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Carbohydrate Research 337 (2002) 2069–2076

CARBOHYDRATE RESEARCH

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Synthesis of glycosides of 3-deoxy-4-thiopentopyranosid-2-uloses and their reduction products: 3-deoxy-4-thiopentopyranosides

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Received 1 April 2002; accepted 22 May 2002

Dedicated to Professor Derek Horton on the occasion of his 70th birthday

Abstract

Michael addition of common thiols to the enone system of (2*S*)-2-benzyloxy-2*H*-pyran-3(6*H*)-one (**1**) afforded the corresponding 3-deoxy-4-thiopentopyranosid-2-ulose derivatives (**2**–**4**). The reaction was highly diastereoselective, and the addition was governed by the quasiaxially disposed 2-benzyloxy substituent of the starting pyranone. As expected from the enantiomeric excess of **1** (ee $>86\%$) the corresponding thiouloses **2**–**4** exhibited the same optical purity. However, the enantiomerically pure thioulose **5** was obtained by reaction of **1** with the chiral thiol, *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester. The thio derivative **7** was also synthesized by reaction of **6** (enantiomer of **1**) with the same chiral thiol. Alternatively, 4-thiopent-2-uloses **9**–**12** were prepared in high optical purity by 1,4-addition of thiols to (2*S*)-[(*S*)-2′-octyloxy]dihydropyranone **8**. Similarly, reaction of **13** (enantiomer of **8**) with benzenemethanethiol afforded **14** (enantiomer of **10**). This way, the stereocontrol exerted by the anomeric center on the starting dihydropyranone led to 4-thiopentuloses of the D and L series. Sodium borohydride reduction of the carbonyl function of uloses **10** and **12** gave the corresponding 3-deoxy-4-thiopentopyranosid-2-uloses (**16**–**19**). The diastereomers having the β-D-*threo* configuration (**16**, **18**) slightly predominated over the β-D-*erythro* (**17**, **19**) analogues. However, the reduction of the enantiomeric pyranones **10** and **14** with K-Selectride® was highly diastereofacial selective in favor of the β-D- and β-L-*threo* isomers **16** and **20**, respectively.

Keywords: Michael addition; Thio sugars; 3-Deoxy-4-thiopentopyranosid-2-uloses; 3-Deoxy-4-thiopentopyranosides

1. Introduction

Thio sugars are gaining attention as potential therapeutics. The new developments, specially in the synthetic and medicinal chemistry of thio sugars, are important for carbohydrate drug design.[1] The older synthetic routes to target thio sugars are complex and low-yielding approaches with questionable stereoselectivity. More recently the conjugated addition of thiols to sugar enones has been employed as a direct and diastereoselective approach to prepare sulfur-containing carbohydrates.[2–8] This reaction has been used for the synthesis of (1→4)-linked 4-thiodisaccharides, as enzymatically non-cleavable analogues of the naturally occurring disaccharides, which act as competitive inhibitors.[8,9] Similarly, (1→2)-2-*S*-thiodisaccarides have been prepared.[10] On the other hand, the products of the coupling of thiols to enuloses showed to be suitable precursors of annelated pyranosides.[5,11] The synthetic usefulness of these Michael additions are limited by the accessibility to the starting sugar enone. For preparative-scale reactions, such versatile building blocks should be prepared in a few, high-yielding steps. In this regard, we have described a convenient one-pot procedure for the synthesis of sugar enones from 2-acetoxyglycal derivatives, readily obtained from common hexoses[12] or pentoses.[13] The resulting enulose derivatives have been employed as chiral templates for the synthesis of modified glycosides,[14] ketonucleosides,[15] and diamino tetradeoxy sugars component of antibi-

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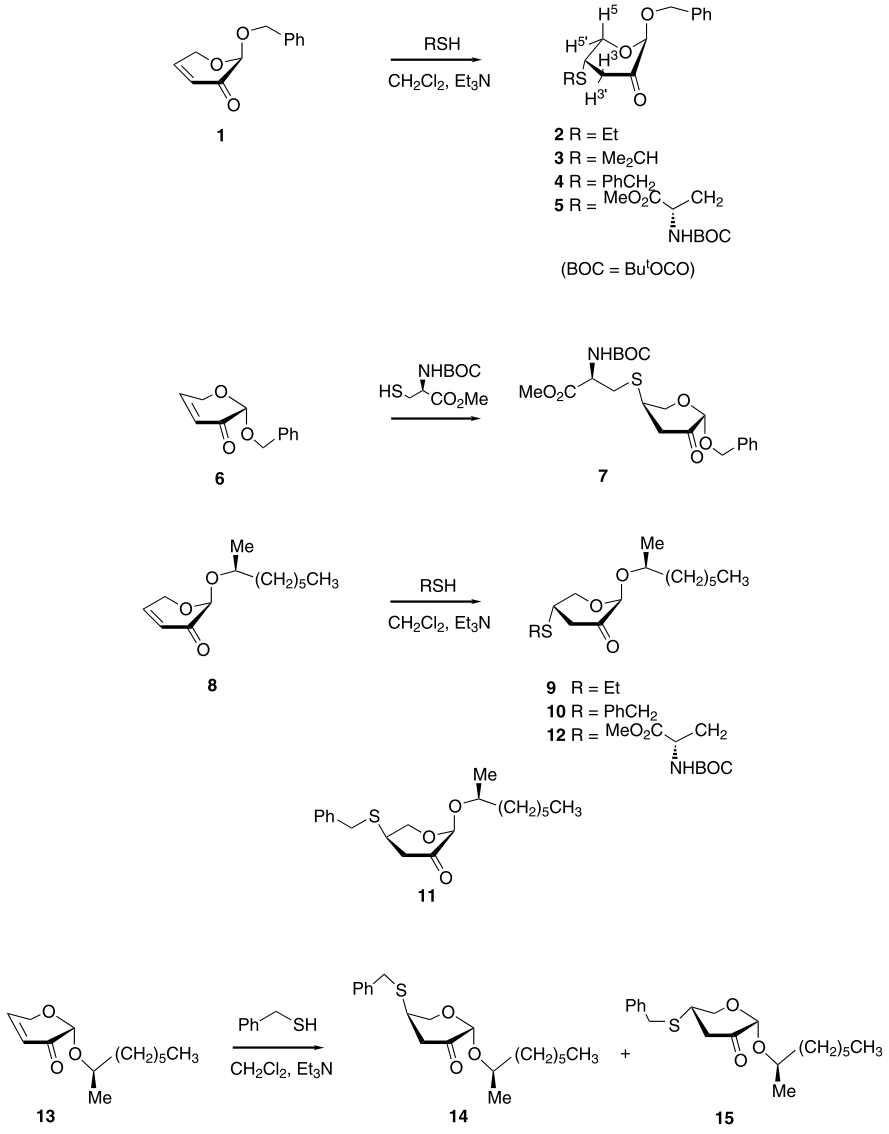
0008-6215/02/$ - see front matter
PII: S0008-6215(02)00292-6

otics.[16,17] More recently, we have studied Diels–Alder cycloadditions[13] and conjugated Michael additions[18] to enuloses. As continuation of such studies, we report here the 1,4-addition of thiols to a number of glycosides of 3,4-dideoxypent-3-enopyranosid-2-uloses having opposite configurations at the anomeric center, to determine the level of stereocontrol exerted by this stereocenter on that generated at C-4. This procedure would constitute a direct and stereoselective route of access to 4-thiopentopyranosy-2-uloses, and hence to 4-thiopentopyranosides, of both the D and L series.

2. Results and discussion

Michael additions were studied using the readily accessible (2*S*)-2-benzyloxy-2*H*-pyran-3-(6*H*)-one (**1**), which was prepared in one step by the tin(IV) chloride-promoted glycosylation and rearrangement of 2-acetoxy-3,4-di-*O*-acetyl-D-xylal.[13] In the presence of catalytic amounts of triethylamine, the α,β-unsaturated carbonyl system of **1** acts as reactive Michael acceptor for the addition of such thiols as ethanethiol, 2-propanethiol, and benzenemethanethiol, to afford the corresponding 4-thiopentopyranosid-2-ulose derivatives **2**–**4** (Scheme 1). As the starting compound **1** exhibited an enantiomeric excess higher than 86% (ee $>86\%$), the conjugated addition products **2**–**4** had the same optical purity, as verified in further experiments (see below).

The configuration of the new stereocenter at C-4 in compounds **2**–**4** was determined as *S*, on the basis of their ^{1}H NMR spectra. Indeed, the small values for the proton–proton coupling constants (*J*) between H-4



Scheme 1.

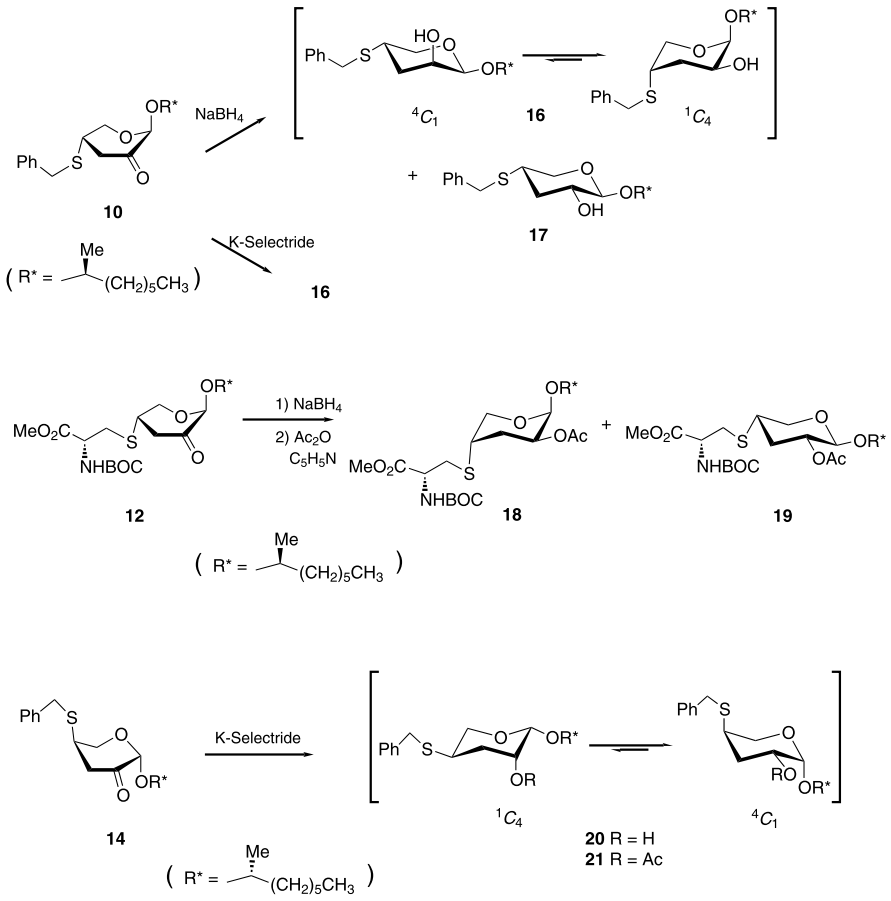
with H-3,3′ and with H-5,5′ indicated an equatorial disposition for H-4. Furthermore, the long-range coupling constant $J_{3',5'}$ (1.8 Hz) confirmed a quasi-equatorial relationship for H-3′ and H-5′ and an axial orientation for the new substituent at C-4. A similar coupling has been observed in related systems having the same relative configuration as **2**–**4**.[8,18] Examination of the ^{1}H NMR spectra of the crude reaction mixtures of preparation of **2**–**4** revealed a negligible formation of the diastereomer having an opposite configuration at C-4. In one instance, such an isomer could be isolated in a very low yield, as described later. The high diastereofacial selectivity in the addition of thiols to enone **1** is governed by the steric bulk of the axially oriented anomeric substituent, in the preferred ^0E conformation. Such a conformation in **1**, as well as in structurally related enones[18] and enolones,[19] is stabilized by the anomeric effect, probably intensified by the vicinal carbonyl group.[13,19]

The exclusive anti-addition mode of the thiols, in respect to the anomeric substituent of **1**, led us to consider the synthesis of 3-deoxy-4-thioulose derivatives in enantiomerically pure form. For this purpose, we conducted the addition of the chiral thiol *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester to **1**. The ^{1}H NMR spectrum of the resulting product revealed, as expected, the formation of a diastereomeric mixture (**5**, **7**), as the signals of H-3 and H-5 of **5** showed small shoulders. Also, the ^{13}C NMR spectrum exhibited small satellites accompanying the resonances of C-3, C-5 and the OMe group of **5** (ratio > 13:1). The signals of lower intensity were attributed to the diastereomer **7**, the product of addition of the chiral thiol to the enantiomeric enone that contaminates **1**. To confirm its structure, compound **7** was synthesized by addition of the chiral thiol employed previously, to the dihydropyranone **6**, the enantiomer of **1**. Compound **6** was prepared by the tin(IV) chloride-promoted glycosylation of 2-acetoxy-3,4-di-*O*-acetyl-L-arabinal with benzyl alcohol (Iriarte Capaccio, C.; Varela, O. unpublished results). The more intense peaks in the NMR spectra of the addition product **7** exactly overlapped with the minor ones present in the crude mixture of preparation of **5**. This way the identity of both diastereomers (**5** and **7**) was conclusively demonstrated. Their ratio in the respective crude mixtures of reaction was in agreement with the optical purity measured for the starting enones (**1** and **6**) using chiral lanthanide shift reagents.[13] Furthermore, compounds **5** and **7** could be isolated as enantiomerically pure adducts (de > 95%) by column chromatography. Therefore, the Michael addition was useful for the synthesis of optically pure thio sugar derivatives, having opposite configuration for the ring stereocenters, even when the starting enones **1** and **6** were not absolutely enantiomerically pure.

An alternative route developed for the synthesis of optically pure glycosides of 3-deoxy-4-thiopentopyranosid-2-uloses was based on the Michael addition of thiols to (2*S*)-[(*S*)-2′-octyloxy]pyranone (**8**), readily prepared by the Lewis acid-promoted reaction of (*S*)-2-octanol with 2-acetoxy-3,4-di-*O*-acetyl-D-xylal.[13] The use of a chiral alcohol for the glycosylation of this glycal derivative led to **8** in a high diastereomeric excess (de > 86%), which can be even increased by careful chromatographic purification of **8**. The addition of ethanethiol, benzenemethanethiol, and *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester to **8** (de > 86%) afforded the respective enantiomerically pure adducts **9**, **10** and **12** highly enriched in the major diastereomer (de 94–97%) after isolation by column chromatography. Similar to the addition of thiols to **1**, the reaction with the analogous pyranone **8** was also highly diastereofacial selective. However, the selectivity was strongly influenced by the temperature; at higher temperatures the reaction was faster but in turn, the selectivity was somewhat lower. For example, only traces of the diastereomer **11** were detected by NMR spectroscopy when the addition of benzenemethanethiol to pure **8** (de > 96%) was conducted at 0–5 °C. The same reaction performed at a higher temperature (40–45 °C) showed by NMR spectroscopy a higher proportion of **11** (~ 8%). This diastereomer arises from the attack of the thiol from the sterically hindered β-face of the enone (syn-addition). In general the syn-addition products were slightly less polar than the major anti-addition products; in particular, **10** and **11** showed a good chromatographic separation that facilitated the isolation of **11**. Its structure was confirmed on the basis of its ^{1}H NMR spectrum, which showed large values for the coupling constants of H-4 with H-3 and H-5, in accordance with their trans-diaxial disposition. Again, the long-range coupling between H-3′ and H-5′ indicated a quasiequatorial relationship for those coupled protons. These data were consistent with an equatorial orientation of the sulfur substituent al C-4.

To obtain a 4-thio-2-ulose derivative of the L series, the addition of benzenemethanethiol was applied to the dihidropyranone **13** (enantiomer of **8**) to give the β-L-*glycero* product **14** (major) and the isomer **15**. The NMR spectra of **14** and **15** were respectively identical to those of **10** and **11**, as expected for enantiomeric products.

Reduction of the carbonyl group of the 3-deoxy-4-thiopentopyranosid-2-uloses will lead to the corresponding 3-deoxy-4-thioglycoside derivatives. Thus, sodium borohydride reduction of **10** gave two products, which exhibited quite different mobilities by TLC. The ^{1}H NMR spectrum of the mixture showed, in the anomeric region, two signals at δ 4.63 ($J_{1,2}$ 2.4 Hz) and 4.24 ($J_{1,2}$ 7.0 Hz), which corresponded, respectively, to the β-D-*threo* (**16**) and β-D-*erythro* (**17**) epimers (1.6:1



Scheme 2.

ratio). The mixture could be readily separated by column chromatography to afford the optically pure 3-deoxy-4-thioglycosides **16** and **17** (Scheme 2). The coupling constants data from the ^{1}H NMR spectrum of **16** showed time-averaged values indicative of a substantial contribution of the $^1C_4$ form in the conformational equilibrium. For example, the values of $J_{3',4}$ (7.6 Hz) and $J_{4,5'}$ (6.5 Hz) were smaller than those expected for the trans-diaxial disposition of such coupled protons in the $^4C_1$ conformer. Derivatives of β-D-*arabino* and β-D-*lyxo*-pentopyranoses, which bear the same configuration for the C-1, C-2 and C-4 stereocenters as **16**, showed also an appreciable proportion of the $^1C_4$ form in the conformational equilibrium.[20,21] In contrast, as observed for analogous pentopyranosides,[20,21] compound **17** adopts preferentially the $^4C_1$ conformation, according to the coupling constant values.

As found for **10**, sodium borohydride reduction of the carbonyl function of **12** led to an epimeric mixture of the 3-deoxy-4-thioglycosides having the β-D-*threo* and β-D-*erythro* configuration (1.5:1 ratio, established by NMR). Due to the difficulty of the chromatographic separation of the components of this mixture, they were directly acetylated under standard conditions. The acetyl derivatives **18** and **19** were readily isolated by column chromatography. Compound **18** exhibited in its ^{1}H NMR spectrum J values indicative of an even stronger preference for the $^1C_4$ conformation, compared with that of **16**. Furthermore, the long-range coupling between H-3′ and H-5′ was consistent with the diequatorial disposition of such protons found in the $^1C_4$ conformer. This conformation is stabilized by the anomeric effect as well as by the lack of 1,3-diaxial interations between the substituents of the ring.

The selectivity observed for the reduction of pyranones **10** and **12** was rather poor, in contrast with the high anomeric stereocontrol reported for the hydride-addition to a carbonyl group vicinal to the anomeric center in enones[14] and enolones.[22] However, compounds **10** and **12** possess in addition a quasiaxially oriented thiobenzyl or thioalkyl group at C-4; hence both faces of the ketone are hindered, resulting in a lower selectivity. The reduction of the carbonyl function of a 4-thiohexopyranone, analogous to **10** and **12**, with a reducing agent having bulky substituents (L-Selectride®) showed to be highly diastereoselective.[8] Therefore, the reduction of the carbonyl group of **10** was conducted with K-Selectride® at low temperature. The reaction proceeded highly stereoselectively with formation of the D-*threo* isomer **16**, which was isolated

in 79% yield. Only traces of the epimer **17** were detected by ^{1}H NMR spectroscopy of the crude mixture. The reduction of **10** seems to be governed by the steric hindrance of the vicinal anomeric substituent rather than by the thiobenzyl group at C-4. Reduction of the pyranone **14** (the enantiomer of **10**) with K-Selectride led, as expected, to the 3-deoxy-4-thiopentopyranoside **20** (enantiomer of **16**) having the β-L-*threo* configuration. For comparative purposes, compound **20** was conventionally acetylated to afford the 2-*O*-acetyl derivative **21**. Diagnostic coupling constants ($J_{2,3}$, $J_{3',4}$, $J_{4,5'}$ and $J_{3',5'}$) from its ^{1}H NMR spectrum indicated a strong preference of **21** (similar to **18**) for the conformer having the substituents at C-1 and C-4 in an axial disposition.

The configurational assignments for the 3-deoxy-4-thiopentopyranosides **16**–**19** were confirmed on the basis of their ^{13}C NMR spectra. Thus, compounds **17** and **19** having the β-D-*erythro* configuration showed the signals of C-1 and C-2 shifted downfield with respect to the same signals of the β-D-*threo* isomers **16** and **18**. These results showed an excellent correlation with the respective analogous methyl 3-deoxypentopyranosides,[23,24] except fot the shifting of the C-4 signal which was shielded because of the replacement of an oxygen by a sulfur-containing substituent.

3. Experimental

General methods.—Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on Silica Gel 60 F_{254} (E. Merck) aluminum-supported plates (layer thickness 0.2 mm). Visualization of the spots was effected by exposure to UV light or by charring with a solution of 5% (v/v) sulfuric acid in EtOH, containing 0.5% *p*-anisaldehyde. Column chromatography was carried out with Silica Gel 60 (230–400 mesh, E. Merck). Optical rotations were measured with a Perkin–Elmer 343 digital polarimeter at 25 °C, for solutions in $CHCl_3$. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AC 200 or, when indicated, with a Bruker AMX 500 instrument, in $CDCl_3$ solutions using tetramethylsilane as an internal standard. The signals from the ^{13}C NMR spectra were assigned by DEPT experiments. Elemental analyses were performed at UMYMFOR-CONICET-University of Buenos Aires. Fast-atom bombardment mass spectra (FABMS) were conducted by LANAIS–EMAR (Buenos Aires, Argentina) using a ZAB-VSEQ mass spectrometer, Cs^+ gun accelerated at 35 eV. Glycerol was employed as matrix and as the standard for calibration.

General procedure for the synthesis of the 3-deoxy-4-thiopentopyranosid-2-ulose glycosides **2**–**5**, **7**, **9**–**12**, **14**, *and* **15**.—To a solution of the 2*H*-pyran-3-(6*H*)-one derivative[13] (**1**, **6**, **8**, or **13**, 1.0 mmol) in dry CH_2Cl_2 (2.0 mL) were added the thiol (1.5 mmol) and a catalytic amount of Et_3N (4 μL). After purging with nitrogen the vial was sealed, and the solution was stirred at 0–5 °C. When TLC monitoring of the reaction mixture revealed complete consumption of the starting material (5–10 h), the solution was concentrated. The residue was purified by column chromatography using the solvent indicated in each individual case. Representative chromatographic fractions obtained in the purification of Michael adducts prepared from **8** or **13** (having de $>86\%$) were monitored by NMR to establish the diastereomeric composition. The purer fractions were collected.

*Benzyl 3-deoxy-4-*S*-ethyl-4-thio-β-*D*-glycero-pentopyranosid-2-ulose* (**2**).—Addition of ethanethiol to **1** (R_f 0.32, 5:1 hexane–EtOAc) afforded, after chromatography with 12:1 hexane–EtOAc, compound **2** (60% yield, ee $>86\%$): R_f 0.36, 5:1 hexane–EtOAc; $[\alpha]_D$ −130.7° (*c* 1.0); ^{1}H NMR: δ 7.36 (bs, 5 H, Ph), 4.82, 4.64 (2 d, 2 H, *J* 11.7 Hz, PhCH_2), 4.79 (bs, 1 H, H-1), 4.44 (dd, 1 H, $J_{4,5}$ 2.9, $J_{5,5'}$ 12.0 Hz, H-5), 3.76 (ddd, 1 H, $J_{3',5'}$ 1.8, $J_{4,5'}$ 3.3 Hz, H-5′), 3.48 (m, 1 H, H-4), 3.15 (dd, 1 H, $J_{3,4}$ 5.1, $J_{3,3'}$ 15.4 Hz, H-3), 2.58 (m, 3 H, H-3′, CH_3CH_2S), 1.27 (t, 3 H, CH_3CH_2S); ^{13}C NMR: δ 199.7 (C-2), 136.6, 128.6, 128.2, 128.1 (Ph), 98.5 (C-1), 70.0 (PhCH_2), 63.0 (C-5), 42.5 (C-4), 41.9 (C-3), 25.0 (CH_3CH_2S), 14.6 (CH_3CH_2S). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81; S, 12.04. Found: C, 63.19; H, 7.04; S, 11.74.

*Benzyl 3-deoxy-4-*S*-(2-propyl)-4-thio-β-*D*-glycero-pentopyranosid-2-ulose* (**3**).—Addition of 2-propanethiol to **1** gave, after chromatographic purification with 12:1 hexane–EtOAc, compound **3** (50% yield, ee $>86\%$); R_f 0.39, 5:1 hexane–EtOAc; $[\alpha]_D$ −118.3° (*c* 1.0); ^{1}H NMR: δ 7.37 (bs, 5 H, Ph), 4.83, 4.64 (2 d, 2 H, *J* 11.7 Hz, PhCH_2), 4.77 (bs, 1 H, H-1), 4.43 (dd, 1 H, $J_{4,5}$ 2.9, $J_{5,5'}$ 12.0 Hz, H-5), 3.74 (ddd, 1 H, $J_{3',5'}$ 1.8, $J_{4,5'}$ 3.6 Hz, H-5′), 3.50 (m, 1 H, H-4), 3.14 (dd, 1 H, $J_{3,4}$ 5.1, $J_{3,3'}$ 15.3 Hz, H-3), 3.00 (m, 1 H, *J* 6.6 Hz, Me_2CHS), 2.56 (ddd, $J_{3',4}$ 4.0 Hz, H-3′), 1.30 (d, 6 H, $(CH_3)_2CHS$); ^{13}C NMR: δ 199.6 (C-2), 136.6, 128.5, 128.1 (Ph), 98.5 (C-1), 70.0 (PhCH_2), 63.5 (C-5), 42.3 (C-3), 41.4 (C-4), 34.3 (Me_2CHS), 23.5, 23.4 ($(CH_3)_2C$). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H 7.19; S, 11.43. Found: C, 64.40; H 7.22; S, 11.76.

*Benzyl 4-*S*-benzyl-3-deoxy-4-thio-β-*D*-glycero-pentopyranosid-2-ulose* (**4**).—Addition of benzenemethanethiol to **1**, followed by chromatographic purification with 15:1 hexane–EtOAc, afforded **4** (86% yield, ee $>86\%$): R_f 0.39, 5:1 hexane–EtOAc; $[\alpha]_D$ −96.4° (*c* 1.0); ^{1}H NMR: δ 7.35, 7.32 (2 bs, 10 H, 2 Ph), 4.81, 4.62 (2 d, 2 H, *J* 11.7 Hz, PhCH_2O), 4.78 (bs,

1 H, H-1), 4.36 (dd, 1 H, $J_{4,5}$ 2.9, $J_{5,5'}$ 12.0 Hz, H-5), 3.82, 3.74 (2 d, 2 H, J 13.6 Hz, PhCH_2S), 3.70 (ddd, 1 H, $J_{3',5'}$ 1.8, $J_{4,5'}$ 3.1 Hz, H-5′), 3.29 (m, 1 H, H-4), 3.08 (dd 1 H, $J_{3,4}$ 5.1, $J_{3,3'}$ 15.0 Hz, H-3), 2.56 (ddd, 1 H, $J_{3',4}$ 2.9 Hz, H-3′); ^{13}C NMR: δ 199.6 (C-2), 137.5, 136.6, 128.8, 128.7, 128.6, 128.2, 127.3 (2 Ph), 98.5 (C-1), 70.0 (PhCH$_2$O), 62.9 (C-5), 42.1, 41.6 (C-3,4), 35.3 (PhCH$_2$S). Anal. Calcd for $C_{19}H_{20}O_3S$: C, 66.49; H, 6.14; S, 9.76. Found: C, 69.50; H, 6.12; S, 9.44.

*Benzyl 3-deoxy-4-*S*-(methyl* N*-(*tert*-*butoxycarbonyl)*-*L*-*cysteinat-3-yl)-4-thio-β-*D*-glycero-*pentopyranosid-2-ulose* (**5**).—The crude mixture of reaction of **1** with *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester (0.35 g, 1.5 mmol) was examined by NMR spectroscopy, indicating a 15:1 ratio of **5** and its diastereomer **7**, which was synthesized independently (see below). Chromatographic purification of the mixture (5:1 hexane–EtOAc) afforded **5** (76% yield): R_f 0.27 (2.5:1 hexane–EtOAc). Crystallized from hexane compound **5** (de >95%) gave mp 95 °C; $[\alpha]_D$ −82.2° (*c* 0.9); ^{1}H NMR (500 MHz): δ 7.33 (m, 5 H, Ph), 5.33 (bs, 1 H, NH), 4.79, 4.61 (2 d, 2 H, J 11.7 Hz, PhCH_2O), 4.73 (bs, 1 H, H-1), 4.53 (m, 1 H, NCHCO$_2$), 4.40 (dd, 1 H, $J_{4,5}$ 2.6, $J_{5,5'}$ 12.2 Hz, H-5), 3.76 (s, 3 H, OCH_3), 3.72 (m, 1 H, $J_{3,5'} \sim J_{4,5'}$ 2.5 Hz, H-5′), 3.50 (bs, 1 H, H-4), 3.13 (dd, 1 H, $J_{3,4}$ 5.2, $J_{3,3'}$ 15.3 Hz, H-3), 3.03 (dd, 1 H, ^3J 5.0, ^2J 13.4 Hz, CCH_aH$_b$S), 2.95 (dd, 1 H, ^3J 5.0 Hz, CCH$_a$$H_b$S), 2.54 (bd, 1 H, $J_{3',4}$ 1.1 Hz, H-3′), 1.45 (s, 9 H, (CH_3)$_3$C); ^{13}C NMR: δ 199.1 (C-2), 171.1 (CO$_2$Me), 155.1 (NCO$_2$), 136.4, 128.5, 128.1 (Ph), 98.3 (C-1), 80.3 (Me$_3$$C$O), 69.9 (Ph$CH_2$O), 62.1 (C-5), 53.2 (N$CHCO_2$), 52.6 (CO$_2$$CH_3$), 43.4 (C-4), 41.6 (C-3), 33.2 (CH$_2$S), 28.2 ((CH$_3$)$_3$C). Anal. Calcd for $C_{21}H_{29}NO_7S$: C, 57.39; H, 6.65; S, 7.29. Found: C, 57.51; H, 6.92; S, 7.56.

*Benzyl 3-deoxy-4-*S*-(methyl* N*-(*tert*-*butoxycarbonyl)*-*L*-*cysteinat-3-yl)-4-thio-β-*L*-glycero-*pentopyranosid-2-ulose* (**7**).—Addition of *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester (1.5 mmol) to **6** afforded **7**, which was purified as described for **5**. Compound **7** (86% yield, de >95%): R_f 0.28 (2.5:1 hexane–EtOAc); mp 86 °C; $[\alpha]_D$ +98.6° (*c* 0.9); ^{1}H NMR (500 MHz): δ 7.33 (m, 5 H, Ph), 5.33 (bs, 1 H, NH), 4.79, 4.61 (2 d, 2 H, J 11.7 Hz, PhCH_2O), 4.73 (s, 1 H, H-1), 4.53 (bs, 1 H, NCHCO$_2$), 4.42 (dd, 1 H, $J_{4,5}$ 2.6, $J_{5,5'}$ 12.2 Hz, H-5), 3.76 (s, 3 H, OCH_3), 3.72 (ddd, 1 H, $J_{3,5'} \sim J_{4,5'}$ 2.5 Hz, H-5′), 3.50 (bs, 1 H, H-4), 3.12 (dd, 1 H, $J_{3,4}$ 5.0, $J_{3,3'}$ 15.3 Hz, H-3), 3.03 (dd, 1 H, ^3J 4.0, ^2J 13.9 Hz, CCH_aH$_b$S), 2.93 (dd, 1 H, ^3J 5.6 Hz, CCH$_a$$H_b$S), 2.56 (bd, 1 H, $J_{3'4}$ 1.1 Hz, H-3′), 1.45 (s, 9 H, (CH_3)$_3$C); ^{13}C NMR: δ 199.1 (C-2), 171.1 (CO$_2$Me), 155.1 (NCO$_2$), 136.4, 128.5, 128.1 (Ph), 98.3 (C-1), 80.3 (Me$_3$$C$O), 69.9 (Ph$CH_2$O), 62.4 (C-5), 53.1 (N$CHCO_2$), 52.7 (CO$_2$$CH_3$), 43.4 (C-4), 41.4 (C-3), 33.2 (CH$_2$S), 28.2 ((CH$_3$)$_3$C). Anal. Calcd for $C_{21}H_{29}NO_7S.0.5\ H_2O$: C, 56.23; H, 6.74; S, 7.15. Found: C, 56.12; H, 6.74; S, 7.09.

*(S)-2-Octyl 3-deoxy-4-*S*-ethyl-4-thio-β-*D*-glycero-pentopyranosid-2-ulose* (**9**).—Chromatographic purification (40:1 hexane–EtOAc) of the reaction mixture of addition of ethanethiol to **8** (de >86%; R_f 0.46, 6:1 hexane–EtOAc) afforded **9** (59% yield; de >95%): R_f 0.49 (6:1 hexane–EtOAc), $[\alpha]_D$ −110.4° (*c* 1.0); ^{1}H NMR: δ 4.73 (bs, 1 H, H-1), 4.44 (dd, 1 H, $J_{4,5}$ 2.9, $J_{5,5'}$ 12.1 Hz, H-5), 3.77 (m, 1 H, J 6.2 Hz, HCO octyl), 3.70 (ddd, 1 H, $J_{3',5'}$ 2.2, $J_{4,5'}$ 3.3 Hz, H-5′), 3.45 (m, 1 H, H-4), 3.10 (dd, 1 H, $J_{3,4}$ 5.1, $J_{3,3'}$ 15.0 Hz, H-3), 2.57 (q, 2 H, J 7.3 Hz, MeCH_2S), 2.50 (ddd, 1 H, $J_{3',4}$ 4.2 Hz, H-3′), 1.63–1.22 (m, 16 H, CH_3CH$_2$S, 5 CH_2 octyl, CH_3-1 octyl), 0.87 (t, 3 H, J 6.4 Hz, CH_3-8 octyl); ^{13}C NMR: δ 199.8 (C-2), 99.1 (C-1), 76.4 (HCO octyl), 62.7 (C-5), 42.6 (C-4), 41.7 (C-3), 36.4, 31.8, 29.3, 25.2, 24.9, 22.6 (MeCH$_2$S, 5 CH$_2$ octyl), 21.3 (CH$_3$-1 octyl), 14.6, 14.1 (CH$_3$-8 octyl, CH$_3$CH$_2$S). Anal. Calcd for $C_{15}H_{28}NO_3S$: C, 62.46; H, 9.78; S, 11.12. Found: C, 62.88; H, 9.90; S, 11.44.

*(S)-2-Octyl 4-*S*-benzyl-3-deoxy-4-thio-β-*D*-glycero-pentopyranosid-2-ulose* (**10**) *and its α-*L*-glycero analogue* (**11**).—The reaction of **8** (de >96%) with benzenemethanethiol was conducted at ~40 °C for 6 h. Monitoring by TLC showed a faint spot (R_f 0.58, 6:1 hexane–EtOAc) and another more intense (R_f 0.49). These two products were separated by column chromatography (40:1 hexane–EtOAc). The less polar compound was identified as **11** (4% yield, de >96%): $[\alpha]_D$ −115.6° (*c* 0.7); ^{1}H NMR: δ 7.31 (bs, 5 H, Ph), 4.63 (bs, 1 H, H-1), 3.96 (apparent t, 1 H, $J_{4,5} \approx J_{5,5'}$ 11.5 Hz, H-5), 3.77 (bs, 2 H, PhCH_2), 3.75 (m, 1 H, HCO octyl), 3.61 (ddd, 1 H, $J_{3',5'}$ 1.9, $J_{4,5'}$ 4.8 Hz, H-5′), 3.08 (dddd, 1 H, $J_{3,4}$ 13.4, $J_{3',4}$ 5.5 Hz, H-4), 2.70 (dd, 1 H, $J_{3,3'}$ 14.2 Hz, H-3), 2.58 (ddd, 1 H, H-3′), 1.63–1.20 (m, 10 H, 5 CH_2 octyl), 1.23 (d, 3 H, J 6.3 Hz, CH_3-1 octyl), 0.87 (t, 3 H, J 6.3 Hz, CH_3-8 octyl); ^{13}C NMR: δ 199.8 (C-2), 137.8, 128.8, 128.7, 127.5 (Ph), 98.4 (C-1), 76.4 (HCO octyl), 62.8 (C-5), 42.6 (C-4), 41.7 (C-3), 36.4, 35.5, 31.7, 29.3, 25.1, 22.6 (PhCH$_2$S, 5 CH$_2$ octyl), 21.3, 14.1 (2 CH$_3$ octyl).

Following fractions from the column afforded **10** (82% yield, de >95%): $[\alpha]_D$ −50.1° (*c* 1.0); ^{1}H NMR: δ 7.30 (bs, 5 H, Ph), 4.73 (bs, 1 H, H-1), 4.35 (dd, 1 H, $J_{4,5}$ 2.6, $J_{5,5'}$ 12.1 Hz, H-5), 3.75 (m, 3 H, PhCH_2S, HCO octyl), 3.64 (ddd, 1 H, $J_{3',5'}$ 2.2, $J_{4,5'}$ 2.9 Hz, H-5′), 3.25 (m, 1 H, H-4), 3.04 (dd, 1 H, $J_{3,4}$ 5.1, $J_{3,3'}$ 15.0 Hz, H-3), 2.49 (ddd, 1 H, $J_{3',4}$ 4.0 Hz, H-3′), 1.65–1.25 (m, 10 H, 5 CH_2 octyl), 1.22 (d, 3 H, J 6.6 Hz, CH_3-1 octyl), 0.87 (t, J 6.3 Hz, CH_3-8 octyl); ^{13}C NMR: δ 199.7 (C-2), 137.6, 128.8, 128.7, 127.3 (Ph), 99.1 (C-1), 76.3 (HCO octyl), 62.6 (C-5), 42.1 (C-4), 41.3 (C-3), 36.4, 35.3, 31.8, 29.3, 25.2, 22.6 (PhCH$_2$, 5 CH$_2$ octyl), 21.3, 14.1 (2 CH$_3$ octyl). Anal. Calcd for $C_{20}H_{30}O_3S$: C, 68.53; H, 8.63; S, 9.15. Found: C, 68.46; H, 8.85; S, 9.43.

(S)-2-Octyl 3-deoxy-4-S-(methyl N-(tert-butoxycarbonyl)-L-cysteinat-3-yl)-4-thio-β-D-glycero-pentopyranosid-2-ulose (**12**).—Reaction of *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester with **8** (de >86%) afforded, after column chromatography with 7.5:1 hexane–EtOAc, the 4-thio derivative **12** (90% yield, de >94%): R_f 0.56 (2.5:1 hexane–EtOAc); $[\alpha]_D$ −39.3° (*c* 0.9); ^{1}H NMR: δ 5.36 (bd, 1 H, *J* 7.0 Hz, N*H*), 4.72 (bs, 1 H, H-1), 4.53 (m, 1 H, NC*H*CO_2), 4.44 (dd, 1 H, $J_{4,5}$ 2.6, $J_{5,5'}$ 12.1 Hz, H-5), 3.79 (m, 1 H, *H*CO octyl), 3.77 (s, 3 H, CO_2CH_3), 3.69 (dt, 1 H, $J_{3',5'} \approx J_{4,5'}$ 2.5 Hz, H-5′), 3.49 (s, 1 H, H-4), 3.12 (dd, 1 H, $J_{3,4}$ 5.1, $J_{3,3'}$ 15.4 Hz, H-3), 2.99 (t, 2 H, *J* 5.5 Hz, CH_2S), 2.51 (bd, 1 H, H-3′), 1.63–1.25 (m, 10 H, 5 CH_2 octyl), 1.45 (s, 9 H, $(CH_3)_3$C), 1.22 (d, 3 H, *J* 6.2 Hz, CH_3-1 octyl), 0.87 (t, 3 H, *J* 6.6 Hz, CH_3-8 octyl); ^{13}C NMR: δ 199.3 (C-2), 171.2 (CO_2Me), 155.0 (N*C*O_2), 99.0 (C-1), 80.3 (Me_3CO), 61.9 (C-5), 53.2 (N*C*HCO_2), 52.6 (CO_2CH_3), 43.6 (C-4), 41.4 (C-3), 36.3, 33.1, 31.7, 29.2, 25.1, 22.5 (*C*H_2S, 5 *C*H_2 octyl), 28.2 ($(CH_3)_3$C), 19.2, 14.0 (2 *C*H_3 octyl). Anal. Calcd for $C_{22}H_{39}NO_7S{\cdot}H_2O$: C, 55.09; H, 8.61; S, 6.68. Found: C, 55.18; H, 8.78; S, 6.49.

(R)-2-Octyl 4-S-benzyl-3-deoxy-4-thio-β-L-glycero-pentopyranosid-2-ulose (**14**) *and its α-D-glycero analogue* (**15**).—The conditions described for the synthesis of **10** and **11** from **8** were applied for the preparation of **14** and **15**, starting from **13** (enantiomer of **8**). Column chromatography of the reaction mixture gave compound **15** (3% yield, de >95%): $[\alpha]_D$ +111.4° (*c* 0.9); ^{1}H and ^{13}C NMR spectra were identical to those of its enantiomer **11**.

From further fractions from the column was isolated the more polar diastereomer **14** (90% yield, de >94%): $[\alpha]_D$ +49.3 (*c* 1.2); ^{1}H and ^{13}C NMR spectra were identical to the enantiomer **10**.

(S)-2-Octyl 4-S-benzyl-3-deoxy-4-thio-β-D-threo- (**16**) *and β-D-erythro-pentopyranoside* (**17**)

(a) Sodium borohydride reduction of **10**. To a solution of thioulose **10** (0.10 g, 0.29 mmol) in MeOH (3 mL) was added $NaBH_4$ (11 mg, 0.29 mmol). The mixture was stirred at room temperature for 20 min. The solution was neutralized with Dowex 50W (H^+) resin, filtered and concentrated. The residue was dissolved in MeOH, and the solvent was evaporated in order to remove boric acid. The procedure was repeated three times to afford a syrup that showed two spots by TLC (5:1 hexane–EtOAc) having R_f 0.53 and 0.47. The ^{1}H NMR spectrum of the crude mixture was recorded in order to establish the ratio of products. Purification by column chromatography (15:1 hexane–EtOAc) afforded first the less polar isomer, which was identified as **16** (50 mg, 50% yield, de >98%): mp 52 °C; $[\alpha]_D$ −86.2° (*c* 0.9); ^{1}HNMR (500 MHz): δ 7.30 (bs, 5 H, Ph), 4.63 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1), 3.95 (dd, 1 H, $J_{4,5}$ 3.3, $J_{5,5'}$ 11.7 Hz, H-5), 3.87 (m, 1 H, H-2), 3.74 (m, 3 H, PhCH_2, *H*CO octyl), 3.34 (dd, 1 H, $J_{4,5'}$ 6.5, $J_{5,5'}$ 11.7 Hz, H-5′), 3.02 (dddd, 1 H, $J_{3,4}$ 4.3, $J_{3',4}$ 7.6 Hz, H-4), 2.10 (ddd, 1 H, $J_{2,3}$ 7.4, $J_{3,3'}$ 13.1 Hz, H-3), 1.77 (ddd, 1 H, $J_{2,3'}$ 4.0, H-3′), 1.62–1.26 (m, 10 H, 5 CH_2 octyl), 1.20 (d, 3 H, *J* 6.2 Hz, CH_3-1 octyl), 0.88 (t, 3 H, *J* 6.3 Hz, CH_3-8 octyl); ^{13}C NMR: δ 138.1, 128.7, 128.5 127.1 (Ph), 98.6 (C-1), 75.2 (H*C*O octyl), 65.9 (C-2), 65.7 (C-5), 38.0 (C-4), 36.4, 35.6, 33.9, 31.8, 29.3, 25.3, 22.5 (C-3, PhCH_2S, 5 *C*H_2 octyl), 21.3, 14.0 (2 *C*H_3 octyl). Anal. Calcd for $C_{20}H_{32}O_3S$: C, 68.14; H, 9.15; S, 9.09. Found: C, 67.85; H, 9.10; S, 9.05.

From the next fraction of the column was isolated **17** (30 mg, 30% yield, de >96%): mp 53 °C; $[\alpha]_D$ −70.0° (*c* 0.5); ^{1}H NMR: δ 7.30 (bs, 5 H, Ph), 4.24 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 3.94 (ddd, 1 H, $J_{3,5}$ 2.2, $J_{4,5}$ 4.4, $J_{5,5'}$ 11.3 Hz, H-5), 3.75 (s, 2 H, PhCH_2), 3.73 (m, 1 H, *J* 6.2 Hz, *H*CO octyl), 3.40 (ddd, 1 H, $J_{2,3}$ 4.6, $J_{2,3'}$ 10.2 Hz, H-2), 3.28 (dd, 1 H, $J_{4,5'}$ 9.9, H-5′), 2.77 (dddd, 1 H, $J_{3,4}$ 4.4, $J_{3',4}$ 11.3 Hz, H-4), 2.27 (dddd, 1 H, $J_{3,3'}$ 12.8 Hz, H-3), 1.65–1.27 (m, 10 H, 5 CH_2 octyl), 1.53 (ddd, 1 H, H-3′), 1.21 (d, 3 H, *J* 6.3 Hz, CH_3-1 octyl), 0.88 (t, 3 H, *J* 6.2 Hz, CH_3-8 octyl); ^{13}C NMR: δ 138.0, 128.7, 128.6, 127.2 (Ph), 104.0 (C-1), 76.2 (H*C*O octyl), 69.3 (C-2), 68.6 (C-5), 38.2 (C-4), 36.5, 35.3, 35.0, 31.7, 29.3, 25.4, 22.6 (C-3, PhCH_2S, 5 *C*H_2 octyl), 21.5, 14.0 (2 *C*H_3 octyl). Anal. Calcd for $C_{20}H_{32}O_3S$: C, 68.14; H, 9.15; S, 9.09. Found: C, 68.38; H, 9.31; S, 9.08.

(b) K-Selectride reduction of **10**.—To a solution of **10** (0.10 g, 0.29 mmol) in anhydrous THF (2 mL), cooled to −78 °C (CO_2–acetone bath), was added under nitrogen a 1 M solution of K-Selectride in THF (0.35 mL, 0.35 mmol). The mixture was stirred at −78 °C for 3 h, and then the temperature was rised to −20 °C, and the stirring was continued for 1 h. The solution was diluted with MeOH (5 mL) and neutralized with Dowex 50W (H^+) resin, filtered and concentrated. The residue was treated and purified as described in (a). Column chromatography afforded the pentopyranoside **16** (80 mg, 79% yield) which showed the same properties as those reported in (a).

(S)-2-Octyl 2-O-acetyl-3-deoxy-4-S-(methyl N-(tert-butoxycarbonyl)-L-cysteinat-3-yl)-4-thio-β-D-threo- (**18**) *and β-D-erythro-pentopyranoside* (**19**).—The sodium borohydride reduction of **12** (0.16 g, 0.35 mmol) was conducted as described for the reduction of **10** to give the mixture of **18** and **19** in a 1.5:1 ratio, according to the ^{1}H NMR spectrum of the crude product. The mixture was acetylated with 1:1 Ac_2O–pyridine for 16 h. After the usual workup, the resulting syrup was purified by column chromatography (9:1 hexane–EtOAc). The less polar isomer (R_f 0.58, 2.5:1 hexane–EtOAc) was identified as **18** (87 mg, 50% yield, de >95%); $[\alpha]_D$ −41.9° (*c* 0.8); ^{1}H NMR: δ 5.38 (bs, 1 H, N*H*), 5.09 (ddd, 1 H, $J_{1,2}$ 2.6, $J_{2,3}$ 9.5, $J_{2,3'}$ 4.0 Hz, H-2), 4.84 (d, 1 H, H-1), 4.52 (m, 1 H, NC*H*CO_2), 4.12 (dd, 1 H, $J_{4,5}$ 2.5, $J_{5,5'}$ 12.1 Hz, H-5), 3.76 (s, 3 H, OCH_3), 3.68 (m, 1 H, *J* 6.2 Hz, *H*CO octyl), 3.45 (ddd,

1 H, $J_{3',5'}$ 1.1, $J_{4,5'}$ 4.3 Hz, H-5′), 3.12 (m, 1 H, H-4), 2.99 (d, 2 H, J 5.2 Hz, SCH_2), 2.26 (ddd, 1 H, $J_{3,4}$ 4.3, $J_{3,3'}$ 13.5 Hz, H-3), 2.08 (s, 3 H, CH_3CO), 1.85 (ddd, 1 H, $J_{3',4}$ 4.8 Hz, H-3′), 1.75–1.26 (m, 10 H, 5 CH_2 octyl), 1.21 (d, 3 H, J 6.2 Hz, CH_3-1 octyl), 0.88 (t, 3 H, J 6.4 Hz, CH_3-8 octyl); ^{13}C NMR: δ 171.3, 170.2 (2 *C*O), 96.6 (C-1), 80.5 (Me$_3$*C*O), 75.6 (H*C*O octyl), 67.5 (C-2), 63.9 (C-5), 53.3 (N*C*HCO$_2$), 52.6 (CO$_2$*C*H$_3$), 40.7 (C-4), 36.5, 33.7, 31.8, 30.2, 29.3, 25.2, 22.6 (C-3, *C*H$_2$S, 5 *C*H$_2$ octyl), 28.2 ((*C*H$_3$)$_3$C), 21.3, 21.0 (*C*H$_3$CO, *C*H$_3$-1 octyl), 14.0 (*C*H$_3$-8 octyl). Anal. Calcd for $C_{24}H_{43}NO_8S$: C, 57.01; H, 8.57; S, 6.33. Found: C, 56.81; H, 8.70; S, 5.85.

The product having R_f 0.54 was isolated from further fractions from the column, and it was characterized as **19** (56 mg, 32% yield); $[\alpha]_D$ −19.2° (*c* 0.5); ^{1}H NMR: δ 5.34 (bs, 1 H, N*H*), 4.64 (ddd, 1 H, $J_{1,2}$ 6.9, $J_{2,3}$ 4.8, $J_{2,3'}$ 9.8 Hz, H-2), 4.53 (m, 1 H, NC*H*CO$_2$), 4.42 (d, 1 H, H-1), 4.03 (ddd, 1 H, $J_{3,5}$ 2.2, $J_{4,5}$ 4.0, $J_{5,5'}$ 11.7 Hz, H-5), 3.77 (s, 3 H, OCH_3), 3.70 (m, 1 H, J 6.2 Hz, *H*CO octyl), 3.29 (dd, 1 H, $J_{4,5'}$ 9.9 Hz, H-5′), 2.99 (t, 2 H, J 4.8 Hz, SCH$_2$), 2.90 (dddd, 1 H, $J_{3,4}$ 4.0, $J_{3',4}$ 9.9 Hz, H-4), 2.42 (dddd, 1 H, $J_{3,3'}$ 12.8 Hz, H-3), 2.05 (s, 3 H, CH_3CO), 1.64–1.24 (m, 11 H, H-3′, 5 CH_2 octyl), 1.20 (d, 3 H, J 6.2 Hz, CH_3-1 octyl), 0.88 (d, 3 H, J 6.3 Hz, CH_3-8 octyl); ^{13}C NMR: δ 171.1, 169.7 (2 *C*O), 101.6 (C-1), 80.6 (Me$_3$*C*O), 76.8 (H*C*O octyl), 70.0 (C-2), 68.3 (C-5), 53.4 (N*C*HCO$_2$), 52.7 (CO$_2$*C*H$_3$), 39.4 (C-4), 36.7, 34.2, 33.6, 31.9, 29.3, 25.1, 22.6 (C-3, *C*H$_2$S, 5 *C*H$_2$ octyl), 28.3 ((*C*H$_3$)$_3$C), 21.7, 21.0 (*C*H$_3$CO, *C*H$_3$-1 octyl), 14.1 (*C*H$_3$-8 octyl). Anal. Calcd for $C_{24}H_{43}NO_8S$: C, 57.01; H, 8.57; S, 6.33. Found: C, 56.69; H, 8.61; S, 5.91.

*(*R*)-2-Octyl 4-*S*-benzyl-3-deoxy-4-thio-β-*L*-threo-pentopyranoside* (**20**) *and its 2-*O*-acetyl derivative* (**21**).—Compound **14** (0.10 g, 0.29 mmol) was reduced with K-Selectride following the procedure described for **10**. Column chromatography in 15:1 hexane–EtOAc afforded **20** (80 mg, 79% yield, de >98%): mp 52 °C; $[\alpha]_D$ +85.8° (*c* 1.0); ^{1}H and ^{13}C NMR spectra were identical to those of the enantiomer **16**.

Conventional acetylation of **20** afforded the 2-*O*-acetyl derivative **21** in almost quantitative yield. Compound **21** gave $[\alpha]_D$ +58.8° (*c* 0.9); ^{1}H NMR: δ 7.31 (bs, 5 H, Ph), 5.10 (ddd, 1 H, $J_{1,2}$ 2.7, $J_{2,3}$ 9.0, $J_{2,3'}$ 3.8 Hz, H-2), 4.81 (d, 1 H, H-1), 4.04 (dd, 1 H, $J_{4,5}$ 3.3, $J_{5,5'}$ 11.9 Hz, H-5), 3.75 (s, 3 H, OCH_3), 3.68 (m, 1 H, J 6.4 Hz, *H*CO octyl), 3.40 (ddd, 1 H, $J_{3',5'}$ 0.9, $J_{4,5'}$ 4.9 Hz, H-5), 2.95 (m, 1 H, H-4), 2.20 (ddd, 1 H, $J_{3,4}$ 4.2, $J_{3,3'}$ 13.4 Hz, H-3), 2.06 (s, 3 H, CH_3CO), 1.81 (dddd, 1 H, $J_{3',4}$ 5.6 Hz, H-3′), 1.65–1.26 (m, 10 H, 5 CH_2 octyl), 1.19 (d, 3 H, J 6.4 Hz, CH_3-1 octyl), 0.87 (t, 3 H, J 6.3 Hz, CH_3-8 octyl); ^{13}C NMR: δ 170.4 (*C*O), 137.9, 128.8, 128.7, 127.0 (Ph), 96.8 (C-1), 75.5 (H*C*O octyl), 67.9 (C-2), 64.4 (C-5), 38.7 (C-4), 36.4, 35.5, 31.8, 30.2, 29.3, 25.1, 22.5 (C-3, *C*H$_2$S, 5 *C*H$_2$ octyl), 21.3, 21.0 (*C*H$_3$CO, *C*H$_3$-1 octyl), 14.0 (*C*H$_3$-8 octyl). FABMS: 395 ($M^+ + 1$).

Acknowledgements

Financial support from the University of Buenos Aires (Project X108) and from The National Research Council of República Argentina (CONICET) is gratefully acknowledged. O. V. is a Research Member of CONICET.

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