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One-pot acetalation–acetylation of sugar derivatives employing perchloric acid immobilised on silica

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Abstract—Perchloric acid immobilised on silica gel has been used as an efficient promoter for per-*O*-acetylation, and acetalation and subsequent *O*-acetylation of glycosides and thioglycosides in one-pot using stoichiometric reagents.

Keywords: Perchloric acid on silica; Acetal–ketal; Acetylation

1. Introduction

Designing synthetic strategies that minimise waste by using stoichiometric reagents and catalytic promoters is central to the principle of atom economy and green chemistry.[1] Our current efforts have been aimed at meeting the demand for various protected sugar building blocks in a fashion that minimises reaction steps, work-up and chromatographic purification.[2] Selective protection of 1,2-*cis*-diols through formation of acetal or ketal groups is one of the most frequently used reactions in carbohydrate chemistry.[3] Generally this reaction is carried out with an aldehyde or ketone in presence of a Lewis acid promoter.[4] To facilitate the reaction, use of the respective dimethyl acetals[5] or ketals,[6] or enol-ethers[7] are also well known in this area. The most frequently used catalysts includes sulfuric acid,[8] formic acid,[9] $CuSO_4$,[10] $ZnCl_2$, [11] *p*-toluenesulfonic acid,[12] camphorsulfonic acid[13] and iodine.[14] Acetalation under basic condition with dibromotoluene[15] in the presence of pyridine has also been used. Most of these reactions use large excess of reagents, which makes extensive work-up and chromatographic purification almost inevitable. A practical synthetic strategy providing access to these important sugar building blocks using stoichiometric reagents would be useful. Noting recent reports of the use of perchloric acid supported on silica gel as an effective promoter for acetylation of simple alcohols[16a] and sugars[16b] and the Ferrier rearrangement of glycals,[17] and the related conversion of carbonyl compounds to dithioacetals by polyphosphoric acid supported on silica gel,[18] we were encouraged to investigate $HClO_4$–silica in carbohydrate chemistry. We now report a facile, one-pot reaction sequence from unprotected sugar glycosides, using stoichiometric reagents, with minimal work-up and purification, that provides straightforward access to per-*O*-acetylated sugar acetals or ketals.

2. Results and discussion

As reported for the acetylation of simple alcohols[16a] and sugars,[16b] we found treatment of methyl α-D-glucopyranoside (**1**) with stoichiometric acetic anhydride and $HClO_4$–silica leads to per-*O*-acetylated derivative (**2**) in excellent yield (Scheme 1). Free reducing sugars and thioglycosides also undergo per-*O*-acetylation in very good to excellent yield. Beyond these obvious applications of immobilised perchloric acid, treatment of methyl α-D-glucopyranoside (**1**) with 1 mol equiv of benzaldehyde dimethylacetal in dry acetonitrile (2 mL per mmol of sugar) in the presence of $HClO_4$–silica

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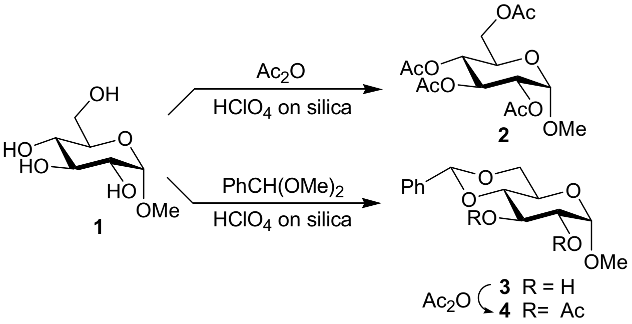
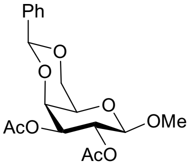
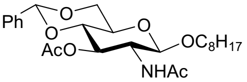
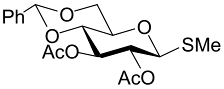
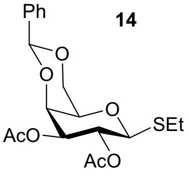
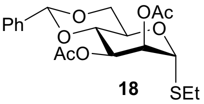


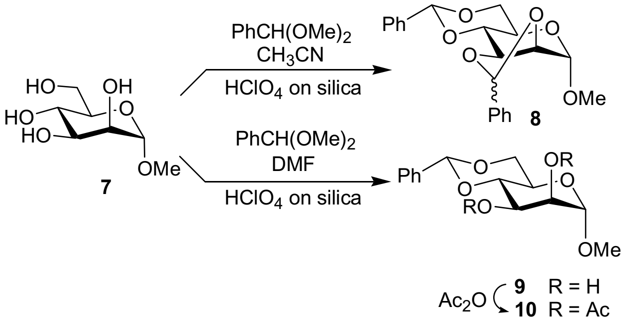
Scheme 1.

(50 mg) leads to complete conversion of the starting material to the corresponding benzylidene acetal derivative (**3**) within 30 min. The resulting product, after filtration and concentration proved to be >98% pure, as judged by NMR spectroscopy and mass spectrometry analysis. After complete formation of benzylidene acetal (**3**), as judged by TLC, 4 mol equiv of acetic anhydride was added to the mixture. Within 30 min at ambient temperature methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside **4**[19] was obtained as essentially a single compound (Scheme 1) in 91% isolated yield. Use of 4 mol equiv of acetic anhydride is necessary due to the fact that 1 mol of benzaldehyde dimethylacetal liberates 2 mol of methanol upon formation of the sugar benzylidene acetal. The methanol produced reacts with 2 mol of acetic anhydride to form volatile methyl acetate as a byproduct. Similarly methyl β-D-galactopyranoside (**5**) led to the corresponding galactose derivative (**6**) (Table 1). This suggests that HClO$_4$–silica is compatible with the pseudo *cis*-decalin system (**6**) as well as the more robust *trans*-decalin equivalent (benzylidenated glucoside **4**). Thioglycosides of hexopyranoses also gave similar results with this reagent system (Table 1). When methyl α-D-mannopyranoside (**7**) was treated with equimolar benzaldehyde dimethyl acetal, TLC showed a mixture of compounds containing mono- and di-benzylidene derivatives and starting material in a ca. 1:2:1 ratio. After addition of another equivalent of reagent, the known bis-benzylidene derivative (**8**) was obtained in 93% yield. When DMF was used as a solvent instead of acetonitrile, treatment with 1.1 equiv of α,α-dimethoxy toluene resulted 4,6-*O*-benzylidene derivative (**9**) in 73% yield, which was transformed into methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**10**) on treatment with acetic anhydride (Scheme 2).

After successful completion of sequential benzylidene acetal formation and acetylation in one-pot, we focused our attention on isopropylidene ketal formation using a similar strategy (Table 2). Thus, methyl α-L-rhamnopyranoside **19** (1 mmol) was treated with 2,2-dimethoxy propane (1 mmol) and HClO$_4$ on silica (30 mg) in acetone (2 mL), after 30 min when TLC showed complete conversion of the starting material to a faster running

Table 1. One-pot benzylidenation–acetylation with HClO$_4$ supported on silica gel

Starting material	Product	Time (min)	Isolated yield (%)
Methyl β-D-galactopyranoside (**5**)	 **6**	60	86
Octyl 2-acetamido-2-deoxy-β-D-glucopyranoside (**11**)	 **12**	90	88
Methyl 1-thio-β-D-glucopyranoside (**13**)	 **14**	60	94
Ethyl 1-thio-β-D-galactopyranoside (**15**)	 **16**	60	83
Ethyl 1-thio-α-D-mannopyranoside (**17**)		80	72

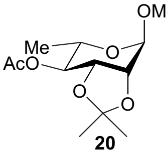
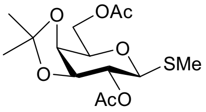
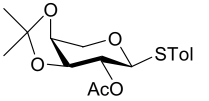
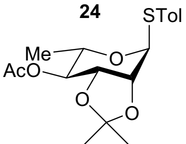
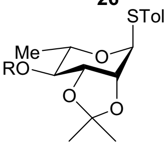
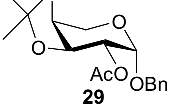
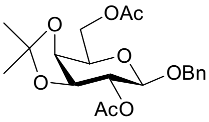


Scheme 2.

component (presumably the corresponding isopropylidene ketal), acetic anhydride (3 mmol) was added and the mixture was stirred for another 30 min. After filtration through Celite and evaporation of the solvent, the expected methyl 4-*O*-acetyl-2,3-*O*-isopropylidene-α-L-rhamnopyranoside **20**[20] was obtained in 92% yield (Table 2). Similarly, methyl glycosides and thioglycosides of D-galactose, L-arabinose and D-mannose are converted to the corresponding isopropylidene ketal derivatives (**22**–**26**) without difficulty (Table 2). In a separate experiment, after formation of the 2,3-*O*-isopropylidene derivative from thiotolyl rhamnoside (**25**), chloroacetic anhydride was added instead of acetic anhydride to form the corresponding chloroacetyl derivative (**27**) in 88% isolated yield. Benzyl α-L-arabinopyranoside and benzyl β-D-galactopyranoside also gave satisfactory results for acetalation–acetylation without cleavage of the anomeric benzyl group.

In conclusion, $HClO_4$–silica is a useful reagent for formation of acetals/ketals coupled with per-*O*-acetylation giving a range of variously protected sugar building blocks. The ease of application of this reagent, the use of stoichiometric reagents, and minimal work-up and

Table 2. One-pot isopropylidenation–acetylation with $HClO_4$ supported on silica gel

Starting material	Product	Time (min)	Isolated yield (%)
Methyl α-L-rhamnopyranoside (**19**)	 OMe, Me, AcO, O **20**	60	92
Methyl-1-thio-β-D-galactopyranoside (**21**)	 OAc, SMe, AcO, O **22**	60	87
p-Tolyl 1-thio-α-L-arabinopyranoside (**23**)	 STol, AcO, O **24**	45	87
p-Tolyl 1-thio α-L-rhamnopyranoside (**25**)	 STol, Me, AcO, O **26**	50	92
p-Tolyl 1-thio α-L-rhamnopyranoside (**25**)	 STol, Me, RO, O R = $ClCH_2CO$ **27**	60	88
Benzyl -L-arabinopyranoside (**28**)	 AcO, OBn, O **29**	45	84
Benzyl β-D-galactopyranoside (**30**)	 OAc, OBn, AcO, O **31**	60	80

purification serves to illustrate the versatility of this practical reagent system.

3. Experimental

3.1. General methods

Methyl glycosides of glucose, galactose and mannose were purchased from Aldrich Chemical Company. Compounds **11**,[21] **13**,[22] **15**,[23] **17**,[24] **19**,[25] **21**,[26] **23**,[27] **28**[28] and **30**[29] were prepared according to the literature procedures. Compound **21** has been prepared in a similar manner to that reported for the corresponding thiomethyl glycoside.[30] ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Plus spectrometer at 400 and 100 MHz, respectively, using Me_4Si as an internal standard. Optical rotations were measured at the Na D-line with a Perkin Elmer 141 polarimeter. Compounds **4**,[19] **6**,[31] **10**,[32] **16**,[33] **20**,[20] **22**[34] and **31**[35] gave ^{1}H and ^{13}C NMR data and optical rotations as reported in the literature. Experimental data for the other products are provided below.

3.2. Preparation of $HClO_4$ supported on silica

Immobilised perchloric acid on silica was prepared essentially as described previously,[16] except it was dried for 2 h at 110 °C instead of 6 h. $HClO_4$ (0.3 mmol, as a 70% aqueous solution) was added to a slurry of silica gel (5 g, 200 mesh) in Et_2O (15 mL) and the solvent was removed under reduced pressure. The resulting powder was kept at 110 °C for 2 h and used directly in reactions.

WARNING: Although there is no specific report about the danger of perchloric acid, care should be taken when handling this potentially explosive material. All reactions have been done in an efficient fumehood and special caution was taken during the drying of the $HClO_4$–silica.

3.3. General procedure for per-*O*-acetylation

To a mixture of the sugar (1 mmol) and Ac_2O, $HClO_4$–silica (50 mg) was added and the mixture was stirred at room temperature. When the reaction was complete as judged by TLC, the mixture was neutralised with Et_3N, diluted with CH_2Cl_2 (10 mL) and filtered through Celite. The filtrate was evaporated and the residue was analysed by ^{1}H and ^{13}C NMR spectroscopy and by mass spectrometry.

3.4. General procedure for formation of benzylidene acetals

To a solution of the starting material (1 mmol) and benzaldehyde dimethylacetal (1 mmol, for mannose derivatives 2 mmol) in acetonitrile (2 mL), $HClO_4$–silica (50 mg) was added and the mixture was stirred at room temperature until TLC (1:1 hexane–ethyl acetate) showed complete conversion. Ac_2O (4 mmol) was added to the mixture and stirring was continued until TLC showed complete reaction. The mixture was then neutralised with Et_3N and filtered through Celite. ^{1}H and ^{13}C NMR spectroscopy of the crude products showed them to be pure, without the need for further purification.

3.5. General procedure for formation of isopropylidene acetals

To a solution of the starting material (1 mmol) and 2,2-dimethoxypropane (2 mmol for hexopyranoses or 1 mmol for deoxy-hexopyranoses and pentopyranoses) in acetone (2 mL), $HClO_4$–silica (50 mg) was added and the mixture was stirred at room temperature until TLC (1:1 hexane–ethyl acetate) showed complete conversion. Ac_2O (4 mmol for hexopyranoses or 3 mmol for deoxy-hexopyranoses and pentopyranoses) was added and the mixture was stirred until TLC showed complete conversion. The product was then isolated as outlined above. No further purification was needed as ^{1}H and ^{13}C NMR spectroscopy confirmed the purity of the compounds.

3.6. Octyl 2-acetamido-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (12)

$[\alpha]_D^{25}$ +49.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ_H, 7.43–7.32 (m, 5H, ArH), 5.76 (d, 1H, $J_{2,NH}$ 9.6 Hz, N*H*COCH$_3$), 5.49 (s, 1H, C*H*Ph), 5.25 (t, 1H, $J_{2,3}$, $J_{3,4}$ 10.0 Hz, H-3), 4.45 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.31 (dd, 1H, $J_{5,6}$ 4.8 Hz, $J_{6a,6b}$ 10.4 Hz, H-6a), 4.05 (m, 1H, H-2), 3.80–3.73 (m, 2H, H-6b, OCH_2), 3.69 (t, 1H, $J_{3,4}$, $J_{4,5}$ H-4), 3.52 (m, 1H, OCH_2), 3.36 (m, 1H, H-5), 2.07 (s, 3H, COCH_3), 1.95 (s, 3H, NHCOCH_3), 1.51 (m, 2H, octyl-CH_2), 1.25 (m, 10H, octyl-CH_2), 0.87 (t, 3H, octyl-CH_3); ^{13}C NMR ($CDCl_3$): δ_C, 171.2 (*C*OCH$_3$), 170.2 (NH*C*OCH$_3$), 137.1, 129.2, 128.3, 126.2 (ArC), 102.1 (*C*HPh), 101.4 (C-1), 78.7, 72.0, 70.1, 68.7, 66.4, 54.6, 31.7, 29.4, 29.2, 29.1, 25.7, 23.2, 22.5 (NHCO*C*H$_3$), 20.8 (CO*C*H$_3$), 13.9; HRMS *m*/*z* calcd for $[C_{25}H_{38}NO_7]H^+$: 464.2643. Found: 464.2643.

3.7. Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (14)

$[\alpha]_D^{25}$ −68.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ_H, 7.44–7.34 (m, 5H, ArH), 5.51 (s, 1H, C*H*Ph), 5.36 (t, 1H, $J_{1,2}$, $J_{2,3}$ 9.3 Hz, H-2), 5.09 (t, 1H, $J_{2,3}$, $J_{3,4}$ 9.3 Hz, H-3), 4.49 (d, 1H, $J_{1,2}$ H-1), 4.40 (dd, 1H, $J_{5,6}$ 4.8 Hz, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.78 (dd, 1H, H-6b), 3.69 (t, 1H, $J_{3,4}$ H-4), 3.62 (m, 1H, H-5), 2.19 (s, 3H, S–CH_3), 2.09 (s, 3H, COCH_3), 2.06 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$):

δ_C, 170.1, 169.8 (2*C*OCH$_3$), 136.8, 128.3, 126.2, 125.3 (ArC), 101.5 (*C*HPh), 83.6 (C-1), 78.4, 72.7, 70.7, 69.8, 68.4, 20.6, 20.5 (2CO*C*H$_3$), 11.4 (S–*C*H$_3$); HRMS *m*/*z* calcd for [C$_{18}$H$_{26}$NO$_7$S]NH$_4^+$: 400.1425. Found: 400.1423.

3.8. Ethyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (18)

$[\alpha]_D^{25}$ +25.0 (*c* 1.1, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ_H, 7.50–7.35 (m, 5H, ArH), 5.60 (s, 1H, C*H*Ph), 5.46 (d, 1H, $J_{2,3}$ 3.3 Hz, H-2), 5.36 (dd, 1H, $J_{2,3}$, $J_{3,4}$ 10.5 Hz, H-3), 4.38–4.24 (m, 2H, H-6a, H-6b), 4.11 (t, 1H, $J_{3,4}$, $J_{4,5}$ 10.5 Hz, H-4), 3.89 (m, 1H, H-5), 2.64 (m, 2H, S–C*H*$_2$–CH$_3$), 2.18 (s, 3H, COC*H*$_3$), 2.01 (s, 3H, COC*H*$_3$), 1.30 (t, 3H, S–CH$_2$–C*H*$_3$); ^{13}C NMR (CDCl$_3$): δ_C, 169.8, 169.7 (2*C*OCH$_3$), 137.0, 128.2, 126.1, 125.2 (ArC), 101.8 (*C*HPh), 83.0 (C-1), 76.6, 71.5, 68.4, 68.3, 64.3, 25.1 (S–*C*H$_2$–CH$_3$), 20.5, 20.4 (2CO*C*H$_3$), 14.5 (S–CH$_2$–*C*H$_3$); HRMS *m*/*z* calcd for [C$_{19}$H$_{28}$NO$_7$S]NH$_4^+$: 414.1581. Found: 414.1580.

3.9. *p*-Tolyl 2-*O*-acetyl-3,4-*O*-isopropylidene-1-thio-α-L-arabinopyranoside (24)

$[\alpha]_D^{25}$ −21.0 (*c* 1.2, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ_H, 7.35, 7.07 (2d, 4H, *J* 8.4 Hz, Ar$_{AB}$), 5.09 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 6.4 Hz, H-2), 4.72 (d, 1H, $J_{1,2}$ H-1), 4.27–4.20 (m, 2H, H-3, H-5a), 4.14 (m, 1H, H-4), 3.74 (m, 1H, H-5b), 2.29 (s, 3H, S–C$_6$H$_4$–C*H*$_3$), 2.10 (s, 3H, COC*H*$_3$), 1.53, 1.33 (2s, 6H, isopropylidene-C*H*$_3$); ^{13}C NMR (CDCl$_3$): δ_C, 169.5 (*C*OCH$_3$), 137.8, 132.4, 130.1, 129.6 (ArC), 110.3 [*C*(CH$_3$)$_2$], 86.1 (C-1), 75.5, 72.0, 71.1, 64.0, 27.5, 26.1 (isopropylidene *C*H$_3$), 20.9 (S–C$_6$H$_4$–*C*H$_3$), 20.8 (CO*C*H$_3$); HRMS *m*/*z* calcd for [C$_{17}$H$_{26}$NO$_5$S]NH$_4^+$: 356.1526. Found: 356.1529.

3.10. *p*-Tolyl 4-*O*-acetyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (26)

$[\alpha]_D^{25}$ −153.0 (*c* 0.9, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ_H, 7.35, 7.12 (2d, 4H, *J* 8.0 Hz, Ar$_{AB}$), 5.68 (s, 1H, H-1), 4.92 (t, 1H, $J_{3,4}$, $J_{4,5}$ 9.0 Hz, H-4), 4.34 (d, 1H, $J_{2,3}$ 5.4 Hz, H-2), 4.23–4.16 (m, 2H, H-3, H-5), 2.32 (s, 3H, S–C$_6$H$_4$–C*H*$_3$), 2.10 (s, 3H, COC*H*$_3$), 1.11 (d, 3H, $J_{5,6}$ 6.0 Hz, H-6); ^{13}C NMR (CDCl$_3$): δ_C, 170.14 (*C*OCH$_3$), 138.0, 132.5, 129.9, 129.4 (ArC), 109.9 [*C*(CH$_3$)$_2$], 83.9 (C-1), 76.6, 75.4, 74.5, 65.3, 27.5, 26.4 (isopropylidene *C*H$_3$), 20.9 (S–C$_6$H$_4$–*C*H$_3$), 20.8 (CO*C*H$_3$), 16.6 (C–*C*H$_3$); HRMS *m*/*z* calcd for [C$_{18}$H$_{28}$NO$_5$S]NH$_4^+$: 370.1683. Found: 370.1683.

3.11. *p*-Tolyl 4-*O*-chloroacetyl-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (27)

$[\alpha]_D^{25}$ −158.0 (*c* 1.0, CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ_H, 7.34, 7.12 (2d, 4H, *J* 8.4 Hz, Ar$_{AB}$), 5.69 (s, 1H, H-1), 4.96 (dd, 1H, $J_{3,4}$ 8.0 Hz, $J_{4,5}$ 10.0 Hz, H-4), 4.35 (d, 1H, $J_{2,3}$ 5.2 Hz, H-2), 4.26–4.20 (m, 2H, H-3, H-5), 4.10 (s, 2H, COC*H*$_2$Cl), 2.32 (s, 3H, SC$_6$H$_4$C*H*$_3$), 1.56, 1.34 (2s, 6H, isopropylidene C*H*$_3$), 1.13 (d, 1H, $J_{5,6}$ 6.0 Hz, C–C*H*$_3$); ^{13}C NMR (CDCl$_3$): δ_C, 166.7 (*C*OCH$_3$), 138.2, 132.6, 130.0, 129.1 (ArC), 110.2 [*C*(CH$_3$)$_2$], 83.9 (C-1), 76.7, 76.6, 75.1, 64.9, 40.7 (CO*C*H$_2$Cl), 27.5, 26.3 (isopropylidene *C*H$_3$), 20.9 (S–C$_6$H$_4$–*C*H$_3$), 16.6 (C–*C*H$_3$); HRMS *m*/*z* calcd for [C$_{18}$H$_{27}$NClO$_5$S]NH$_4^+$: 404.1293. Found: 404.1296.

3.12. Benzyl 2-*O*-acetyl-3,4-*O*-isopropylidene-β-L-arabinopyranoside (29)

$[\alpha]_D^{25}$ −43.0 (*c* 1.1, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ_H, 7.34–7.25 (m, 5H, ArH), 4.97 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1), 4.90 (dd, 1H, $J_{1,2}$, $J_{2,3}$ 8.1 Hz, H-2), 4.71, 4.48 (2d, 2H, *J* 12.3 Hz, CH$_2$Ph), 4.36 (dd, 1H, $J_{2,3}$, $J_{3,4}$ 5.7 Hz, H-3), 4.24 (m, 1H, H-4), 4.00 (m, 2H, H-5a, H-5b), 2.06 (s, 3H, COC*H*$_3$), 1.52, 1.34 (2s, 6H, isopropylidene C*H*$_3$); ^{13}C NMR (CDCl$_3$): δ_C, 170.5 (*C*OCH$_3$), 137.2, 128.5, 127.9, 127.6 (ArC), 109.3 [C(CH$_3$)$_2$], 95.2 (C-1), 73.4, 72.8, 72.1, 69.4, 58.7, 27.8, 26.2 (isopropylidene *C*H$_3$), 20.7 (CO*C*H$_3$); HRMS *m*/*z* calcd for [C$_{17}$H$_{26}$NO$_6$]NH$_4^+$: 340.1755. Found: 340.1756.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2005.02.012.

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