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Carbohydrate Research 339 (2004) 1219–1223
Carbohydrate RESEARCH

Note

A facile preparation of uronates via selective oxidation with TEMPO/KBr/$Ca(OCl)_2$ under aqueous conditions

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Received 31 October 2003; accepted 3 February 2004

Abstract—Addition of solid $Ca(OCl)_2$ as the terminal oxidant in the TEMPO-mediated selective oxidation has the benefit of easier operation. A variety of partially protected saccharide derivatives (**1a**–**l**) have been successfully converted into the corresponding uronate derivatives, including disaccharide building blocks for GAG fragments and precursors to saponins. The beneficial effect of Aliquat 336 was also disclosed in the oxidation of certain substrates.

Keywords: Uronate; Oxidation; TEMPO; $Ca(OCl)_2$; Saponin

Repeating disaccharides composed of a uronic acid and a 2-amino sugar constitute glycosaminoglycans (GAGs), that is, hyaluronan, chondroitin, dermatan, heparin, and heparan sulfate, which are ubiquitous in extracellular matrix of animals and play essential roles in various cellular processes, including cell growth and cell–cell interactions.[1] Uronates also occur as a important structural units in a number of bacterial capsular polysaccharides and plant glycosides that show a variety of biological activities.[2,3] Furthermore, glucuronates are frequently the final form of a drug or xenobiotic eliminated from the body, performing a detoxification role.[4] A key step in the synthesis of uronates usually employs the oxidation of the primary hydroxyl groups of the sugar moieties to carboxylic acids.[4,5] A selective oxidation in the presence of secondary hydroxyl groups would greatly simplify the protecting group manipulations.[6] This idea has been realized mostly resorting to the oxidation protocol developed by Anelli and co-workers in 1987 employing a TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) (cat)–KBr (cat)–NaOCl system under aqueous conditions.[6–8] Here we applied a modified protocol with $Ca(OCl)_2$ as the terminal oxidant for the selective oxidation of the substrates (**1a**–**l**) with a variety of aqueous solubilities.

In the TEMPO–Br^-–NaOCl oxidation system, the primary hydroxyl groups are oxidized to aldehydes by the oxoammonium salt of TEMPO generated in situ via oxidation with ClO^- and/or BrO^-. The hypohalogenous species then oxidize the resulting aldehydes to carboxylic acids.[7,8] The latter oxidation takes place in the aqueous phase; thus phase-transfer catalysts are required for hydrophobic substrates. The pH is critically important to the oxidation, which determines the interconversion of the oxidation species in the system. In addition, oxidation of a hydroxymethyl group to an aldehyde involves release of a H^+ so as to drop the pH sharply. Therefore, the reaction medium is usually buffered with $NaHCO_3$ at pH 8.6–9.5. In some cases, higher pH was carefully controlled to execute the oxidation via adding dilute NaOH solution during the reaction.[6c,d,h,j,k] NaOCl is commercially available in dilute aqueous solution that deteriorates rather rapidly; thus the solution needs titration before use to define the quantity of oxidant present.[9a] Alternatively, $Ca(OCl)_2$ is a stable and inexpensive solid hypochlorite oxidant.[9b] Its use as an

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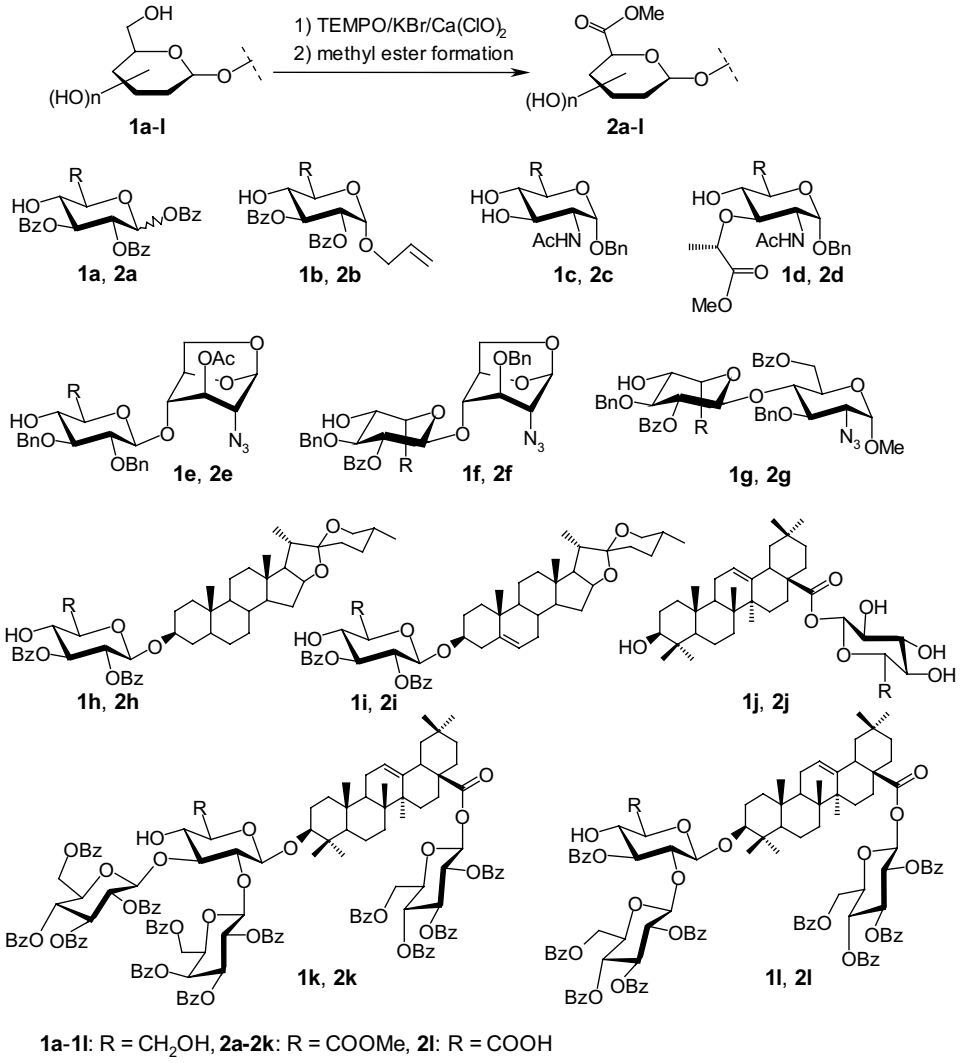
0008-6215/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2004.02.001



Scheme 1.

alternative to NaOCl in the TEMPO-mediated oxidation has been demonstrated by Torii and co-workers.[10] However, only two papers have so far reported the oxidation of two monosaccharide 4,6-diols with the TEMPO–KBr–$Ca(OCl)_2$ system.[11] In addition, these authors dissolved $Ca(OCl)_2$ in an aqueous $NaHCO_3$ solution before use, and in fact a NaOCl solution was prepared.[9b,c] Addition of aqueous NaOCl solution dilutes the reaction system so as to cause pH change and the precipitation of certain substrates in the biphasic reaction medium. We found the addition of $Ca(OCl)_2$ solid to be more convenient and controllable. In fact, substrates **1a**–**l** were reliably oxidized into the corresponding uronates (**2a**–**l**) in satisfactory yields under the present modified operation conditions (Scheme 1, Table 1).

The present typical procedure is nicely applicable to the partially protected monosaccharides **1a**,**b**, and **1d**, disaccharides **1e** and **1f**, and the saponin derivatives **1h**,**k**, and **1l**, affording the desired uronates, after methylation (except for **2l**), in satisfactory 71–89% yields (entries 1, 2, 4–6, 8, 11, 12).[†] For the water-soluble GluNAc 3,4,6-triol **1c**, the oxidation was carried out in an aqueous solution free of the organic solvent, giving methyl uronate **2c** in 85% yield after methylation with MeI (Na_2CO_3, DMF, 50 °C) (entry 3). Glucosyl oleanolic ester **1j** is insoluble in either water or CH_2Cl_2; therefore 1:4 H_2O–*t*-BuOH was used as the reaction medium. The oxidation was completed with 4 equiv of $Ca(OCl)_2$ at 10 °C, affording after methylation the desired uronate **2j** in a satisfactory 65% yield, where the three secondary OHs on the glucose

[†] The ^1H NMR signal changes from the starting pyranosides to the resulting methyl uronates are very diagnostic: the H-5 signal moves downfield from a multiplet to a doublet ($J = \sim 9.6$ Hz, for glucuronates), the two H-6 signals disappear, and the nascent COOMe singlet appears downfield (3.74–3.88 ppm).

Table 1. Selective oxidation to prepare uronates with TEMPO–KBr–$Ca(OCl)_2$ under aqueous conditions

Entry	Substrate	Conditions[a,b]	Product	Yield (%)
1	**1a**	A	**2a**	83
2	**1b**	A	**2b**	70
3	**1c**	B[b]	**2c**	85
4	**1d**	A[b]	**2d**	71
5	**1e**	A	**2e**	73
6	**1f**	A	**2f**	83
7	**1g**	A; C	**2g**	54; 93
8	**1h**	A	**2h**	78
9	**1i**	A; C	**2i**	0; 51
10	**1j**	D[b]	**2j**	65
11	**1k**	A	**2k**	72
12	**1l**	A[c]	**2l**	89

[a] Conditions: (A) TEMPO (0.02 equiv), KBr (0.2 equiv), $Ca(OCl)_2$ (2 equiv), $Bu_4N^+Br^-$ (0.2 equiv), 1:1 CH_2Cl_2–aq $NaHCO_3$, 0 °C, 45 min; then CH_2N_2, THF, rt. See the typical procedure for detailed experiment. (B) Free of organic solvent (CH_2Cl_2). (C) Aliquat 336 ($CH_3(C_8H_{17})_3N^+Cl^-$, 0.2 equiv) was used in place of $Bu_4N^+Br^-$. (D) The solvent was changed to 1:4 H_2O–*t*-BuOH; 4 equiv of $Ca(OCl)_2$ was required to complete the oxidation.

[b] Subsequent methylation was carried out with MeI in DMF in the presence of Na_2CO_3 (1 equiv) at 50 °C for 3 h.

[c] Methylation was not carried out.

moiety and the secondary 3-OH of the aglycone remained intact (entry 10). Although, subjection of the steroidal glycosides **1h** to the present typical oxidation procedure gave, after methylation, the expected uronate **2h** in good yield (78%) (entry 8), oxidation of **1i**, which bears an additional 5,6-double bond on the steroid, under the similar conditions failed to provide the desired uronate (**2i**). In the major products isolated the 5,6-double bond was absent as indicated by ^1H NMR spectroscopy.[12] It is noted that the double bonds in **1b** and **1j–l** remained intact during oxidation under similar conditions. Interestingly, when Aliquat 336 ($CH_3(C_8H_{17})_3N^+Cl^-$) was employed in place of the previous phase-transfer catalyst, $Bu_4N^+Br^-$, oxidation of **1i** provided **2i** in 51% yield (entry 9). The Aliquat 336 is capable of forming inverted micelles[13] that might provide accommodations to the lipophilic steroidal moiety so as to prevent the double bond from attack by the halogenous species. The beneficial effect of using Aliquat 336 instead of $Bu_4N^+Br^-$ was also found when oxidizing disaccharide **1g**, where the yield of uronate **2g** increased from 54% to 93% (entry 7).

In summary, the use of solid $Ca(OCl)_2$ in place of NaOCl in the TEMPO-mediated oxidation has the benefit of easier operation. The present modified operation has been reliably applied to a variety of substrates to prepare uronates, where disaccharides **2e–g** are important building blocks for the synthesis of heparin and heparan sulfate fragments, and **2h–l** are advanced precursors to the synthesis of glucuronic acid-containing saponins.[14] This is the first application of the TEMPO-mediated selective oxidation to the saponin substrates. It shall be also valuable to disclose the beneficial effect of Aliquat 336 in the oxidation of certain substrates.

1. Experimental

1.1. General methods

See Ref. 15.

A typical procedure is as follows: To a solution of the alcohol **1f** (0.6 mmol) in CH_2Cl_2 (1.5 mL) containing TEMPO (2 mg, 0.02 equiv) was added a solution of satd aq $NaHCO_3$ (1.5 mL, its pH was adjusted to 9.5 with satd aq Na_2CO_3) containing KBr (11 mg, 0.2 equiv), and $Bu_4N^+Br^-$ (14 mg, 0.2 equiv). The mixture was cooled to 0 °C. Under vigorous stirring, $Ca(OCl)_2$ was added

Table 2. ^1H NMR and MS data for compounds **2a–l**

Compound	^1H NMR (300 MHz, $CDCl_3$): δ	ESIMS (*m*/*z*)
2a	α-Isomer: 6.82 (d, 1H, *J* 3.9 Hz, H-1), 4.58 (d, 1H, *J* 10.2 Hz, H-5), 3.86 (s, 3H, OMe); β-isomer: 6.21 (d, 1H, *J* 7.5 Hz, H-1), 3.83 (s, 3H, OMe).	543.4 [M+Na^+]
2b	5.89 (dd, 1H, *J* 9.6 Hz, H-3), 5.86 (m, 1H, OCH_2CH=CH_2), 5.37 (d, 1H, *J* 3.6 Hz, H-1), 5.32 (m, 1H, OCH_2CH=CH_2), 5.27 (m, 1H, OCH_2CH=CH_2), 5.17 (d, 1H, *J* 10.5 Hz, H-2), 4.45 (d, 1H, *J* 9.6 Hz, H-5), 4.30 (m, 1H, OCH_2CH=CH_2), 4.04 (m, 2H), 3.88 (s, 3H, OMe).	479.1303 [M+Na^+] (calcd 479.1313)
2c	($(CD_3)_2CO$): 7.40–7.29 (m, 5H, Ph), 4.95 (d, 1H, *J* 3.6 Hz, H-1), 4.75 and 4.52 (AB, 2H, *J* 12.3 Hz), 4.13 (d, 1H, *J* 9.3 Hz, H-5), 4.00 (m, 1H, H-2), 3.74 (s, 3H, OMe), 3.76–3.66 (m, 2 H), 1.91 (s, 3H, Ac).	362.1221 [M+Na^+] (calcd 362.1210)
2d	7.42–7.27 (5H, Ph), 5.59 (d, 1H, *J* 9.6 Hz, N*H*), 5.06 (s, 1H, OH), 4.89 (d, 1H, *J* 3.9 Hz, H-1), 4.75 and 4.46 (AB, 2H, *J* 11.4 Hz), 4.39 (m, 1H, H-3), 4.22 (d, 1H, *J* 9.6 Hz, H-5), 4.13 (m, 1H, H-2), 3.88 (m, 1H), 3.85 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.40 (t, 1H, *J* 9.3 Hz, H-4), 1.96 (s, 3H, Ac), 1.38 (d, 3H, *J* 6.0 Hz, Me).	448.1558 [M+Na^+] (calcd 448.1578)
2e	5.49 (br s, 1H, H-1), 5.29 (dd, 1H, *J* 1.5 Hz, H-3), 4.99 (AB, 1H, *J* 10.8 Hz), 4.87 (AB, 2H, *J* 11.4 Hz), 4.77 (AB, 1H, *J* 10.8 Hz), 4.64 (d, 1H, *J* 7.5 Hz, H-1′), 4.57 (d, 1H, *J* 5.1 Hz, H-5), 4.02 (dd, 1H, *J* 7.5, 0.9 Hz, H-4), 3.88 (dd, 1H, *J* 8.0 Hz), 3.84 (d, 1H, *J* 9.6 Hz, H-5′), 3.79 (s, 3H, OMe), 3.76 (m, 1H), 3.65 (br s, 1H), 3.55 (m, 2H), 3.20 (br, 1H, H-2), 2.12 (s, 3H, OAc).	622.2 [M+Na^+]

(*continued on next page*)

Table 2 (*continued*)

Compound	^{1}H NMR (300 MHz, $CDCl_3$): δ	ESIMS (m/z)
2f	5.52 (s, 1H, H-1), 5.36 (s, 1H, H-1′), 5.31 (m, 1H, H-2′), 4.90 (s, 1H, H-5′), 4.88 (AB, 1H, *J* 12.0 Hz), 4.75 (d, 1H, *J* 5.5 Hz, H-5), 4.68 (AB, 1H, *J* 12.0 Hz), 4.57 (d, 1H, *J* 7.0 Hz, C*H*$_2$Ph), 4.13 (d, 1H, *J* 7.0 Hz), 4.05 (d, 1H, *J* 7.2 Hz, H-4), 3.92(br, 1H), 3.82 (m, 1H), 3.79 (s, 3H, OMe), 3.77 (m, 1H), 3.68 (m, 1H), 3.26 (d, 1H, *J* 3 Hz, H-2).	684.2 [M+Na$^+$]
2g	8.10–7.25 (m, 20H, Ph), 5.37 (s, 1H, H-1′), 5.21 (br, 1H, H-2′), 4.97 (d, 1H, *J* 2.1 Hz, H-5′), 4.76 (AB, 2H, *J* 11.4 Hz), 4.81–4.67 (m, 4H), 4.48 (AB, 1H, *J* 12.0 Hz), 4.02 (d, 1H, *J* 7.8 Hz), 4.13–3.96 (m, 2H), 3.92–3.86 (m, 2H), 3.48 (s, 3H, OMe), 3.45 (s, 3H, OMe), 3.44 (m, 1H), 2.66 (d, 1H, *J* 9.0 Hz, OH).	820.3 [M+Na$^+$]
2h	7.97–7.37 (m, 10H, Ph), 5.51 (dd, 1H, *J* 9.5 Hz, H-3′), 5.39 (dd, 1H, *J* 8.6 Hz, H-2′), 4.86 (d, 1H, *J* 7.8 Hz, H-1′), 4.39 (m, 1H, H-16), 4.19 (dd, 1H, *J* 9.3 Hz, H-4′), 4.07 (d, 1H, *J* 9.6 Hz, H-5′), 3.86 (s, 3H, OMe), 3.62 (m, 1H, H-3), 3.47–3.30 (m, 2H), 0.74 (d, 3H, *J* 6.9 Hz), 0.78 (d, 3H, *J* 6.0 Hz), 0.72, 0.68 (s each, 2 × Me).	832.5 [M+NH$_4^+$]
2i	8.01–7.35 (m, 10H, Ph), 5.53 (dd, 1H, *J* 10.2 Hz, H-3′), 5.41 (dd, 1H, *J* 9.6 Hz, H-2′), 5.26 (d, 1H, *J* 4.8 Hz, H-6), 4.87 (d, 1H, *J* 5.4 Hz, H-1′), 4.40 (m, 1H, H-16), 4.19 (m, 1H), 4.08 (d, 1H, *J* 9.9 Hz, H-5′), 3.86 (s, 3H, OMe), 3.59–3.34 (m, 3H), 0.98 (d, 3H, *J* 6.6 Hz, Me), 0.92 (s, 3H, Me), 0.79 (d, 3H, *J* 6.6 Hz, Me), 0.76 (s, 3H, Me).	835.4 [M+Na$^+$]
2j	(CD_3OD): 5.43 (d, 1H, *J* 7.7 Hz, H-1′), 5.26 (t, 1H, *J* 3.6 Hz, H-12), 3.91 (d, 1H, *J* 9.6 Hz, H-5′), 3.77 (s, 3H, OMe), 3.57 (t, 1H, *J* 9.1 Hz), 3.45 (t, 1H, *J* 8.4 Hz), 3.39 (t, 1H, *J* 9.1 Hz), 3.15 (m, 1H, H-3), 2.88 (m, 1H, H-18), 1.28, 1.16, 0.98, 0.95, 0.92, 0.78, 0.77 (7 × s, 7 × Me).	669.4 [M+Na$^+$]
2k	5.97 (t, 1H, *J* 9.6 Hz), 5.94 (d, 1H, *J* 8.5 Hz), 5.90 (t, 1H, *J* 9.8 Hz), 5.78–5.69 (m, 2H), 5.58 (t, 2H, *J* 8.4 Hz), 5.52–5.43 (m, 2H), 5.38 (d, 1H, *J* 3.6 Hz), 5.27 (s, 1H), 4.68 (d, 1H, *J* 7.7 Hz), 4.60 (d, 1H, *J* 8.0 Hz), 4.56 (dd, 1H, *J* 12.4, 2.8 Hz), 4.45 (dd, 1H, *J* 12.2, 4.8 Hz), 4.42–4.30 (m, 2H), 4.28–4.16 (m, 2H), 4.03 (dd, 1H, *J* 11.0, 7.7 Hz), 3.88–3.75 (m, 2H), 3.78 (s, 3H), 3.70 (d, 1H, *J* 9.6 Hz), 3.58 (t, 1H, *J* 8.6 Hz), 3.53 (s, 1H), 3.02 (dd, 1H, *J* 15.7, 4.2 Hz), 2.78 (d, 1H, *J* 9.0 Hz), 2.62 (m, 1H), 2.33 (t, 1H, *J* 6.9 Hz), 1.16, 1.02, 0.98, 0.95, 0.86, 0.82, 0.42 (7 × s, 7 × Me).	2403.3 [M+Na$^+$]
2l	See Ref. 14.	

slowly in small portions. After 45 min at 0 °C, the reaction was quenched with $Na_2S_2O_3$ (100 mg). After addition of water (1.5 mL) and CH_2Cl_2 (4 mL), aq HCl (6 N) was added to adjust the final pH to pH 3. Then the organic phase was separated, and the remaining aq phase was extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried with Na_2SO_4, and then concentrated in vacuo. In order to facilitate the purification and characterization, the corresponding methyl uronate was prepared via treating the crude uronate with CH_2N_2 in THF at rt. Chromatography on a silica gel column provided the desired **2f** (329 mg, 83%). See Table 2 for characterization data for compounds **2a**–**l**.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (29925203) and the Committee of Science and Technology of Shanghai (02QMA1401).

References

1. (a) Bhavanandan, V. P.; Davidson, E. A. In *Glycoconjugates*; Allen, H. J., Kisailus, E. C., Eds.; Marcel Dekker: New York, 1992; p 167; (b) Kjellen, L.; Lindahl, U. *Ann. Rev. Biochem.* **1991**, *60*, 443.
2. (a) Lindberg, B.; Kenne, L. In *The Polysaccharides*; Academic: New York, 1985; Vol. 2, p 287; (b) Lindberg, B. *Adv. Carbohydr. Chem. Biochem.* **1990**, *48*, 279.
3. Hostettmann, K.; Marston, A. *Saponins*; Cambridge, UK: Cambridge University Press, 1995.
4. For a comprehensive review on glucuronide synthesis, see: Stachulski, A. V.; Jenkins, A. N. *Nat. Prod. Rep.* **1998**, 173–186.
5. Relevant Ref. cited in: Yu, B.; Zhu, X.; Hui, Y. *Org. Lett.* **2000**, *2*, 2539–2541.
6. For selective oxidation of saccharides to uronates with TEMPO–Br$^-$–NaOCl, see, for example: (a) Davis, N. J.; Flitsch, S. L. *Tetrahedron Lett.* **1993**, *34*, 1181–1184; (b) Davis, N. J.; Flitsch, S. L. *J. Chem. Soc., Perkin Trans. 1* **1994**, 359–368; (c) de Nooy, A. E. J.; Besemer, A. C.; van Bekkum, H. *Carbohydr. Res.* **1995**, *269*, 89–98; (d) Heeres, A.; van Doren, H. A.; Gotlieb, K. F.; Bleeker, I. P. *Carbohydr. Res.* **1997**, *299*, 221–227; (e) Battistelli, C. L.; De Castro, C.; Iadonisi, A.; Lanzetta, R.; Mangoni, L.; Parrilli, M. *J. Carbohydr. Chem.* **1999**, *18*, 69–86; (f) Garegg, P. J.; Oscarson, S.; Tedebark, U. *J. Carbohydr. Chem.* **1998**, *17*, 587–594; (g) Yeung, B. K. S.; Hill, D. C.; Janicka, M.; Petillo, P. A. *Org. Lett.* **2000**, *2*, 1279–1282; (h) Kraus, T.; Budesinsky, M.; Zavada, J. *Eur. J. Org. Chem.* **2000**, 3133–3137; (i) Haller, M.; Boons, G.-J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 814–822; (j) Thaburet, J.-F.; Merbouh, N.; Ibert, M.; Marsais, F.; Queguiner, G. *Carbohydr. Res.* **2001**, *330*, 21–29; (k) Soderman, P.; Widmalm, G. *Eur. J. Org. Chem.* **2001**, 3453–3456; (l) Lefeber, D. J.; Arevalo, E. A.; Kamerling, J. P.; Vliegenthart, J. F. G. *Can. J. Chem.* **2002**, *80*, 76–81; (m) Bouktaib, M.; Atmani, A.; Rolando, C. *Tetrahedron Lett.* **2002**, *43*, 6263–6266; (n) Brochette-Lemoine, S.; Joannard, D.; Descotes, G.; Bouchu, A.; Queneau, Y. *J. Mol. Catalysis*

1999, *150*, 31–36; (o) Lemoine, S.; Thomazeau, C.; Joannard, D.; Trombotto, S.; Descotes, G.; Bouchu, A.; Queneau, Y. *Carbohydr. Res.* **2000**, *326*, 176–184.
7. (a) Anelli, P. L.; Biffi, C.; Montanari, F.; Quici, S. *J. Org. Chem.* **1987**, *52*, 2559–2562; (b) Anelli, P. L.; Banfi, S.; Montanari, F.; Quici, S. *J. Org. Chem.* **1989**, *54*, 2970–2972.
8. For a comprehensive review on the TEMPO-mediated oxidation of alcohols, see: de Nooy, A. E. J.; Besemer, A. C.; van Bekkum, H. *Synthesis* **1996**, 1153–1174.
9. (a) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons, 1995; Vol. 7, p 4580; (b) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons, 1995; Vol. 2, p 966; (c) *Gmelins Handbuch der Anorganischen Chemie*; Verlag Chemie, GmbH 1964; System-number 21, p 156.
10. Inokuchi, T.; Matsumoto, S.; Nishiyama, T.; Torii, S. *J. Org. Chem.* **1990**, *55*, 462–466.
11. (a) Magaud, D.; Grandjean, C.; Doutheau, A.; Anker, D.; Shevchik, V.; Cotte-Pattat, N.; Robert-Baudouy, J. *Carbohydr. Res.* **1998**, *314*, 189–199; (b) Karst, N.; Jacquinet, J.-C. *Eur. J. Org. Chem.* **2002**, 815–825.
12. Addition of hypohalogenous acids to the double bond has been mentioned, see: Ref. 7a and Dalcanale, E.; Montanari, F. *J. Org. Chem.* **1986**, *51*, 567–569.
13. Neumann, R.; Khenkin, A. M. *J. Org. Chem.* **1994**, *59*, 7577–7579.
14. Peng, W.; Sun, J.; Lin, F.; Han, X.; Yu, B. *Synlett* **2004**, 259–262.
15. Sun, J.; Han, X.; Yu, B. *Carbohydr. Res.* **2003**, *338*, 827–833.