Chemistry of Natural Compounds, Bioorganic, and Biomolecular Chemistry

Selective preparation of glycosyl sulfone or glycal by treatment of phenyl thioglycoside of *N*-acetylneuraminic acid with *m*-chloroperbenzoic acid

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Treatment of acetylated phenyl thioglycoside of *N*-acetylneuraminic acid with *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 affords quantitatively mixtures of the respective sulfone and glycal free from the sulfoxide. The outcome of the reaction does not depend on the anomeric configuration of the starting thioglycoside. The sulfone can be selectively prepared (yield ~100%) by oxidation with an excess of MCPBA and $NaHCO_3$. In the presence of pyridine (2 equiv.) and MCPBA (2 equiv.), the major product is glycal (yields 81—88%). This version of the reaction can be regarded as a new method for the preparation of sialic acid glycals.

Key words: sialic acids; phenyl thioglycoside of *N*-acetylneuraminic acid; oxidation with *m*-chloroperbenzoic acid; sulfone; *N*-acetylneuraminic acid glycal.

The development of effective methods for the synthesis of complex oligosaccharides and glycoconjugates containing *N*-acetylneuraminic acid (Neu5Ac) is an important area of modern synthetic carbohydrate chemistry because these structures determine the course of a whole series of immunological, neurobiological, oncological, and other biological processes.[1a]

Many known glycosylation methods[1b,2,3a,4,5] were used successfully to prepare Neu5Ac glycosides (for a review see Ref. 6). However, glycosyl sulfoxides, popular in recent years, which proved to be highly efficient in the case of other types of monosaccharides (for reviews, see Refs. 3b, 4, and 5), have not been employed as glycosyl donors in the synthesis of Neu5Ac glycosides. We decided to fill this gap and, as the first step, we attempted to synthesize glycosyl sulfoxide based on Neu5Ac. This paper describes the results obtained along this line.

Results and Discussion

Usually, anomeric glycosyl sulfoxides are synthesized by oxidation of thioglycosides with *m*-chloroperbenzoic

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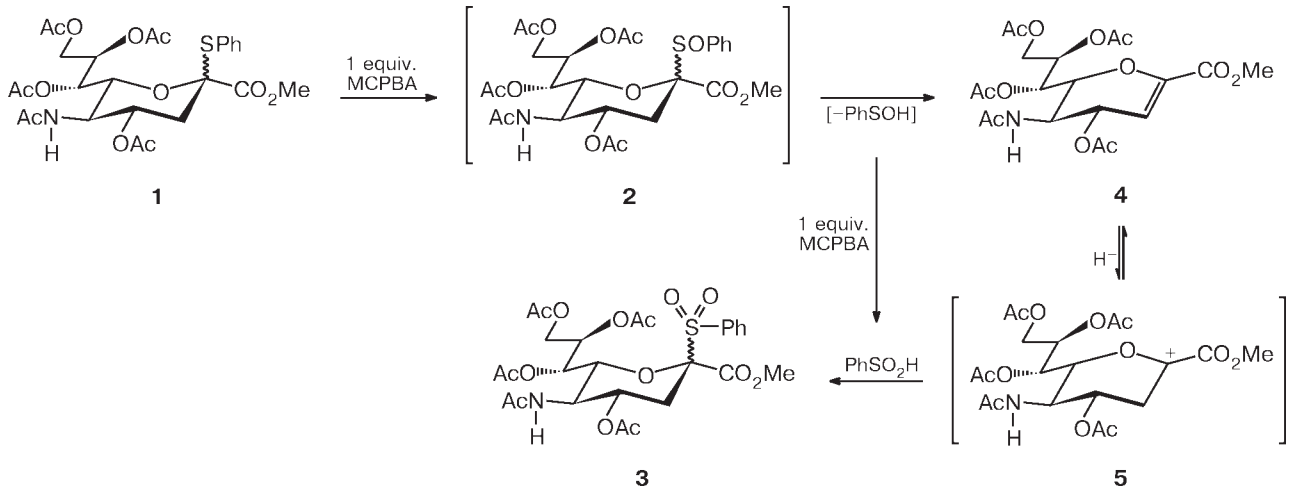
Scheme 1



acid (MCPBA) in CH_2Cl_2 [7] (for other methods of preparation of glycosyl sulfoxides, see Ref. 8). However, the use of this approach for the oxidation of acetylated phenyl thioglycoside of *N*-acetylneuraminic acid (**1**)[9] did not result in the formation of the target sulfoxide **2** (Scheme 1). The reaction carried out in CH_2Cl_2 in the presence of an excess of solid $NaHCO_3$ gave only one product, *viz.*, the known sulfone **3** (Table 1, entry 1) as a mixture of anomers ($\beta : \alpha \approx 7 : 3$). The ^{1}H NMR spectra of the α- and β-isomers of sulfone **3** (in C_6D_6) virtually coincided with the data published previously;[9] the observed small differences can be attributed to the fact that we recorded the spectra of **3** in C_6D_6 at elevated temperature (at 308 K; see Experimental). The mass spectrum of sulfone **3** exhibited a quasi-molecular ion peak (*m/z* 616 $[M + H]^+$ and 617 $[M + 1 + H]^+$) and the fragment peaks, in particular, a peak for the glycosyl cation (*m/z* 474 $[M - PhSO_2]^+$ and 475 $[M + 1 - PhSO_2]^+$) and peaks formed from it (identified using the MS/MS data) upon consecutive elimination of acetic acid residues (*m/z* 414, 415, 354, 294).

The formation of sulfones along with sulfoxides in the oxidation of sulfides under the action of MCPBA is a well-known process attributable to the "overoxidation" of the intermediate sulfoxide.[8,10a,11] Often, the proportion of sulfone can be decreased by using precise amounts of the oxidant or by changing the reaction conditions. However, we were unable to detect glycosyl sulfoxide **2** under any of the conditions used (see below); this must be due to the instability of this compound under the reaction conditions. Unlike other α-alkoxy sulfoxides,[10d] glycosyl sulfoxides derived from many simple monosaccharides are fairly stable compounds: they are prepared by oxidation of thioglycosides in the temperature range from –78 to 25 °C (see, for example, Refs. 7, 12), hexopyranosyl sulfoxides are isolated from reaction mixtures at room temperature (in particular, by chromatography[8]). The problem of partial "overoxidation" of phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside to the corresponding glycosyl sulfone on treatment with MCPBA at room temperature has been mentioned in a publication;[8] however, no relevant experimental details have been presented to confirm the structure of the oxidation products obtained with MCPBA.

Oxidation carried out without $NaHCO_3$ (Table 1, entry 2), including the reaction using only 2 equiv. of the oxidant (Table 1, entry 3), gave (according to ^{1}H NMR data for the reaction mixture after workup) the known *N*-acetylneuraminic acid glycal (**4**),[13–17] in addition to sulfone **3**. Glycal **4** could have been formed upon thermal elimination from both sulfoxide **2** [10b] (see Scheme 1) and sulfone **3**.[10c] The results of oxidation of sulfide **1** with deficiency of the oxidant (0.5 equiv. MCPBA, Table 1, entry 4) suggest that glycal **4** is apparently formed directly from sulfoxide **2**, because the reaction products were found to contain approximately equal amounts of glycal **4** and the starting sulfide **1** (in addition to traces of sulfone **3**). Glycal **4** is not produced from sulfone **3** upon thermal elimination because refluxing in toluene (Table 1, entry 6) of the reaction mixture, after workup, containing approximately equal amounts of sulfone **3** and glycal **4** (Table 1, entry 5) did not result in any substantial change in its composition.

However, the results of experiments show that sulfone **3** can be produced from glycal **4**. Direct oxidation of sulfoxide **2** under the reaction conditions used makes a smaller contribution to the formation of sulfone **3**. Indeed, it can be seen from the data of Table 1 that the yield of the sulfone increased with an increase in the reaction time and was not directly related to the amount of oxidant taken (*cf.* entries 3, 5, and 7, Table 1), which would not have been the case if the elimination and

Table 1. Transformation of thioglycoside **1** upon treatment with MCPBA

Entry	Anomeric configuration of thioglycoside **1** (α : β)	Reaction conditions[a]			Reaction products (%)[b]		
		B/equiv.	MCPBA (equiv.)	τ/h	**4**	**3**[c]	Recovered **1**
1	1 : 2.3	$NaHCO_3$ (40)	10.0	23.5	—	~100	—
2	0 : 1	—	1.7 + 10.0[d]	23	29	71	—
3	1 : 2.9	—	2.00	18[e]	33	67	—
4	0 : 1	—	0.50	22	55	2	43
5	1 : 2.3	—	1.20	4	55	45	—
6	[f]	—	—	2[g]	50	50	—
7	0 : 1	—	1.90	0.5	82	18	—
8[h]	1 : 2.3	$NaHCO_3$ (10)	2.00	[i]	84	16	—
				0.25	82	18	—
				0.5	79	21	—
				2	73	27	—
9	1 : 2.3	Py (0.99)	1.11	20	67	4	29
10	1 : 2.3	Py (1.59)	1.70	22.3	80	5	15
11[h]	1 : 2.3	Py (10)	2.00	0—2	~50[j]	—	~50[j]
12	1 : 2.3	Py (1.98)	2.01	23.5	87[k]	13[k]	—
13	1 : 2.3	Py (1.97)	1.98	23.5	88[k]	12[k]	—
14[l]	1 : 2.3	Py (1.91)	1.92	22	83[m,n]	10[m]	7[m]

[a] B is a base, τ is the reaction time. Solvent CH_2Cl_2, +4 °C, 0.05 mmol of thioglycoside **1** (for details, see Experimental).
[b] According to ^{1}H NMR. The integral intensities of the singlets (in ^{1}H NMR spectra recorded in $CDCl_3$) of the methoxycarbonyl groups in the starting thioglycoside **1** (δ 3.60 (β-anomer), δ 3.56 (α-anomer)), in sulfone **3** (δ 3.57 (β-anomer) and δ 3.88 (α-anomer)) and in glycal **4** (δ 3.78) were compared; the integral intensities of the H(3) signals in the spectra of glycal **4** (δ 6.00) and H_{eq}(3) signals of sulfone **3** (δ 3.23 (β-anomer) and δ 3.02 (α-anomer)) and in thioglycoside **1** (δ 2.68 (β-anomer) and δ 2.81 (α-anomer)) were additionally taken into account.
[c] Sulfone **3** was formed in all cases as an anomeric mixture (α : β ≈ 2 : 8—3 : 7, ^{1}H NMR).
[d] The second portion of MCPBA (10 equiv.) was added 2 h after beginning of the reaction.
[e] The reactants were mixed at +4 °C and the reaction mixture was allowed to warm up (in a bath) to +20 °C.
[f] The reaction mixture of entry 5.
[g] Refluxing in toluene (110 °C).
[h] The samples were taken from the reaction mixture 5, 15, 30, and 120 min after the addition of MCPBA.
[i] 5 min.
[j] The ratio does not change with time.
[k] Chromatographic purification (SiO_2, AcOEt) of the combined reaction mixtures (entries 12 and 13) gave a mixture of glycal **4** (yield 81%) and sulfone **3** (yield 11%).
[l] Preparative experiment (0.52 mmol of thioglycoside **1**); for details, see Experimental.
[m] After column chromatography (SiO_2, AcOEt).
[n] The yield of glycal **4** was 92% based on the consumed thioglycoside **1**.

oxidation of sulfoxide **2** to sulfone **3** had proceeded in parallel, independently of each other.

A support for the assumption that sulfone **3** is mainly formed from glycal **4** is provided by the results of ^{1}H NMR analysis of samples taken from the same reaction mixture 5, 15, 30, and 120 min after the addition of the oxidant (Table 1, entry 8). Under these conditions, the reaction mixture contained glycal **4** and sulfone **3**, while the starting sulfide **1** was not detected by ^{1}H NMR. It is significant that the amount of sulfone **3** in the reaction mixture gradually increased as the reaction advanced; correspondingly, the amount of glycal gradually decreased (after 2 h of the reaction, the **4** : **3** ratio decreased from 5.1 : 1 to 2.7 : 1).

On the basis of these results, the following reaction scheme can be proposed (see Scheme 1). First, MCPBA is consumed for the transformation of sulfide **1** to sulfoxide **2**, which is oxidized to a minor extent to give sulfone **3** but mainly eliminates sulfenic acid PhSOH to give glycal **4**. Benzenesulfenic acid PhSOH is a weak acid ($pK_a > 6$);[10e] it cannot induce substantial transformations of glycal **4** (Table 1, entry 4). When the amount of MCPBA increases, oxidation of PhSOH to stronger sulfinic acid $PhSO_2H$ (pK_a 2.97)[18] starts to play an important role; this acid causes further transformation of glycal **4**, which takes place in parallel with its formation (Table 1, entry 5). Protonation of glycal **4** with sulfinic acid $PhSO_2H$ results in the formation of the corresponding glycosyl cation **5**, which is attacked by the nucleophile ($PhSO_2H$) to give sulfone **3**. In the presence of $NaHCO_3$, more nucleophilic sulfinate anion $PhSO_2^-$ is generated from sulfinic acid $PhSO_2H$; this ultimately

results in complete transformation of glycal **4** into sulfone **3** (Table 1, entry 1). The intermediate formation of the glycosyl cation **5** is confirmed additionally by the fact that the configuration of the anomeric center in sulfone **3** does not depend on the configuration of this center in the starting thioglycoside **1**; in all cases, a mixture of anomers of **3** is produced (β : α ≈ 7 : 3—8 : 2).

Thus, it can be inferred that after the primary oxidation of thioglycoside **1** to sulfoxide **2** and elimination giving glycal **4**, the reaction proceeds as acid-catalyzed nucleophilic addition to vinyl ethers (in this particular case, to glycal **4**). The more common Michael addition of sulfinic acids and their anions to the double bonds of α,β-unsaturated esters giving rise to 1,4-adducts[10f] does not take place in this case, most likely, due to high stability of the glycosyl cation **5**.[6]

Currently, *N*-acetylneuraminic acid glycal (**4**) is the key intermediate in the synthesis of the most efficient sialosyl donors with the stereocontrolling group at the C(3) atom of the *N*-acetylneuraminic acid.[6] Therefore, we decided to study the oxidation of thioglycoside **1** in more detail and to find out whether it could be converted selectively into glycal **4**.

One might expect that the reaction between thioglycoside **1** and MCPBA would stop after the formation of glycal **4** (see Scheme 1) if exactly 2 equiv. of the oxidant are used (one equivalent for the oxidation of sulfide **1** to sulfoxide **2**, and the other, for the oxidation of PhSOH to $PhSO_2H$; recall that both processes occur simultaneously, see Table 1, entry 5) and an acidic medium favorable for the generation of the glycosyl cation is avoided.

Indeed, oxidation of **1** in the presence of Py, which neutralizes $PhSO_2H$ and hence decreases the probability of protonation of glycal **4** to yield the glycosyl cation **5**, sharply decreased the amount of sulfone **3** formed. In conformity with the reaction mechanism, the use of less than two equivalents of MCPBA did not result in complete disappearance of the starting thioglycoside **1**; an increase in the amount of the oxidant entailed both a higher degree of conversion of the starting sulfide and a higher yield of glycal **4** (*cf.* entries 9 and 10). An excess of Py prevented complete oxidation of the starting thioglycoside **1** (entry 11), which may be caused by the consumption of some of the MCPBA for the oxidation of Py to the corresponding *N*-oxide.[10g] These findings indicate that the results of experiments on the oxidation in the presence of Py can, in principle, be explained by assuming that Py reduces some of the oxidant and thus prevents oxidation of the sulfide to sulfoxide and then to sulfone. However, the observed fact of formation of glycal **4** in the presence of Py indicates that the oxidation of sulfide **1** to sulfoxide **2**, elimination to give glycal **4**, and the acid-base reaction between Py and $PhSO_2H$ proceed much faster than the oxidation of Py.

By using exactly measured amounts of MCPBA and Py taken in the reaction, we succeeded in attaining both the complete conversion of the starting thioglycoside **1** and high yields (87—88%) of glycal **4** (*cf.* entries 12 and 13, Table 1). The workup of the combined reaction mixtures (entries 12 and 13 in Table 1) and chromatographic purification of the product afforded an inseparable mixture of glycal **4** (yield 81%) and sulfone **3** (yield 11%). A special preparative experiment (*cf.* run 14, Table 1 and Experimental) carried out with slightly different amounts of the reactants (1.92 equiv. of MCPBA, 1.91 equiv. of Py) gave similar results (the yield of glycal **4** was 83%, *i.e.*, 92% based on the consumed thioglycoside **1**).

These results mean that we succeeded in finding new conditions for the synthesis of glycal **4**, which is an important intermediate in the chemistry of sialic acids.[6,19] From the preparative standpoint, the presence of a small amount of sulfone **3** (or starting thioglycoside **1**) in glycal **4** should not interfere with its further use, for example, for the synthesis of efficient glycosyl donors based on Neu5Ac.[6] This approach can also be used for the synthesis of glycals of other sialic acids.

The outcome of the reaction between **1** and MCPBA in the presence of $NaHCO_3$ deserves special attention. In our opinion, the main specific features of the reaction in the presence of $NaHCO_3$ are related to the heterogeneity of the reaction mixture. Apparently, the acid-base reaction between $NaHCO_3$ and $PhSO_2H$ in CH_2Cl_2 proceeds at a rate comparable with that of protonation of glycal **4**. As a consequence, on the one hand, the reaction mixture contains the glycosyl cation **5** and, on the other hand, the reaction between $NaHCO_3$ and $PhSO_2H$ gradually yields the sulfinate anion, which adds to cation **5** to give sulfone **3**.

Thus, the study of oxidation of acetylated phenyl thioglycoside of *N*-acetylneuraminic acid (**1**) on treatment with MCPBA in CH_2Cl_2 showed that the detectable reaction products include glycal **4** and sulfone **3** produced from **4**; the corresponding glycosyl sulfoxide **2** was not found in the reaction mixture. Conditions for the preparative synthesis of both sulfone **3** and glycal **4** were proposed.

Experimental

The general experimental techniques, solvent purification procedures, and the instruments used were described previously.[20] The content of *m*-chloroperbenzoic acid (MCPBA, 70%) in the commercial reagent (Fluka) was determined by iodometric titration. The starting thioglycoside **1** was prepared by a known procedure;[9] samples with different anomeric ratios (determined by ^{1}H NMR) were isolated from the reaction mixture by chromatography.

Oxidation of thioglycoside 1 with MCPBA (general procedure). [Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranosyl)onate] phenyl

sulfone (3) and methyl (2,6-anhydro-5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ene)onate (4).
A. (Table 1, entries 2—5, 7). MCPBA was added in one portion (the amounts are given in Table 1) to a solution of thioglycoside **1** (0.05 mmol) in anhydrous CH_2Cl_2 (2 mL) stirred at +4 °C (ice-water bath). The homogeneous reaction mixture was stirred at the same temperature (see Table 1) for the specified period of time (see Table 1), a cold saturated solution of Na_2SO_3 was added (5 mL), and a mixture was stirred for an additional 30 min at the same temperature and for 1 h at ~20 °C. The organic layer was washed with a mixture of equal volumes of saturated solutions of Na_2SO_3 and $NaHCO_3$ and with brine, filtered through cotton wool plug, and the solvent was evaporated *in vacuo*. The residue was dried *in vacuo*, dissolved in $CDCl_3$ or C_6D_6 (0.4 mL), and analyzed by ^{1}H NMR, the recorded spectra being compared with the known spectra of sulfone **3** (in C_6D_6 [9] and in $CDCl_3$) and glycal **4** (in $CDCl_3$[13]). The spectra of **3** and **4** in reaction mixtures coincided with the known spectra of individual compounds.

B. Oxidation was carried out as described in procedure ***A*** but the initial reaction mixture contained also pyridine (Table 1, entries 9, 10, 12, and 13).

C. Oxidation was carried out as described in procedure ***A*** but the initial reaction mixture contained also solid $NaHCO_3$ (Table 1, entry 1).

D. Oxidation was carried out as described in procedures ***B*** (Table 1, entry 11) or ***C*** (Table 1, entry 8). Aliquots were taken from the reaction mixture (5, 15, 30, and 120 min after the addition of the oxidant); they were worked-up and analyzed as described in procedure ***A***.

E. Oxidation of thioglycoside **1** (304 mg, 0.52 mmol) in CH_2Cl_2 (20 mL) with MCPBA (247 mg, 1.00 mmol, 1.92 equiv.) in the presence of Py (80 μL, 0.993 mmol, 1.91 equiv.) carried out as described in procedure ***B*** resulted, after chromatography on silica gel (with AcOEt as the eluent), in a mixture (248 mg) containing, according to ^{1}H NMR, glycal **4** (83%), sulfone **3** (10%), and unconsumed thioglycoside **1** (7%) (Table 1, entry 14).

Sulfone 3 (Table 1, entry 1; β : α = 7 : 3). MS (APCI), *m/z* (I_{rel} (%)): 294 $[M - PhSO_2 - 3\,AcOH]^+$ (6), 354 $[M - PhSO_2 - 2\,AcOH]^+$ (12), 414 $[M - PhSO_2 - AcOH]^+$ (55), 415 $[M + 1 - PhSO_2 - AcOH]^+$ (100), 474 $[M - PhSO_2]^+$ (21), 475 $[M + 1 - PhSO_2]^+$ (8), 616 $[M + H]^+$ (21), 617 $[M + 1 + H]^+$ (19). $C_{26}H_{33}NO_{14}S$. Calculated: M = 615.16.

^{1}H NMR (C_6D_6, 308 K), δ:* **β-anomer**, 2.21 [2.14] (dd, 1 H, $H(3)_{ax}$, $J_{3ax,4}$ = 10.7 Hz [10.6], $J_{3eq,3ax}$ = 15.0 [15.0]); 3.33 [3.36] (dd, $H(3)_{eq}$, $J_{3eq,4}$ = 4.8 [4.8] Hz); 3.13 [3.05] (s, 3 H, CO_2Me); 4.82 [4.89] (dd, 1 H, H(9′), $J_{8,9'}$ = 2.3 [2.4] Hz, $J_{9,9'}$ = 12.4 [12.5] Hz); 5.28 [5.23] (dd, 1 H, H(6), $J_{6,7}$ = 2.2 [2.5] Hz, $J_{5,6}$ = 10.7 [10.7] Hz); 5.83 [5.79] (ddd, 1 H, H(4), $J_{4,5}$ = 10.3 [10.0] Hz); 6.16 (d, 1H, C(5)NH, $J_{5,NH}$ = 10.1 Hz); **α-anomer**, 2.39 [2.36] (dd, 1 H, $H(3)_{ax}$, $J_{3ax,4}$ = 12.5 [11.7] Hz); 3.26 [3.28] (dd, 1 H, $H(3)_{eq}$, $J_{3eq,4}$ = 5.4 [4.5] Hz, $J_{3eq,3ax}$ = 12.1 [12.8] Hz), 3.54 [3.42] (s, 3 H, CO_2Me).

^{1}H NMR ($CDCl_3$, 297 K, ^{1}H—^{1}H COSY), δ: **β-anomer**, 1.94 (s, 3 H, NHAc); 2.02, 2.04, 2.12, 2.13 (all s, each 3 H, OAc); 2.29 (dd, 1 H, $H(3)_{ax}$, $J_{3ax,4}$ = 10.3 Hz, $J_{3eq,3ax}$ = 15.0 Hz); 3.23 (dd, $H(3)_{eq}$, $J_{3eq,4}$ = 4.8 Hz); 3.57 (s, 3 H, CO_2Me); 4.00 (m, 1 H, H(5)); 4.11 (dd, 1 H, H(9), $J_{8,9}$ = 6.8 Hz, $J_{9,9'}$ = 12.1 Hz); 4.44 (dd, 1 H, H(9′), $J_{8,9'}$ = 2.3 Hz); 4.99 (dd, 1 H, H(6), $J_{6,7}$ = 2.3 Hz, $J_{5,6}$ = 10.8 Hz); 5.27 (ddd, 1 H, H(8)); 5.39 (dd, 1 H, H(7), $J_{7,8}$ = 5.0 Hz); 5.61 (ddd, 1 H, H(4), $J_{4,5}$ = 9.6 Hz); 6.63 (d, 1 H, C(5)NH, $J_{5,NH}$ = 10.0 Hz); 7.15—7.95 (m, 5 H, Ph);* **α-anomer****, 2.18 (m, $H(3)_{ax}$***); 3.02 (dd, 1 H, $H(3)_{eq}$, $J_{3eq,4}$ = 4.4 Hz, $J_{3eq,3ax}$ = 12.8 Hz), 3.88 (s, 3 H, CO_2Me); 4.90 (m, 1 H, H(4)); 6.08 (d, 1 H, C(5)NH, $J_{5,NH}$ = 10.0 Hz); 7.15—7.95 (m, 5 H, Ph).*

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* Only identified characteristic signals are presented; the values in brackets are published data (the temperature of recording the spectrum is unknown).[9]

* The signal overlaps with the corresponding signal of the other anomer.

** Only identified signals are given.

*** The signal overlaps with the signals of the acetyl groups.

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