Available online at www.sciencedirect.com
SCIENCE DIRECT®
Carbohydrate Research 339 (2004) 885–890
Carbohydrate RESEARCH

Note

Chloramine-T-mediated chemoselective hydrolysis of thioglycosides into glycosyl hemiacetals under neutral conditions ☆

Anup Kumar Misra* and Geetanjali Agnihotri

Medicinal Chemistry Division, Central Drug Research Institute, Lucknow 226-001, India

Received 1 September 2003; accepted 21 December 2003

This paper is dedicated to my mentor Prof. Nirmolendu Roy, Indian Association for the Cultivation of Science, Kolkata

Abstract—A metal-free, mild, efficient and chemoselective hydrolysis of several thioalkylglycosides (**1**) into their corresponding 1-hydroxy sugars (**2**) using sodium *N*-chloro-*p*-toluenesulfonamide trihydrate (chloramine-T) without affecting other functional groups is reported.

Keywords: Chloramine-T; Thioglycoside; Hemiacetal

A judicious choice of anomeric protecting groups is often of decisive importance in planning strategy for synthesizing complex oligosaccharides. In addition to the obvious requirement of stability towards the reaction conditions employed, it is desirable that the anomeric protecting group should be removed selectively or that it can be transformed into an activated derivative for further glycosylation.[1] Suitably protected 1-hydroxy sugars are useful synthons for synthesizing various glycosyl donors to be used in glycosylation reactions. Protected glycosyl hemiacetals can be prepared from (a) peracylated sugars by using toxic hydrazine salts or organic bases like benzylamine or butylamine;[2] (b) alkyl glycosides by acid hydrolysis of the glycosidic bond[3] or (c) by hydrolysis of thioglycosides. The generation of glycosyl hemiacetals from their corresponding thioglycosides is more convenient due to their availability and stability under various reaction conditions such as in the protection and deprotection steps for hydroxyl groups of saccharide molecules. Under hydrolytic conditions a thioglycoside is converted to its corresponding hemiacetal, which may either be converted to another glycosyl donor such as a trichloroacetimidate,[4] or the hemiacetal can be utilized as a substrate for Wittig or Horner–Emmons or related reactions for chiral[5] syntheses of various natural products. Therefore, the hydrolysis of thioglycosides is quite often used for preparation of desired glycosyl hemiacetals. The reported methodologies[6a–e] for this conversion includes the involvement of (a) toxic thiophilic heavy metal salts, (b) *N*-bromosuccinimide in moist acetone, (c) a combination of trityl tetrakis(pentafluorophenyl)borate, sodium periodate and a Lewis acid, (d) $Hg(CF_3COO)_2$ in moist THF, (e) vanadium pentoxide–H_2O_2–NH_4Br and (f) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$–$H_2O_2$ or $H_2MoO_4\cdot H_2O$–H_2O_2, $HClO_4$–NH_4Br. However, in spite of their potential utility, many of these methods suffer from drawbacks such as relatively low yields, use of expensive reagents, incompatibility with other functional groups and relatively harsh reaction conditions. Therefore, the development of mild, efficient, metal-free and neutral reaction conditions would extend the scope of this conversion.

Sodium *N*-chloro-*p*-toluenesulfonamide trihydrate (chloramine-T) has long been known for its oxidizing

☆ C.D.R.I. communication no. 6448.

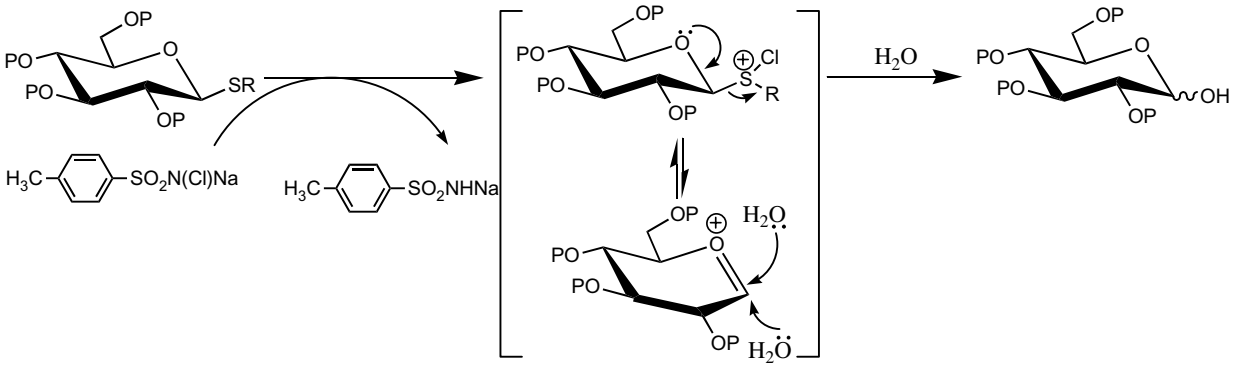
* Corresponding author. Fax: +91-0522-223938; e-mail: akmisra69@rediffmail.com

0008-6215/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.carres.2003.12.020

capability in cycloaddition reactions[7] of oximes with dipolarophiles, for example, alkenes or alkynes and as a nitrogen-atom transferring agent.[8] The usefulness of chloramine-T is that it behaves as sources of both a 'halonium' cation as well as a 'nitrogen anion'. The synthetic applications of chloramine-T have been well documented for aminohydroxylations, amino chalcogenation of alkenes, allylic aminations and aziridination of alkenes.[9]

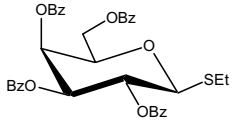
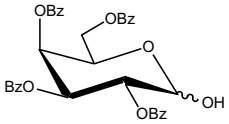
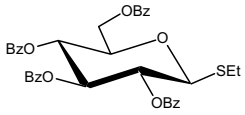
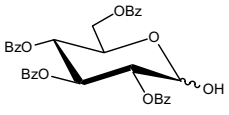
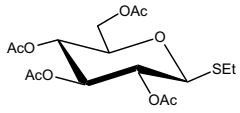
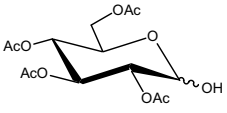
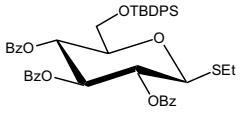
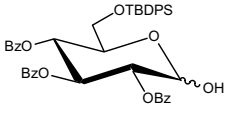
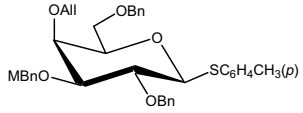
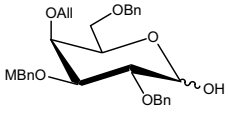
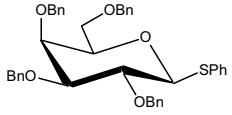
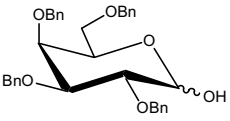
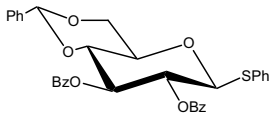
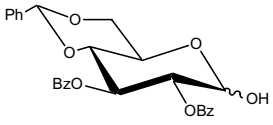
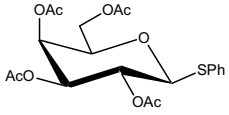
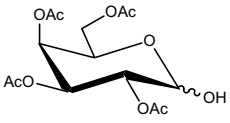
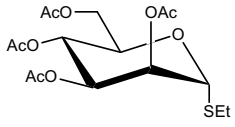
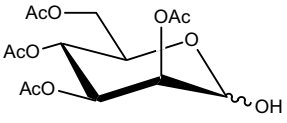
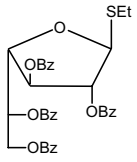
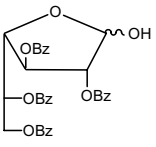
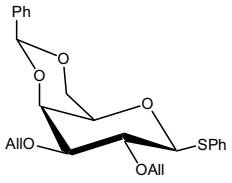
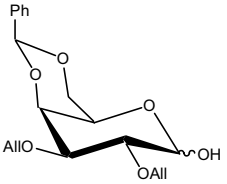
As a part of our ongoing program to prepare 1-hydroxy sugars for their use in the synthesis of enantiomerically pure natural products, it was envisioned that the activation of a thioglycoside by chloramine-T may lead to the formation of a 1-hydroxy sugar through in situ formation of a chlorosulfonium ion intermediate, followed by its hydrolysis in which chloramine-T acts as a chloronium ion source (Scheme 1). We are pleased to report here an easy, practically metal-free protocol for the hydrolysis of thioglycosides into their corresponding hemiacetals using chloramine-T. The reaction is carried out without requirement of any additive, leaving a variety of functional groups attached to the substrate intact. This straightforward operation that involves a low-cost, neutral activator, short reaction times and a simple purification of products are the key points of this methodology.

A wide variety of thioglycosides were transformed in excellent yields into their corresponding hemiacetals using 1.5 M equiv of chloramine-T trihydrate in commercial grade acetonitrile as a solvent at ambient temperature. Subsequently, we have attempted to optimize the reaction conditions by varying the quantity of chloramine-T. Upon treatment with 0.5 M equiv of the activator, the reaction did not reach completion. However, the use of a stoichiometric quantity of the activator takes considerably longer reaction time (~48 h) to furnish the expected product. After some experimentation with respect to the molar ratio of the activator, the reaction conditions (temperature/time) and the nature of the solvent, it was observed that the use of 1.5 M equiv of chloramine-T in acetonitrile as a solvent consistently produced excellent yields of 1-hydroxy sugars without affecting a variety of protecting groups. It is noteworthy that no direct oxidation of sulfur atoms or formation of aziridines in the double bonds present as a protecting group of the substrate was observed, and silyl and acetal protecting groups were quite stable under these reaction conditions (Table 1, entries 4, 7, 11). Formation of a 2,3-unsaturated glycosyl hemiacetal by activation of a 2,3-unsaturated thioglycoside (a Ferrier product) without formation of any Perlin aldehyde or 2-deoxy-3-thioalkyl products is an added advantage of this methodology (Table 1, entry 21). In order to study the rate of hydrolysis of differentialy functionalized thioglycosides, a series of alkyl- and acyl-protected thioethyl, thiophenyl, thiotolyl and thiobenzyl glycosides were tested (Table 1), and it was observed that the rate of hydrolysis for acyl-protected thioglycosides is slightly slower than that for an alkyl-protected one, which may be explained by considering the activation of 'armed' or activated and 'disarmed' or deactivated thioglycoside concept. Being armed, the thioglycosides having an alkyl group at the C-2 position are more reactive towards the Cl^+ ion and thereby form the desired product at a faster rate compared to their 2-*O*-acyl counterparts. In another approach, a series of peracetylated benzyl thioglycosides were tested for their reactivity towards chloramine-T, and it was found that all benzyl thioglycosides afforded their corresponding hemiacetals in excellent yields. The observed rate of hydrolysis of the substituted benzyl thioglycosides (benzyl thioglycoside ≈ 3,4-dimethylbenzyl thioglycoside > *p*-methoxybenzyl thioglycoside > *p*-nitrobenzyl thioglycoside) may be explained by considering the presence of electron-donating and -withdrawing groups present on the benzene nucleus of the benzyl groups; however, the substitutions on the benzene nucleus of substituted benzyl thioglycosides have a little influence on the overall rate of hydrolysis (Table 1). A series of solvents were tested for their efficacy under the reaction conditions, and CH_3CN was found as the one best-



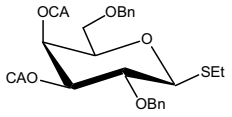
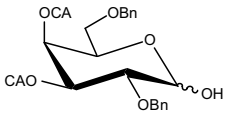
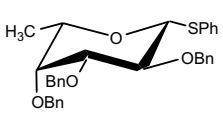
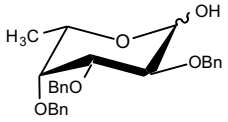
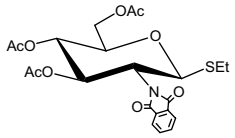
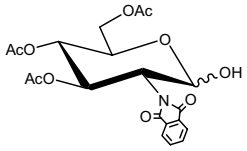
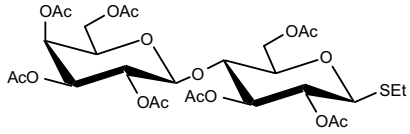
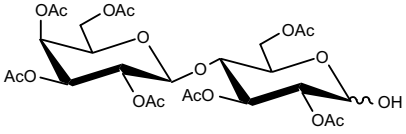
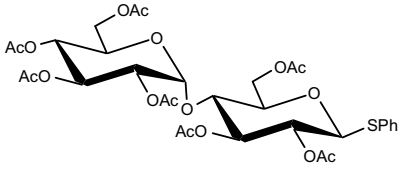
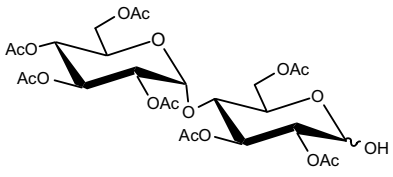
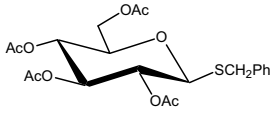
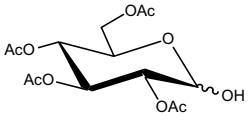
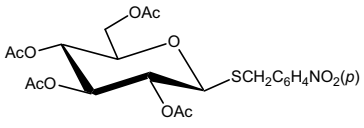
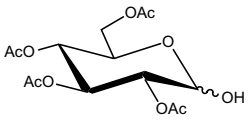
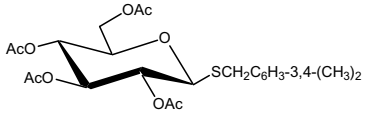
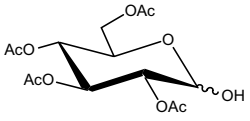
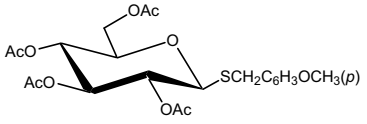
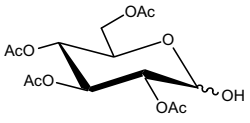
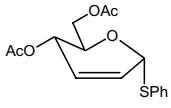
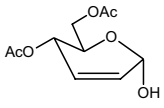
Scheme 1. Plausible mechanism for the hydrolysis of thioglycoside.

Table 1. Hydrolysis of thioglycosides using Chloramine-T in CH_3CN at room temperature[a]

Entry	Thioglycosides (1)	Products (2)	Time (h)	Yield (%)[b]	Reference
1			2.0	92	6e
2			2.0	87	6e
3			1.5	85	6f
4			2.5	86	10
5			1.0	76	—
6			0.5	92	6f
7			1.5	88	11
8			2.0	90	6f
9			2.0	92	—
10			2.5	84	—
11			1.5	86	12

(*continued on next page*)

Table 1 (*continued*)

Entry	Thioglycosides (1)	Products (2)	Time (h)	Yield (%)[b]	Reference
12			1.0	80	—
13			1.0	86	—
14			1.5	86	—
15			2.5	80	—
16			3.0	76	—
17			1.0	87	6f
18			2.5	80	6f
19			1.0	90	6f
20			1.5	92	6f
21			1.0	78	—

[a] Products all known compounds gave acceptable ^{1}H NMR spectra that matched data reported in the cited references. New compounds are characterized according to identity and purity (see data in Experimental section).
[b] Isolated yield.

suited solvent in comparison to other commonly used solvents like dichloromethane and THF. The formation of the hydrolyzed products from the corresponding thioglycosides can be explained as follows: Chloramine-

T produces an active chloronium ion (Cl^+) that reacts with the sulfur atom to form a chlorosulfonium complex, which is then finally hydrolyzed to furnish the 1-hydroxy compound (Scheme 1).

In conclusion, a simple and useful methodology has been devised for chemoselective hydrolysis of thioglycosides to their corresponding 1-hydroxy counterparts using chloramine-T under very mild, metal-free conditions. It is significant to mention that addition of any extra additive is not required for this reaction, and most of the functional groups used for protection of glycosyl hydroxyl groups, including acid-labile acetal protecting groups and base-labile silyl protecting groups, are quite stable under these conditions. Due to its operational simplicity, generality, efficacy and cost effectiveness, this method is expected to have much wider applicability for the chemoselective hydrolysis of thioglycosides. A study on stereoselective glycosylation by extending this methodology is currently in progress.

1. Experimental

1.1. General methods

NMR spectra were measured with an Avance DPX 200 FT Bruker Robotics Spectrometer for solutions in $CDCl_3$ using Me_4Si as the internal reference. FAB mass spectra were recorded on a Jeol SX 102/DA 6000 mass spectrometer using Argo/xenon (6 kV, 10 mA) as the FAB gas. Aluminium sheets coated with Silica Gel 60 F_{254} (E. Merck) were used for TLC. Viewing under a short wavelength UV lamp, followed by heating the plates sprayed with 5% H_2SO_4 in EtOH, effected detection of reaction products. Column chromatography was performed with Silica Gel 100–200 mesh (SRL, India). Chloramine-T trihydrate was purchased from Aldrich Chemical Company, USA.

1.2. Typical experimental protocol

1.2.1. 2,3,4,6-Tetra-*O*-acetyl-α,β-D-galactopyranose. To a well-stirred solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (440.0 mg, 1.0 mmol) in CH_3CN (5.0 mL) was added chloramine-T trihydrate (425.0 mg, 1.5 mmol) at room temperature. The reaction mixture was allowed to stir at room temperature until the reaction was complete (2.0 h) (Table 1, entry 8). When TLC indicated the disappearance of starting material, the mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on SiO_2 using 2:1 hexane–EtOAc to furnish pure 2,3,4,6-tetra-*O*-acetyl-α,β-D-galactopyranose (315.0 mg, 90%). Mp: 143–145 °C; ^{1}H NMR: δ 2.03–2.21 (4s, 12H, 4COCH_3), 4.07–4.16 (m, 3H), 4.19 (m, 1H), 4.29 (m, 1H), 5.18 (dd, $J = 3.4$ and 10.8 Hz, 1H), 5.44 (d, 1H, $J = 2.2$ Hz), 6.32 (d, 1H, $J = 3.6$ Hz). FABMS: calcd for $C_{14}H_{20}O_{10}$, m/z 348; found, m/z 331 [(M−H_2O)+1].

^{1}H NMR and mass spectroscopic data for the hemiacetal products are as follows:[†]

1.2.2. 2,3,4,6-Tetra-*O*-benzoyl-α-D-galactopyranose. ^{1}H NMR: δ 7.34–8.13 (m, 20H), 6.08 (m, 2H), 5.90 (dd, 1H), 5.75 (m, 1H), 4.60 (m, 2H), 4.45 (m, 1H). FABMS: calcd for $C_{34}H_{28}O_{10}$, m/z 596; found, m/z 579 [(M−H_2O)+1].

1.2.3. 2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranose. ^{1}H NMR: δ 7.28–8.06 (m, 20H), 6.24 (t, 1H), 5.76 (d, J 3.0 Hz, 1H), 5.73 (t, 1H), 5.28 (dd, 1H), 4.62 (m, 2H), 4.46 (m, 1H). FABMS: calcd for $C_{34}H_{28}O_{10}$, m/z 596; found, m/z 579 [(M−H_2O)+1].

1.2.4. 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranose. ^{1}H NMR: δ 6.25 (d, J 2.0 Hz, 1H), 5.46 (t, 1H), 5.44 (d, J 1.5 Hz, 1H), 5.08 (t, 1H), 4.95 (dd, 1H), 4.14 (m, 2H), 2.01–2.12 (4s, 12H). FABMS: calcd for $C_{14}H_{20}O_{10}$, m/z 348; found, m/z 331 [(M−H_2O)+1].

1.2.5. 4-*O*-Allyl-2,6-di-*O*-benzyl-3-*O*-(*p*-methoxybenzyl)-α-D-glucopyranose. ^{1}H NMR: δ 6.84–7.73 (m, 14H), 5.90 (m, 1H), 5.14–5.24 (m, 3H), 4.52–4.79 (m, 8H), 4.18 (m, 2H), 3.80 (s, 3H, OCH_3), 3.50–3.63 (m, 3H). FABMS: calcd for $C_{31}H_{36}O_7$, m/z 520; found, m/z 503 [(M−H_2O)+1].

1.2.6. 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranose. ^{1}H NMR: δ 7.26–7.34 (m, 20H), 5.24 (br s, 1H), 4.98 (m, 1H), 4.48–4.88 (4dd, 8H), 3.97 (m, 2H), 3.63 (m, 3H). FABMS: calcd for $C_{34}H_{36}O_6$, m/z 540; found, m/z 523 [(M−H_2O)+1].

1.2.7. 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranose. ^{1}H NMR: δ 5.41 (dd, 1H), 5.27 (m, 3H), 4.24 (m, 2H), 4.14 (m, 1H), 2.00–2.22 (4s, 12H). FABMS: calcd for $C_{14}H_{20}O_{10}$, m/z 348; found, m/z 331 [(M−H_2O)+1].

1.2.8. 2,3,5,6-Tetra-*O*-benzoyl-α-D-galactofuranose. ^{1}H NMR: δ 7.19–8.10 (m, 20H), 6.11 (m, 2H), 5.85 (d, J 3.0 Hz, 1H), 5.72 (br s, 1H), 4.88 (t, 1H), 4.61 (m, 1H), 4.38 (m, 1H). FABMS: calcd for $C_{34}H_{28}O_{10}$, m/z 596; found, m/z 579 [(M−H_2O)+1].

1.2.9. 3,4-Di-*O*-chloroacetyl-2, 6-di-*O*-benzyl-α-D-galactopyranose. ^{1}H NMR: δ 7.24–7.35 (m, 10H), 5.54 (d, J

[†] Although, both α- and β-anomers formed under the reaction conditions, spectral data for the α-anomers are given for the sake of simplicity.

3.0 Hz, 1H), 5.38 (dd, 1H), 5.30 (d, *J* 3.0 Hz, 1H), 4.68 (s, 2H), 4.56 (dd, 2H), 4.40 (dd, 1H), 3.94 (m, 4H), 3.81 (m, 2H), 3.48 (m, 1H). FABMS: calcd for *m/z* 513; found, *m/z* 496 [(M−H_2O)+1].

1.2.10. 2,3,4-Tri-*O*-benzyl-α-L-fucopyranose. ^{1}H NMR: δ 7.23–7.35 (m, 15H), 5.23 (d, *J* 3 Hz, 1H), 4.60–4.96 (3dd, 6H), 4.07 (m, 1H), 4.01 (dd, 1H), 3.98 (dd, 1H), 3.55 (m, 1H), 1.15 (d, 3H). FABMS: calcd for $C_{27}H_{30}O_5$, *m/z* 434; found, *m/z* 417 [(M−H_2O)+1].

1.2.11. 2-Deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-β-D-glucopyranose. ^{1}H NMR: δ 7.70–7.92 (m, 4H), 5.85 (t, 1H), 5.65 (m, 1H), 5.20 (t, 1H), 4.25 (m, 3H), 3.90 (m, 1H), 1.87, 2.05, 2.10 (3s, 9H). FABMS: calcd for $C_{20}H_{21}NO_{10}$, *m/z* 435; found, *m/z* 418 [(M−H_2O)+1].

1.2.12. 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranose. ^{1}H NMR: δ 5.45 (t, 1H), 5.26 (br s, 2H), 4.89 (dd, 1H), 4.88 (dd, 1H), 4.47 (m, 1H), 4.37 (m, 2H), 4.13 (m, 3H), 4.03 (m, 1H), 3.88 (m, 1H), 1.88–2.08 (7s, 21H). FABMS: calcd for $C_{26}H_{36}O_{18}$, *m/z* 636; found, *m/z* 619 [(M−H_2O)+1].

1.2.13. 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl-(1 → 4)-*O*-2,3,6-tri-*O*-acetyl-α-D-glucopyranose. ^{1}H NMR: δ 5.57 (d, *J* 3.0 Hz, 1H), 5.39 (m, 1H), 5.33 (d, *J* 3.0 Hz, 1H), 5.03 (m, 1H), 4.89 (m, 1H), 4.70 (m, 1H), 4.52 (m, 2H), 3.90–4.15 (m, 5H), 3.77 (m, 1H), 1.92–2.18 (7s, 21H). FABMS: calcd for $C_{26}H_{36}O_{18}$, *m/z* 636; found, *m/z* 619 [(M−H_2O)+1].

1.2.14. 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranose. ^{1}H NMR: δ 5.90 (m, 2H), 5.46 (br s, 1H), 5.28 (m, 1H), 4.22 (m, 3H), 2.05, 2.08 (2s, 6H). FABMS: calcd for $C_{10}H_{14}O_6$, *m/z* 230; found, *m/z* 213 [(M−H_2O)+1].

Acknowledgements

The authors thank the Director, Central Drug Research Institute (C.D.R.I.) for his encouragement and support. R.S.I.C., C.D.R.I. is gratefully acknowledged for use of its instrumentation facilities. This work is partly supported by DST, New Delhi (Project no. SR/FTP/CSA-10/2002).

References

1. (a) Garegg, P. J. *Acc. Chem. Res.* **1992**, *25*, 575–580; (b) Kunz, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 294–308; (c) Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 823–856.
2. (a) Roush, W. R.; Lin, X.-F. *J. Am. Chem. Soc.* **1995**, *117*, 2236–2251; (b) Nikolaev, A. V.; Ivanova, I. A.; Shibaev, V. N.; Kochetkov, N. K. *Carbohydr. Res.* **1990**, *204*, 65–78; (c) Ivanova, I. A.; Ross, A. J.; Ferguson, M. A. J.; Nikolaev, A. V. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1743–1754; (d) Yashunsky, D. V.; Tsvetkov, Y. E.; Ferguson, M. A. J.; Nikolaev, A. V. *J. Chem. Soc., Perkin Trans. 1* **2002**, 242–256; (e) Ruhela, D.; Vishwakarma, R. A. *J. Org. Chem.* **2003**, *68*, 4446–4456.
3. Koto, S.; Morishima, N.; Miyata, Y.; Zen, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2639–2640.
4. Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212–235.
5. (a) Hanession, S. In *Total Synthesis of Natural Products; The Chiron Approach*; Baldwin, J. E., Ed.; Pergamon: Oxford, 1983; (b) Ousset, J. B.; Mioskowski, C.; Yang, Y. L.; Falck, J. R. *Tetrahedron Lett.* **1984**, *25*, 5903–5906; (c) Lakhrissi, M.; Chapleur, Y. *Angew. Chem., Int. Ed.* **1996**, *35*, 750–752; (d) Liberknecht, A.; Griesser, H.; Bravo, R. D.; Colinas, P. A.; Grigera, R. J. *Tetrahedron* **1998**, *54*, 3159–3168; (e) Gothelf, K. V.; Jorgensen, K. A. *Chem. Rev.* **1998**, *98*, 863–909.
6. (a) Motawis, M. S.; Marcussan, J.; Moeller, B. L. *J. Carbohydr. Chem.* **1995**, *14*, 1279; (b) Kaesbeck, L.; Kessler, H. *Liebigs Ann. Chem.* **1997**, 169; (c) Uchiro, H.; Wakiyama, Y.; Mukaiyama, T. *Chem. Lett.* **1998**, 567–568; (d) Xie, J.; Molina, A.; Czernecki, S. *J. Carbohydr. Chem.* **1999**, *18*, 481–498; (e) Mondal, E.; Barua, P. M. B.; Bose, G.; Khan, A. T. *Chem. Lett.* **2002**, 210–211; (f) Barua, P. M. B.; Sahu, P. R.; Mondal, E.; Bose, G.; Khan, A. T. *Synlett* **2002**, 81–84.
7. (a) Hassner, A.; Rai, K. M. L. *Synthesis* **1989**, 57–59; (b) Pal, A.; Bhattacharjee, A.; Bhattacharjya, A.; Patra, A. *Tetrahedron* **1999**, *55*, 4123–4132; (c) Pal, A.; Bhattacharjee, A.; Bhattacharjya, A. *Synthesis* **1999**, 1569–1572; (d) Osborn, H. M. I.; Gemmell, N.; Harwood, L. M. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2419–2438.
8. (a) Ando, T.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron Lett.* **1998**, *39*, 309–312; (b) Minakata, S.; Kano, D.; Fukuoka, R.; Oderaotoshi, Y.; Komatsu, M. *Heterocycles* **2003**, *60*, 289–298; (c) Jain, S. L.; Sain, B. *Tetrahedron Lett.* **2003**, *44*, 575–577; (d) Brandt, P.; Sodergren, M. J.; Anderson, P. O.; Norrby, P. O. *J. Am. Chem. Soc.* **2000**, *122*, 8013–8020; (e) Albone, D. P.; Aujla, P. S.; Taylor, P. C.; Challenger, S.; Derrick, A. M. *J. Org. Chem.* **1998**, *63*, 9569–9571.
9. (a) Campbell, M. M.; Johnson, G. *Chem. Rev.* **1978**, *78*, 65–79; (b) Sharpless, K. B.; Chong, A. O.; Oshima, K. *J. Org. Chem.* **1976**, *41*, 177–179; (c) Barton, D. H. R.; Britten-Kelly, M. R.; Ferreira, D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1090–1100; (d) Li, G.; Angert, H. H.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **1996**, *35*, 2813–2817; (e) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. *J. Am. Chem. Soc.* **1976**, *98*, 269–271; (f) Jeong, J. U.; Tao, B.; Sagasser, I.; Hennings, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844–6845.
10. Nicolaou, K. C.; Winssinger, N.; Pastor, J.; DeRoose, F. *J. Am. Chem. Soc.* **1997**, *119*, 449–450.
11. Lefeber, D. J.; Kamerling, J. P.; Vliegenthart, J. F. G. *Chem. Eur. J.* **2001**, *7*, 4411–4421.
12. Mootoo, D. R.; Date, V.; Fraser-reid, B. *J. Am. Chem. Soc.* **1988**, *110*, 2662–2663.