *Synlett*, 1992, 927.
[29] Rodebaugh, R., and Fraser-Reid, B., *J. Am. Chem. Soc.*, 1994, **116**, 3155.
[30] Toyokuni, T., Ogawa, S., and Suami, T., *Bull. Chem. Soc. Jpn*, 1983, **56**, 1161.
[31] Ogawa, S., Miyamoto, Y., and Nakajima, A., *Chem. Lett.*, 1989, 725.
[32] Takeo, K., Fukatsu, T., and Yasato, T., *Carbohydr. Res.*, 1982, **107**, 71.