46. Synthesis of Methyl 2-Acetamido-4,6-di-*O*-acetyl-3-*S*-acetyl-2-deoxy-3-thio-α-D-mannopyranoside[1])

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Summary

Methyl 2-acetamido-4,6-di-*O*-acetyl-3-*S*-acetyl-2-deoxy-3-thio-α-D-mannopyranoside has been synthesized by conversion of methyl 2-amino-2-deoxy-4,6-*O*-benzylidene-α-D-altropyranoside into the corresponding 3-*O*-methanesulfonyl-2-*N*-[(methylthio)thiocarbonyl]derivative followed by intramolecular displacement of the 3-*O*-methanesulfonyloxy group with the (methylthio)thiocarbamoyl group.

For studies directed toward the synthesis of 6-thiosialic acid and related analogs, a 2-amino-2-deoxy-3-thio-D-mannose derivative was required as a precursor. Since the first described synthesis [2] was complex and gave the desired 3-thio-analog of 2-amino-2-deoxy-D-mannose in rather low overall yield (less than 17%), we developed an alternative approach, which is the subject of this communication. Enhanced interest in this area is noted since similar synthetic goals have been recently reported by other laboratories [3] [4].

The synthesis of 2-acetamido-2-deoxy-3-thio-D-mannose derivatives has been accomplished either by direct nucleophilic displacement with potassium thioacetate of the 3-*O*-trifluoromethanesulfonyloxy group of methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-trifluoromethanesulfonyl-α-D-altropyranoside [4], or by displacement of a 3-*O*-*p*-toluenesulfonyloxy group *via* neighboring-group participation of the thioureido group of methyl 4,6-*O*-benzylidene-2-deoxy-2-thioureido-3-*O*-*p*-toluenesulfonyl-α-D-altropyranoside [2], or of the thioacetamido group of methyl 4,6-*O*-benzylidene-2-deoxy-2-thioacetamido-3-*O*-*p*-toluenesulfonyl-α-D-altropyranoside [3].

The approach described herein is based on displacement of the 3-*O*-methanesulfonyloxy group of methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-2-*N*-[(methylthio)thiocarbonyl]-3-*O*-methanesulfonyl-α-D-altropyranoside **3** *via* neighboring-group participation of the thiocarbonyl group.

Methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (**1**), obtained by $NaBH_4$-reduction [5] of methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-altro-

[1]) Part VI. of neighboring-group participation in carbohydrate chemistry. For Part V see [1].

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[3]) Taken in part from the Ph.D. thesis of P.H.

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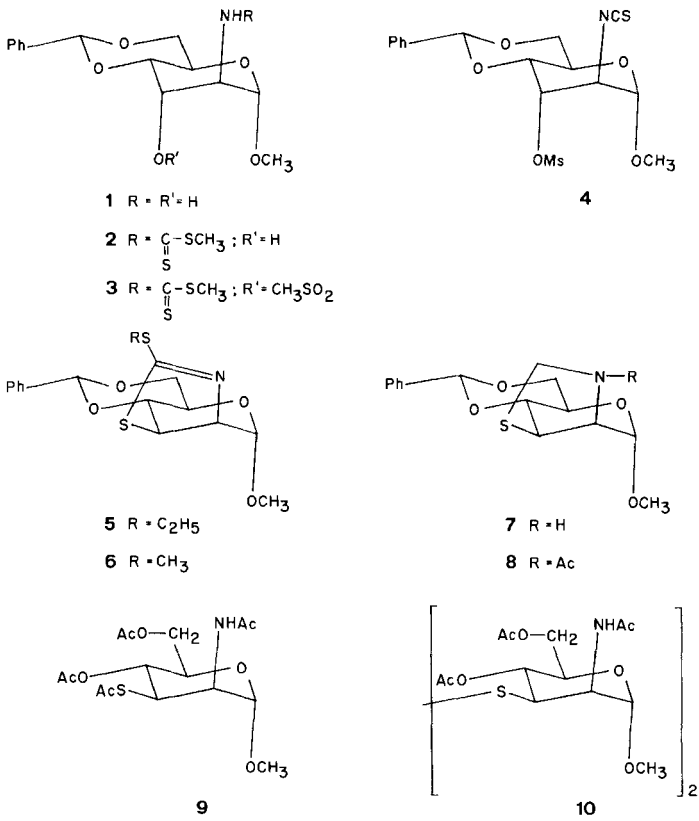

pyranoside [6] was converted in 89% yield into the methyl dithiocarbamate **2** by treating an anhydrous pyridine solution of **1** with equimolar amounts of CS_2 and $(C_2H_5)_3N$ at 0° (90 min), followed by methylation with CH_3I (14 h at 4°) [7].

Mesylation of **2** with CH_3SO_2Cl in anhydrous pyridine at room temperature afforded methyl 4,6-*O*-benzylidene-2-deoxy-2-isothiocyano-3-*O*-methanesulfonyl-*α*-D-altropyranoside (**4**) as the major product (66%), and methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-2-*N*-[(methylthio)thiocarbonyl]-3-*O*-methanesulfonyl-*α*-D-altropyranoside (**3**) as the minor product. The isothiocyano sugar **4** was fully characterized spectroscopically and also chemically by conversion into 4′,6′-*O*-benzylidene-1′-*O*-methyl-*α*-D-mannopyrano[2′,3′:4,5]-2-ethylthio-2-thiazoline (**5**) by refluxing **4** with ethanethiol in pyridine in 86% yield. Mesylation of **2** with methanesulfonyl chloride in pyridine[4]) at 0° (12 h), afforded the desired 3-*O*-methanesulfonyl-2-deoxy-2-*N*-[(methylthio)thiocarbonyl] derivative **3** as essentially the only product. The isolated crude product was dissolved in anhydrous pyridine and heated for 2½ h at 80° to form 4′,6′-*O*-benzylidene-1′-*O*-methyl-*α*-D-mannopyrano[2′,3′:4,5]-2-methylthio-2-thiazoline (**6**) in 71% yield (based on **2**).

[4]) It is very important not to add CH_3SO_2Cl in one portion, but slowly, over a period of 1 h, since otherwise the yield of **3** is decreased considerably.

Reduction of the 2-thiazoline **6** with freshly prepared Al-amalgam [8] in aqueous tetrahydrofuran gave 4′,6′ - *O* - benzylidene - 1′ - *O* - methyl - α - D - mannopyrano - [2′,3′: 4,5]-thiazolidine (**7**) which was directly acetylated with acetic anhydride (1 h at room temperature) into *N*-acetyl-4′,6′-*O*-benzylidene-1′-*O*-methyl-α-D-mannopyrano[2′,3′: 4,5]-thiazolidine (**8**) (81% overall yield.

Finally, the thiazolidine ring was opened in acetone/H_2O 97:3 by refluxing **8** for 16 h with a 1:1 $HgCl_2$/HgO mixture. The product without prior purification was dissolved in pyridine containing ethanethiol[5]) and acetylated with acetic anhydride (16 h at room temperature) to give methyl 2-acetamido-4,6-di-*O*-acetyl-3-*S*-acetyl-2-deoxy-3-thio-α-D-mannopyranoside (**9**) in 84% yield.

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Experimental Part

General. The silica gel used for all column chromatography was *E. Merck* (Darmstadt, W. Germany) silica gel 60, particle size less than 0.063 mm. The melting points (m.p.) are uncorrected. Optical rotation were determined with a *Cary 60* spectropolarimeter using a 1.0-cm cell. The IR. spectra were recorded in $CHCl_3$ with a *Perkin-Elmer* infrared spectrophotometer, Model 267 (λ_{max}, cm^{-1}). ^{1}H-NMR. spectra were recorded in $CDCl_3$ with a *Brucker* HX-360[6]) and a *Varian* T-60 spectrometer using tetramethylsilane (TMS.) as the internal standard. Chemical shifts (δ) are expressed in parts per million (ppm).

*Preparation of methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-2-*N*-[(methylthio)thiocarbonyl]-α-*D*-altropyranoside* (**2**). To a stirred cold (0°) solution of *methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-*D*-altropyranoside* (**1**) [5] (300 mg; 1.01 mmol) in dry pyridine (5 ml), $(C_2H_5)_3N$ (0.14 ml; 1.01 mmol) and CS_2 (0.07 ml; 1.16 mmol) were added. After keeping the reaction mixture at 0° for 90 min, CH_3I (0.075 ml; 1.20 mmol) was added and the reaction was continued at 4° for another 14 h. The pyridine solution was then poured into ice-water and the aq. phase was extracted with $CHCl_3$. The combined $CHCl_3$-extract was successively washed with ice-cold H_2SO_4/H_2O 1:99-sat. aq. $NaHCO_3$-solution and with water. After drying over anhydrous $MgSO_4$, the $CHCl_3$-extract was evaporated *i.v.* The obtained yellowish syrupy residue was first freed from traces of residual pyridine by dissolving it in small amounts of benzene and evaporating the benzene solution *i.v.* (three times) and then dried in high vacuum for 2 h yielding slightly yellow crystals (379 mg; 100%; m.p. 195–199°). Recrystallization of this product from ethyl acetate/petroleum ether afforded the chromatographically pure **2** as almost colorless needles (338 mg; 89%), m.p. 200–201°. Analytical sample was obtained by two more recrystallizations from ethyl acetate, m.p. 201–203° (dec.); $[\alpha]_D^{27} = +9°$ ($c = 1.01$, $CHCl_3$). – IR.: 3520 and 3360 (H-bonded and free OH-group); 1480 and 1130 (dithiocarbamoyl group). – ^{1}H-NMR.: 9.16 (*d*, $J(2,NH) = 7.93$, 1 H, NH); 7.49–7.32 (*m*, 5 H, arom. H); 5.63 (*s*, 1 H, methine H-atom from benzylidene group); 5.03 (*d*×*d*, $J(2,NH) = 7.93$ and $J(2,3) = 3.05$, 1 H, H–C(2)); 4.73 (*s*, 1 H, H–C(1)); 4.33 (*d*×*d*, $J(5,6eq) = 4.88$ and $J(6ax,6eq) = 9.76$, 1 H, H_{eq}–C(6)); 4.33–4.23 (*m*, 1 H, H–C(3)); 4.25 (*d*×*d*×*d*, $J(4,5) = 9.46$, $J(5,6eq) = 4.88$ and $J(5,6ax) = 9.76$, 1 H, H–C(5)); 3.94 (*d*×*d*, $J(3,4) = 3.05$ and $J(4,5) = 9.46$, 1 H, H–C(4)); 3.85 (*t*, $J(5,6ax) = J(6ax,6eq) = 9.76$, 1 H, H_{ax}–C(6)); 3.67 (*d*, $J(3,OH) = 6.41$, 1 H, OH); 3.43 (*s*, 3 H, OCH_3); 2.63 (*s*, 3 H, SCH_3).

$C_{16}H_{21}NO_5S_2$	Calc.	C 51.75	H 5.70	N 3.77	S 17.26%
(371.5)	Found	„ 51.94	„ 5.83	„ 3.77	„ 17.30%

[5]) Without prior treatment of the crude reaction mixture with ethanethiol, acetylation with acetic anhydride/pyridine mixture gave **9** in only 24% yield, whereas the disulfide **10** was obtained in 51% yield. Reduction of the pyridine solution of disulfide **10** with ethanethiol and subsequent acetylation with acetic anhydride afforded **9** in 88% yield.

[6]) We are greatly indebted to Dr. *Charles De Brosse* for recording the 360 MHz ^{1}H-NMR. spectra.

Preparation of 4',6'-O-Benzylidene-1'-O-methyl-α-D-mannopyrano[2':3':4,5]-2-methylthio-2-thiazoline (**6**). To a stirred cold (0°) solution of **2** (1.00 g; 2.7 mmol) in dry pyridine (30 ml) a solution of methanesulfonyl chloride (0.27 ml; 3.49 mmol) in dry pyridine (5 ml) was added dropwise and the reaction mixture was kept in ice-bath for 12 h. According to TLC. (benzene/ethyl acetate 1:1), in addition to small amounts of starting material **2** (Rf 0.45) and *methyl-4,6-O-benzylidene-2-deoxy-2-isothiocyano-3-O-methanesulfonyl-α-D-altropyranoside* (**4**) (Rf 0.72), the solution contained *methyl-2-amino-4,6-O-benzylidene-2-deoxy-3-O-methanesulfonyl-2-N-[(methylthio)thiocarbonyl]-α-D-altropyranoside* (**3**) (Rf 0.58) as the major product. The reaction mixture was poured into ice-water and stirred for 1 h, during which time a pale yellow viscous mass separated. The aq. phase was decanted, extracted with $CHCl_3$ and the combined extract was used to dissolve the residue. The $CHCl_3$-phase was washed once with water, dried over anh. $MgSO_4$ and evaporated *i.v.* keeping the water bath at 30°. The residue was dissolved in dry pyridine (10 ml) and heated at 80° for 2.5 h. The dark reaction mixture, which according to TLC. (benzene/ethyl acetate 1:1) indicated the presence of only one major product (Rf 0.72) was evaporated *i.v.* and the dark brown residue was freed from residual pyridine by dissolving it in benzene and evaporating the benzene solution *i.v.* Chromatography of the crude product on silica gel (50 gm) gave on elution with benzene/ethyl acetate 3:1 a chromatographically homogeneous faintly yellow syrup (672 mg; 70%) which crystallized on standing. Recrystallization (twice) from 2-propanol gave an analytically pure **6**, m.p. 116–116.5°; $[\alpha]^{27} = -202$ ($c = 1.00$, $CHCl_3$). – ^{1}H-NMR.: 7.48–7.24 (*m*, 5 H, arom. H); 5.52 (*s*, 1 H, methine H-atom from benzylidene group); 5.41 (*s*, 1 H, H–C(1)); 4.28 (*d* × *d*, $J(5,6eq) = 4.88$ and $J(6ax,6eq) = 10.07$, 1 H, H_{eq}–C(6)); 4.18 (*d*, $J(2,3) = 6.10$, 1 H, H–C(2)); 3.86 (*d* × *d*, $J(2,3) = 6.10$ and $J(3,4) = 10.07$, 1 H, H–C(3)); 3.82 (*m*, $J(4,5) = 9.77$, $J(5,6eq) = 4.88$ and $J(5,6ax) = 10.07$, 1 H, H–C(5)); 3.49 (*d* × *d*, $J(3,4) = 10.07$ and $J(4,5) = 9.77$, 1 H, H–C(4)); 3.43 (*s*, 3 H, OCH_3); 2.55 (*s*, 3 H, SCH_3).

$C_{16}H_{19}NO_4S_2$	Calc.	C 54.37	H 5.42	N 3.96	S 18.14%
(353.5)	Found	,, 54.54	,, 5.48	,, 3.93	,, 18.28%

Preparation of methyl-4,6-O-benzylidene-2-deoxy-2-isothiocyano-3-O-methanesulfonyl-α-D-altropyranoside (**4**). To a solution of **2** (250 mg; 0.67 mmol) in anh. pyridine (10 ml), CH_3SO_2Cl (0.1 ml; 1.23 mmol) was added under vigorous stirring and the reaction mixture, was kept at RT. for 48 h. The pyridine solution, which, according to TLC. (benzene/ethyl acetate 9:1) contained, in addition to small amounts of **6** (Rf 0.36) and traces of an unidentified very polar material (Rf 0.00–0.04), only one major product (Rf 0.59), was poured onto ice-water and stirred whereby an oily precipitate separated. The aq. phase was decanted, extracted with $CHCl_3$ and the combined $CHCl_3$-phase was used to dissolve the oily residue. The obtained $CHCl_3$-phase was washed once with water, dried over anh. $MgSO_4$ and evaporated *i.v.* The black tarry residue was chromatographed on silica gel (15 g). Elution with benzene/ethyl acetate 25:1 gave chromatographically homogeneous **4** (178 mg; 66%) as a faintly yellow syrup and the thiazoline derivative **6** as an almost colorless syrup (29 mg; 12%), which crystallized on trituration with 2-propanol. Recrystallization of **6** from 2-propanol yielded colorless needless (22 mg), m.p. 114–115°. The analytical sample of **4** was obtained by chromatography on silica gel using benzene/acetone 35:1 as eluant: $[\alpha]^{27} = -47°$ ($c = 0.82$, $CHCl_3$). – IR. 2037 (asymmetric stretch of NCS) and 2110 *S*; 1357 and 1190 (asymmetric and symmetric stretch of sulfonate). – ^{1}H-NMR.: 7.45–7.35 (*m*, 5 H, arom. H); 5.65 (*s*, 1 H, methine H-atom from benzylidene group); 5.01 (*d* × *d*, $J(2,3) = J(3,4) = 2.75$, 1 H, H–C(3)); 4.78 (*s*, 1 H, H–C(1)); 4.35 (*d* × *d*, $J(5,6eq) = 5.19$ and $J(6ax,6eq) = 10.38$, 1 H, H*eq*–C(6)); 4.24 (*m*, $J(5,6eq) = 5.19$ and $J(5,6ax) = J(6ax,6eq) = 10.38$, 1 H, H–C(5)); 4.23 (*d*, $J(2,3) = 2.75$, 1 H, H–C(2)); 4.03 (*d* × *d*, $J(3,4) = 2.75$ and $J(4,5) = 10.38$, 1 H, H–C(4)); 3.82 (*d* × *d*, $J(5,6ax) = J(6ax,6eq) = 10.38$, 1 H, H*ax*–C(6)); 3.42 (*s*, 3 H, OCH_3); 2.95 (*s*, 3 H, methyl from methanesulfonyl group).

$C_{16}H_{19}NO_7S_2$ (401.5) Calc. C 47.87 H 4.77% Found C 48.01 H 4.79%

Preparation of 4',6'-O-benzylidene-1'-O-methyl-α-D-mannopyrano[2',3':4,5]-2-ethylthio-2-thiazoline (**5**). A solution (4 ml) of **4** (600 mg; 1.49 mmol) in anhydrous pyridine/ethanethiol 1:1 was refluxed for 6 h. The reaction mixture, which according to TLC. (benzene/ethyl acetate 9:1) contained only one product (Rf 0.43) was evaporated *i.v.*; the brown syrupy residue was dissolved in $CHCl_3$ and the insoluble white solid was filtered off and discarded. The filtrate was evaporated i.v. and the crude **5** was chromatographed on silica gel (30 g). Elution with benzene/ethyl acetate 30:1 gave a faintly yellow syrup (510 mg; 93%) which crystallized after standing overnight (m.p. 82–85°). Recrystallization from 2-propanol yielded thiazoline derivative **5** as white needles (463 mg; 84%), m.p. 85–87°. Analytical sample was obtained by two more recrystallizations from 2-propanol, m.p. 88–88.5°; $[\alpha]^{27} = -205°$ ($c = 1.00$, $CHCl_3$). – ^{1}H-NMR.: 7.49–7.26 (*m*, 5 H, arom. H);

5.54 (*s*, 1 H, methine H-atom from benzylidene group); 5.42 (*s*, 1 H, H–C(1)); 4.29 (*d*×*d*, *J*(5,6*eq*) = 4.88 and *J*(6*ax*,6*eq*) = 10.07, 1 H, H*ax*–C(6)); 4.19 (*d*, *J*(2,3) = 6.10, 1 H, H–C(2)); 3.85 (*d*×*d*, *J*(2,3) = 6.10 and *J*(3,4) = 10.07, 1 H, H–C(3)); 3.85 (*m*, *J*(4,5) = 9.77, *J*(5,6*eq*) = 4.88 and *J*(5,6*ax*) = 10.38, 1 H, H–C(5)); 3.71 (*d*×*d*, *J*(5,6*ax*) = 10.38 and *J*(6*ax*,6*eq*) = 10.07, 1 H, H*ax*–C(6)); 3.49 (*d*×*d*, *J*(3,4) = 10.07 and *J*(4,5) = 9.77, 1 H, H–C(4)); 3.45 (*s*, 3 H, OCH_3).

$C_{17}H_{21}NO_4S_2$ (367.5) Calc. C 55.56 H 5.76% Found C 55.72 H 5.90%

Preparation of N-*acetyl-4′,6′*-O-*benzylidene-1′*-O-*methyl-α*-D-*mannopyrano[2′,3′:4,5]thiazolidine* (**8**). To the Al-amalgam, prepared from Al-foil (2.0 g) according to *Vogel* [8], was added a solution of **6** (472 mg; 1.34 mmol) in THF. (25 ml) and to the stirred mixture water was added dropwise (7 ml), causing vigorous evolution of a gas. The resulting reaction mixture was refluxed for 24 h at which point the TLC. (benzene/methanol 9:1) indicated the presence of only one product (Rf 0.32) together with traces of unreacted **6** (Rf 0.60). After filtering the reaction mixture through a layer of *Celite (Johns Manville)*, the filtrate was evaporated *i.v.* to dryness. Slightly yellow syrupy residue (455 mg) was dissolved in ethanol (20 ml) and to the solution was added acetic anhydride (3 ml). After keeping the reaction mixture at RT. for 1 h, TLC. (benzene/ethyl acetate 1:1) indicated the presence of one major product (Rf 0.43). Ethanol, the excess of acetic anhydride and the formed acetic acid were removed *i.v.* and the syrupy residue was chromatographed on silica gel (15 g). Elution with benzene/ethyl acetate 2:1 gave chromatographically pure **8** (381 mg; 81%) as a colorless syrup, which crystallized on standing, m.p. 171–173. Analytical sample was obtained by recrystallization from acetone/hexane, white plates, m.p. 174–175°, $[\alpha]_D^{27} = -307$ (*c* = 1.03, $CHCl_3$). – IR.: 1650 (strong (C=O)-stretching typical of disubstituted amides). – ^{1}H-NMR.: 7.52–7.35 (*m*, 5 H, arom.H); 5.60 (*s*, 1 H, methine H-atom from benzylidene group); 5.23 (*s*, 1 H, H–C(1)); 4.30 (*d*×*d*, *J*(5,6*ax*) = 4.88 and *J*(6*ax*,6*eq*) = 10.07, 1 H, H*eq*–C(6)); 4.27 (*d*, *J*(2,3) = 6.41, 1 H, H–C(2)); 3.94 (*m*, *J*(4,5) = *J*(5,6*ax*) = 9.77 and *J*(5,6*eq*) = 4.88 1 H, H–C(5)); 3.75 (*d*×*d*, *J*(2,3) = 6.41 and *J*(3,4) = 10.38, 1 H, H–C(3)); 3.70 (*d*×*d*, *J*(3,4) = 10.38 and *J*(4,5) = 9.77, 1 H, H–C(4)); 3.48 (*d*×*d*, *J*(5,6*ax*) = 9.77 and *J*(6*ax*,6*eq*) = 10.07, 1 H, H*ax*–C(6)); 3.40 (*s*, 3 H, OCH_3); 2.18 (*s*, 3 H, *N*-acetyl group).

$C_{17}H_{21}NO_5S$ (351.4) Calc. C 58.10 H 6.02% Found C 58.27 H 6.05%

Reduction of **5** *with Al-amalgam.* Thiazoline derivative **5** (410 mg; 1.12 mmol) was reduced with Al-amalgam and the reaction mixture was worked up and acetylated as previously described for **6** *(vide supra)*. The crude product was purified by chromatography on silica gel (12 g). Elution with benzene/ethyl acetate 2:1 gave colorless syrup (211 mg; 54%) which crystallized on standing (m.p. 172–174°). Recrystallization from acetone/hexane gave white plates, m.p. 175°, which showed no depression of m.p. when mixed with **8** (mixed m.p. 174–175°). The obtained product was also spectroscopically (IR. and NMR.) identical with **8**. It is interesting to note that relatively large amount of unreacted thiazoline **5** was recovered (137 mg; 33%).

*Preparation of methyl-2-acetamido-4,6-di-*O-*acetyl-3-*S-*acetyl-2-deoxy-3-thio-α*-D-*mannopyranoside* (**9**). To a solution of **8** (250 mg; 0.71 mmol) in acetone/water 97:3 (10 ml) $HgCl_2$ and red HgO were added (1.0 g of each) and the obtained suspension was stirred vigorously at reflux for 16 h, at which point TLC. (benzene/ethyl acetate 1:1) indicated the absence of starting material. The reaction mixture was cooled to RT., ethanethiol (5 ml) was added and after continuing stirring at RT. for another 30 min, the precipitate was filtered off and washed with three 10-ml portions of $CHCl_3$ and five 10-ml portions of CH_3OH. The combined filtrate and washings was stirred with $NaHCO_3$ (3 g) for 2 h, the solid was filtered off and the filtrate was evaporated *i.v.* The residue (348 mg) was dissolved in anh. pyridine (5 ml) and to the solution acetic anhydride (5 ml) and ethanethiol (1 ml) were added. After keeping the reaction mixture at RT. for 16 h, methanol was added and the mixture evaporated *i.v.* The syrupy residue was chromatographed on silica gel (10 g). Elution with benzene/ethyl acetate 2:1 gave chromatographically homogeneous **9** as a colorless syrup (226 mg; 84%), which crystallized on standing (m.p. 148–150°). Analytical sample of **9** was obtained by recrystallization from acetone/hexane, white needles, m.p. 149.5–150°; $[\alpha]_D^{27} = +41°$ (*c* = 1.02 $CHCl_3$). – IR.: 3420 (strong NH-stretch), 1740 (strong (C=O)-stretch, *O*-acetate) and 1685 (strong (C=O)-stretch, *N*-monosubstituted amide). – ^{1}H-NMR.: 6.17 (*d*, *J*(2,NH) = 10.38, 1 H, NH); 4.94 (*d*×*d*, *J*(3,4) = 11.29 and *J*(4,5) = 9.77, 1 H, H–C(4)); 4.54 (*d*, *J*(1,2) = 1.22, 1 H, H–C(1)); 4.48 (*d*×*d*×*d*, *J*(1,2) = 1.22, *J*(2,3) = 4.27 and *J*(2,NH) = 10.38, 1 H, H–C(2)); 4.24 (*d*×*d*, *J*(2,3) = 4.27 and *J*(3,4) = 11.29, 1 H, H–C(3)); 4.22 (*d*×*d*, *J*(5,6*eq*) = 6.10 and *J*(6*ax*,6*eq*) = 12.21, 1 H, H*eq*–C(6)); 4.04–3.98 (unresolved *m*, 2 H, H–C(5) and H*ax*–C(6)); 3.38 (*s*, 3 H, OCH_3); 2.27 (*s*, 3 H, CH_3 from *N*-acetyl group), 2.06, 2.00 and 1.99 (3*s*, 9 H, CH_3 groups from two *O*-acetyl and one *S*-acetyl group).

$C_{15}H_{23}NO_8S$ (377.4) Calc. C 47.74 H 6.14% Found C 47.90 H 6.20%

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