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Direct Preparation of N-Glycosidic Bond-Linked Nonionic Carbohydrate-Based Surfactant (NICBS) via Ritter Reaction

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Dedicated to the memory of Professor Ramiro Sanchez

Keywords: Ritter reaction / Carbohydrates / Surfactants / Carbocations / Acylation

The Ritter reaction has been successfully extended to the direct preparation of N-glycosidic bond-linked nonionic carbohydrate-based surfactants from carbohydrates and nitriles in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and silver perchlorate ($AgClO_4$) on a high-speed mechanical shaker. The new surfactant molecules have the features of low toxicity, environmental compatibility and biodegradability.

Introduction

Although polyethyleneglycol (PEG)[1] based nonionic surfactants have found many applications in metal recovery,[2] soil bioremediation,[3] preparation of nanosized particles,[4] and detergents (e.g., Triton X-100),[5] etc., nonionic carbohydrate-based surfactants (NICBS) including alkyl polyglycosides (APGs)[6] and *N*-acyl-*N*-methylglucamides[7] have become increasingly important today. Such a trend is possibly because PEG-type surfactants possess a cloud point[8] and separate into two phases at somewhat elevated temperature due to the dehydration of the hydrophilic headgroup.[9] Other drawbacks of PEG-type surfactants include persisting environmental concerns, a forseeable shortage originating from petrochemical resources,[10] and the high solubility of APGs in lipophilic media which necessitates large amounts of surfactant for solubilization, emulsification and detergency.[8] In contrast, NICBSs are sustainably available, biocompatible, biodegradable[6a] and low (or non-) toxic. In addition, they do not possess cloud points because of the highly hydrophilic carbohydrate headgroups.[8] The increasing demand for NICBSs are also evidenced by the inauguration of a 23000 tons per annum (tpa) production plant for APGs by the Henkel Corporation in USA in 1992, and Henkel KGaA in Germany in 1995 with equal production capacity of APGs,[6b] as well as a 40000 tpa capacity for *N*-acyl-*N*-methylglucamides.[11] Notably, *N*-acyl-*N*-methylglucamides (simplified as glucamides, vide infra), the second largest used carbohydrate-based surfactants, have found wide applications, mainly because of their mildness,[12] stability, rinsability,[13] synergistic effect with anionic surfactants,[14] and particularly their excellent functions in foaming, thickening, emulsifying[12] and degreasing.[15] For example, glucamides have been applied as sole surfactants[7c] or in combination with sodium dodecyl sulfate (SDS) in toothpaste;[16] and are used in shampoo and soap bar for foaming.[17] More importantly, due to strong hydrogen bonding among hydrophilic headgroups, glucamides have been applied to accelerate emulsion polymerization[18] and to prepare technical membranes,[12] especially the stable monolayers used for the solubilization of membrane proteins from animal cells.[7d] Additionally, glucamides are readily biodegradable, as evidenced by 99 % of primary degradation and more than 98 % of DOC removal from the standard degradation test using a batch-activated sludge system and the modified Sturm test.[19]

Results and Discussion

Reported in this work is a new type of nonionic carbohydrate-based surfactant, and its simple preparation method. The new surfactant molecules have a β-N-glycosidic bond connecting to a hydrophobic tail, and are quite different from the known glucamide surfactants (Figure 1). Conventionally, glucamide surfactants are usually prepared from reductive amination of glucose and methylamine by hydrogenation over Raney nickel,[20] followed by amidation under the Schotten–Bauman condition,[21] so that the C1 of the carbohydrate moiety is in an alcohol oxidation state

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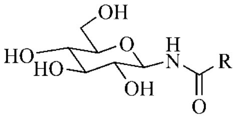
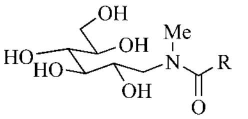
rather than an aldehyde oxidation state, and the carbohydrate ring is opened after the amination.[20] In contrast, the C1 of the carbohydrate moiety in our case is still in an aldehyde oxidation state with one proton on the nitrogen atom.



N-acyl-1-deoxyglucopyranosylamines

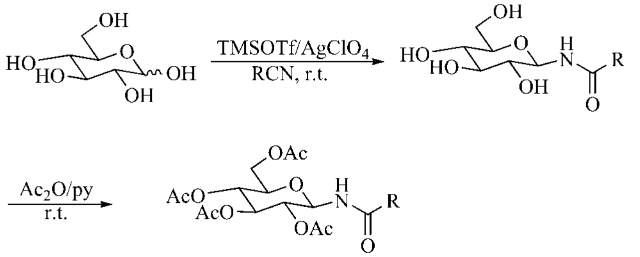


glucamides

Figure 1. The general structure of *N*-acyl-1-deoxyglucopyranosylamines and glucamides.

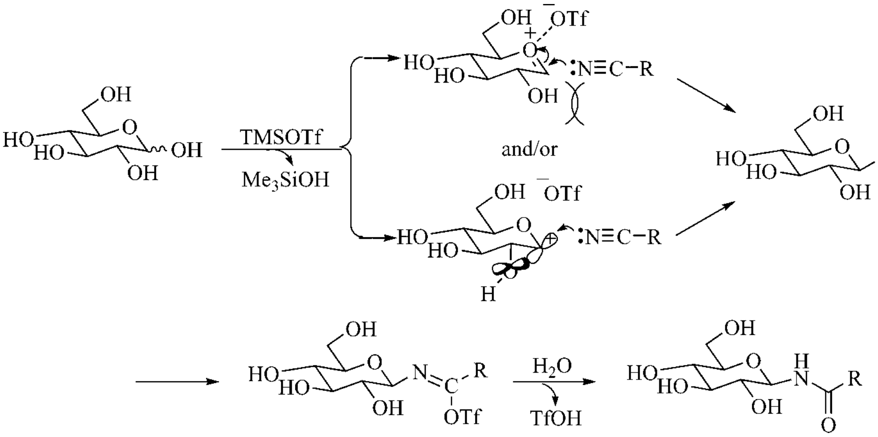
We believe that the new surfactants would have similar applications to those glucamides, and in some points, they are superior to those glucamides for the following reasons. First, the new compounds are stable enough to be applied as surfactants, as indicated by the wide distribution of similar N-glycosidic bonds in glycopeptides,[22] glycoproteins[23] and nucleotides. Second, NICBSs should be more hydrophilic and, thus, form more stable micelles than glucamides do. Greater hydrophilicity is expected because there is one more proton on the nitrogen atom of the amide bond in NICBS, which can participiate in hydrogen bonding as with the peptide bonds of protein in forming β-sheet; whereas in glucamides the hydrogen is replaced by a methyl group, and the carbonyl group in such amido group might not be accessible for hydrogen bonding due to the increased steric hindrance. Moreover, even though the glucamides are readily biodegradable,[19] the new surfactant molecules should be more benign to the environment because the amide linkage in our case is connected to a carbohydrate moiety via a *N*-glycosidic bond, which is more labile for degradation than a normal amide bond, as in peptides and glucamides. In addition, the new molecules would have lower toxicity, if any, than the glucamides, because the new surfactant molecules degrade into fatty acid and glucosylamine. In comparison, the glucamides may be converted into fatty acids and *N*-methylglucosylamine after degradation, and methylamines are generally considered to be toxic.[24]

We also report here a facile preparation of such surfactant molecules directly from carbohydrate and nitriles in the presence of a Lewis acid, under mechanical agitation from a high speed shaker,[25] as shown in Scheme 1. The resulting molecules are then acetylated for the sake of structural characterization. The product can also be prepared directly from β-D-glucose pentaacetate and nitrile under the same reaction conditions. The presence of hydrogen on the N-glycosidic linkage is clearly indicated from the combination of ^{1}H NMR, H-H COSY and H-C HSQC spectra, where the NH signal is not correlated to the carbon signal in the HSQC spectrum, as shown in the supporting information (for supporting information see also the footnote on the first page of this paper).



Scheme 1. The preparation of *N*-acyl-1-deoxy-β-*D*-glucopyranosylamines and their derivatives.

Such facile preparation of NICBS has the following features. First, the reaction is carried out under mechanochemical treatment that has been verified to accelerate reaction rate.[26] Our results have shown that carbohydrates in the solid state can be efficiently acylated to peresters of a single configuration with good to high yields under mechanical force.[25] In this work, the mixture of carbohydrate, TMSOTf and an excess of nitrile was vigorously vibrated on a high-speed shaker at room temperature, and was worked-up after 7 to 24 h. However, the same reaction under magnetic stirring was remarkably slow. Comparing to the mechanochemical force, microwave has also been widely applied in organic synthesis to accelerate chemical reactions.[27] One such example is the preparation of glycosylation from Kochetkov amination under microwave irradiation at 40 °C, for which the reaction time has been shortened from typically 5 d to only 90 min. By treatment of 2-iminothiolane, Seeberger et al., have converted the resulting glycosylamines into almidine derivatives[28] that are similar to but not exactly the same as our NICBSs with amido linkage between the carbohydrate and the hydrocarbon tail. Second, even though protection and deprotection are usually required for most carbohydrate transformations,[29] the carbohydrate was used directly in our case without any protection. Regarding another feature of our preparation of NICBSs, activation of the carbohydrate is not necessary, although it is common that glycol donors are usually activated by means of conversion into glycosyl halides,[30] sulfides,[31] or trichloroacetimidates,[32] etc., then reacted with glycol acceptors in the presence of a Lewis acid. Furthermore, such a one-step reaction is facile but justifiable between carbohydrates and nitriles. Although in many organic reactions nitriles are applied as either solvents (e.g., acetonitrile[33]) or electrophiles[34] to give compounds such as imidates[33] or ketones,[34] there are also many examples in which nitriles function as nucleophiles in the presence of even stronger electrophiles (e.g., carbocations). Under these conditions, carbocations have one empty p orbital, and the nitrogen atoms of nitriles have one pair of electrons, so that the lone pair electrons can fill into the empty p orbital of the carbocations to form nitrilium cations. The resulting nitrilium cations in the presence of water are converted into amides.[35] This type of reaction is generally referred to as



Scheme 2. Possible mechanism for the formation of N-glycosidic surfactant.

a Ritter reaction,[35,36] and has been observed for alcohols and olefins,[35] as well as trioxanes,[37] *N*-tosylazetidines,[38] aziridines[36d] and epoxides.[36c]

In addition, the Ritter reaction is not new for carbohydrate chemists either, though it has not been explored extensively. As an example, Hindsgaul et al., have applied the Ritter reaction to the combinatorial synthesis of a small β-peptide library from three different ketoses and three different amines in the presence of a nitrile.[39] In fact, the formation of the nitrilium cation in carbohydrate chemistry has been noted as early as 1991 by Sinaÿ who rationalized the β-selectivity for the glycosylation of thioglycosides in acetonitrile in the presence of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (TBPA$^{\cdot+}$), a stable radical cation that functions as a one-electron transfer reagent.[31d] Recently, Crich et al., have applied the Ritter reaction to enhance the β-selectivity of the L-rhamnopyranosylation of thioglycosides by addition of 5% of acetonitrile or propionitrile to the reaction solution, using 1-(phenylsulfinyl)piperidine/trifluoromethanesulfonic anhydride as the promoter.[40] In addition, even in the presence of such a little amount of acetonitrile or propionitrile in dichloromethane, the competing Ritter reaction with the desired glycosylation is still detectable, though the intermediate decomposes immediately. Our study probably is the second to actually isolate the Ritter reaction product involving carbohydrate, which indicates the feasibility of preparation of carbohydrate-containing nonionic surfactant molecules directly from nitriles of long hydrocarbon tails and simple carbohydrates without prior protection and activation. It is known that the outcome of the Ritter reaction depends on the reactivity of nitriles as well as the stability of carbocations,[42] thus tertiary alcohols give much higher yields of Ritter products than primary or secondary alcohols.[41] Similarly, in our reaction, C1 of the carbohydrate forms the most stable carbocation to react with nitrile. It is worth noting that the electron-rich nitriles readily react with carbohydrate, whereas electron-deficient nitriles (e.g., benzonitrile) react poorly or do not react at all.

Another feature of our study is that all the N-glycosidic bonds are proven to be of β-configuration from NMR spectra. This is as would be expected being that carbohydrate in the presence of Lewis acid (e.g., TMSOTf) is converted into an oxonium cation, and nitrile adds to the oxonium double bond preferably from the top of the carbohydrate ring because of the blockage of 2-OH at the bottom of the ring, as shown in Scheme 2. Alternatively, the empty p orbital of the carbocation intermediate may partially share an electron from the lone pair electrons of oxygen at the C2 position, and the other side of the p orbital is more electron-deficient, thus the nitrogen atom can approach from the top of the ring, leading to the formation of β-N-glycosidic bond. This result is consistent with the results of Sinaÿ, Crich, as well as others where nitriles favor the β-selectivity.[43] Additionally, like other Ritter reactions, the Ritter reaction with carbohydrates can also take place in the presence of TMSOTf without the addition of $AgClO_4$. However, the addition of $AgClO_4$ generally gives a cleaner reaction. Moreover, it should be pointed out that the Ritter reaction is also competed with other side reactions involving carbocations, such as the ring-enlargement of cyclic carbocations,[35c] the rearrangement of carbocations,[43] etc. The Ritter reaction of a carbohydrate having more than one OH group may lead to the formation of many carbocation centers and give side products; however, often the acylamino glycosides are isolated as major products. Finally, our reaction condition is very close to many reported glycosylations carried out in acetonitrile in the presence of TMSOTf or other Lewis acids.[44] This study indicates the potential complication of glycosylation when carried out in acetonitrile.

Conclusions

In conclusion, we report herein a new type of nonionic carbohydrate-based surfactant that holds many structural features of interest and is benign to the environment. Concurrently, this type of surfactant molecule can be simply prepared by the Ritter reaction between carbohydrates and nitriles of long hydrocarbon chain under mechanochemical force without prior protection and activation.

Experimental Section

Typical Experimental Procedure: D-Glucose (0.225 g, 1.25 mmol), acetonitrile (10 mL, 191.5 mmol), $AgClO_4$ (66 mg, 0.3 mmol), and TMSOTf (d = 1.228 g/mL, 0.4 mL, 2.2 mmol) were added to an 18-mL scintillation vial. The vial was capped and mounted to the high-speed shaker. After 3 h of vigorous vibration at room temperature, solid glucose disappeared, and a rose or red purple solution formed. After 24 h, 0.5 mL of Et_3N was added to quench the reaction, and the mixture was directly loaded to a 10-cm silica gel column and washed with hexane/EtOAc (2:1 to 1:1) to remove unreacted acetonitrile and Et_3N, and then eluted with EtOAc/MeOH (3:1). Upon evaporation, 0.237 g of viscous oil was obtained 85.8% and the oil was directly acetylated with 2 mL of Ac_2O in 2 mL of pyridine. The reaction mixture was diluted with 50 mL of EtOAc and washed with 1 N HCl (3 × 20 mL), saturated $NaHCO_3$ aqueous solution (2 × 20 mL) and brine (20 mL), and dried with $CaCl_2$. After removal of solvent, the residue was purified by silica gel column chromatography using hexane/EtOAc (5:1 to 3:2) to afford 0.113 g of 1-acetamido-2,3,4,6-tetraacetyl-1-deoxy-β-D-glucopyranose, in yield of 27.1%.

Supporting Information (see footnote on the first page of this article): Experimental procedures for other nitriles, the characterization of synthesized molecules by both HRMS and NMR (^{1}H NMR, ^{13}C NMR, H-H COSY and H-C HSQC).

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