



Oxidation and degradation of native wheat starch by acidic bromate in water at room temperature

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ABSTRACT

Native wheat starch was oxidized by benign acidic bromate in water at room temperature. HPLC-ELSD study indicated that starch degraded in the course of oxidation but it still had a polymeric structure characterized by ¹H, ¹³C, HSQC and HMBC NMR measurements. Products were generally water-soluble fragments but the use of a short reaction time and dilute reaction mixture yielded water-insoluble products. Titration of the products showed, that the increase of the starch content and reaction time increased the content of carbonyl and carboxyl groups in the range of 0.5–2.5% and 1.7–17.2%, respectively, in the product fragments. A mechanism for the oxidation reaction was proposed.

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1. Introduction

Starch is a natural carbohydrate polymer obtained from numerous botanical sources like cereals, roots and tubers (Tharanathan, 2005). It is biodegradable, abundantly available and contains various possibilities for modification (Serrero et al., 2010; Zhang, Zhang, Wang, & Wang, 2009). Starch has a granular structure, which consists of a practically linear amylose whose glucose units are linked by $\alpha(1 \rightarrow 4)$ bonds and a highly branched amylopectin with a $\alpha(1 \rightarrow 4)$ backbone containing $\alpha(1 \rightarrow 6)$ branches (Izydorczyk, 2005; Tavares et al., 2004). Starch and its derivatives are widely used in many fields including plastics, food and medical industry (Zhang, Wang, Zhang, Yang, & Wang, 2010), cosmetics and pharmaceuticals (Rinaudo, 2008).

Oxidized starch (Kato, Matsuo, & Isogai, 2003; Wing & Willett, 1997; Zhu, Sjöholm, Nurmi, & Bertoft, 1998) is one of most studied starch derivatives and dialdehyde starch (DAS) is most valuable one (Du et al., 2008). Oxidized starch is useful for its low viscosity, high stability, film forming and binding properties (Kuakpetoon & Wang, 2006) and therefore widely used in paper (Teleman, Kruus, Ämmälähti, Buchert, & Nurmi, 1999) and textile (Kuakpetoon & Wang, 2006) industry for coating and surface sizing purposes. It also interests food industry as a coating and sealing agent in confectionary, as a conditioner of bread as well as a binding agent in batter applications (Kuakpetoon & Wang, 2006).

Dialdehyde starch is usually prepared by oxidation like with sodium periodate (Serrero et al., 2010; Tharanathan, 2005) or sodium hypochlorite (Kuakpetoon & Wang, 2006; Tharanathan, 2005; Wang & Wang, 2003) and it has been further oxidized to a dicarboxylic acid derivative (Teleman et al., 1999). Primary hydroxyl groups of starch glucose units can be selectively oxidized with TEMPO–NaOCl–NaBr system carboxyl groups (Kato et al., 2003).

Bromate is a benign oxidant which has been used for oxidation of secondary alcohols (Natarajan & Venkatasubramanian, 1969; Gupta, Banerjee, & Chatterjee, 1992) together with a metal catalyst (Tomioka, Oshima, & Nozaki, 1982; Yamamoto, Suzuki, & Morooka, 1985) or in plain water with bromide (Pääkkönen, Pursiainen, & Lajunen, 2010, 2012). Bromate cleaves and oxidates C–C bond to ketones (Gupta, Kumar, Sen, Banerjee, & Chatterjee, 1991) or dicarboxylic acids (Bierenstiel, D'Hondt, & Schlaf, 2005). Besides bromate has been used to oxidate primary C-6 hydroxyl groups of a polysaccharide to carboxyl groups in strongly acidic (80–85% H₃PO₄) medium (Pagliaro, 1998; Varela, 2003).

Under neutral conditions molecular bromine has oxidated C-2–C-3 carbon bond of glucose unit via a ketone intermediate (Salomonsson, Andersson, Tornepport, & Theander, 1991; Tornepport, Salomonsson, & Theander, 1990). The increase of the bromine amount in the oxidation mixture has lowered the molecular weight of starch (Muhrbeck, Eliasson, & Salomonsson, 1990). Optimum conditions for a hypobromite (BrOH) oxidation are alkaline (pH 9) (Hollingsworth & El-Gewely, 1996). Bromine based oxidants are much less studied in starch oxidations than other corresponding halogen compounds even

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thought they are stronger oxidants than chloro compounds (Hollingsworth & El-Gewely, 1996) and less expensive than iodo compounds. Bromate has been used as a modifier for flour (<http://www.inchem.org/documents/jecfa/jecmono/v024je03.htm>; <http://www.fda.gov/Food/FoodIngredientsPackaging/FoodAdditives/ucm191033.htm>) but information about products or oxidation mechanism was slight.

We have shown that bromate with bromide in plain acidic water is a rapid and sensitive method for oxidation of secondary alcohols yielding only a negligible amount of side products (Pääkkönen et al., 2012). In this study we have examined the bromate oxidation of native wheat starch in acidic water at room temperature in order to produce water-soluble oxidized starch for a metal complexation studies (Komulainen, Pursiainen, Perämäki, & Lajunen, under review). Besides the oxidation of primary hydroxyl groups, the cleavage of glucose ring between C-2 and C-3 occurred. Products were generally water-soluble, degraded oxidized fragments. A short reaction time with a dilute reaction mixture yielded products insoluble to water. Oxidation products were characterized by HPLC, NMR and titration methods, and a mechanism for the oxidation was proposed.

2. Experimental

2.1. General

All commercially available reagents (Sigma–Aldrich, FF Chemicals, Baker, Ciba, Fluka) were reagent grade and used as received without further purification. Oxidation reactions were performed at room temperature. The oxidized starch precipitated by ethanol was dried at 35 °C for 2 days. NMR spectrum of samples was measured by a Bruker DPX 400 spectrometer at room temperature and the spectrum was reported in ppm the solvent residue with ^1H (D_2O , $\delta_{\text{H}} = 4.80$ ppm, when DMSO , $\delta_{\text{H}} = 0$) as the internal standard and ^{13}C (DMSO , $\delta_{\text{C}} = 39.51$ ppm and EtOH as a secondary standard, $\delta_{\text{CH}_3} = 18.01$) as the internal standard. The HPLC-ELSD instrument (Shimadzu) consisted of three isocratic pumps (LC-10AD) equipped with a control unit (SCL-10A), a degasser (DGU-14A), an automatic sampler (SIL-10AD), an evaporative light scattering detector (Polymer Laboratories PL-ELS 2100), a guard column (Phenomenex PolySep-GFC-P) and an analytical column (Phenomenex Poly Sep-GFC-Linear 300 mm \times 7.8 mm).

2.2. General oxidation procedure and isolation of product

The native wheat starch (3.0 g) was weight out into a flask, 25 mL or 10 mL of distilled water (oxidations A or B, respectively) and 1.05 equiv. of NaBrO_3 (2.927 g) per glucose unit was added to each. H_2SO_4 (5.5 mL, 1.77 M) was manually added by dropwise within 60 min. The reaction was stopped by neutralizing the mixture with NaOH (1 M) until pH 9. Addition of ethanol (100 or 250 mL) precipitated the oxidation product, which was filtered under vacuum through sintered glass funnel #4 (porosity 10–16 μm), washed three times with a water–ethanol mixture (30 mL of distilled H_2O and 300 mL of cold ethanol). Ethanol used in the precipitation was evaporated from the filtrate and reused in the next isolation.

2.2.1. Determination of carboxyl group content of oxidized starch

The carboxyl content of the oxidized, water-soluble starch was determined by a titration typical for weak acids (Wing & Willett, 1997). Starch solution (0.5 g of dry, oxidized starch in 300 mL of distilled water) was adjusted to pH 2.5 with 0.1 M HCl at room temperature, stirred for 15 min and titrated to pH 8.3 with standardized 0.1 M NaOH . Native wheat starch was used as blank sample of the determination. The known contents of acetic and citric acid (0.025 and 0.012 M, respectively) were used as standards of the procedure.

Carboxyl content of the sample was calculated as follows (Kuakpetoon & Wang, 2006):

Percentage of carboxyl content

$$= \frac{[(\text{Sample} - \text{Blank})\text{mL} \times \text{molarity of NaOH} \times 100 \times 0.045]}{\text{Sample weight in grams}}$$

2.2.2. Determination of carbonyl group content of oxidized starch

The carbonyl content of the oxidized starches was determined by the following titrimetric method (Kuakpetoon & Wang, 2006): a dry sample of oxidized starch (0.5 g) was suspended into 100 mL of distilled water in a flask and the solution was adjusted to pH 3.2 with 0.1 M HCl . Hydroxylamine reagent (20 mL) (prepared by dissolving 25 g of hydroxylamine hydrochloride in 100 mL of 0.5 M NaOH in a volumetric flask (500 mL) and filled with distilled water to the mark) was added. The reaction mixture was stirred for 4 h. The unreacted hydroxylamine was determined by a rapid titration to pH 3.2 with standardized 0.1 M HCl . A blank experiment with native wheat starch and hydroxylamine reagent was performed similarly.

Carbonyl content of the sample was calculated as follows (Kuakpetoon & Wang, 2006):

Percentage of carboxyl content

$$= \frac{[(\text{Blank} - \text{Sample})\text{mL} \times \text{molarity of HCl} \times 100 \times 0.028]}{\text{Sample weight in grams}}$$

2.3. NMR spectroscopy

For a 1D NMR measurement a sample (ca. 0.3 mL) from the neutralized oxidized mixture A or B was taken, evaporated to dry and dissolved into D_2O . 2D NMR measurements were performed with isolated, oven dried oxidized starch (20 mg in 0.5 mL). All the measurements were performed at room temperature.

2.4. Determination of water-solubility of oxidized starch

Water-solubility of oxidized starches was determined by dissolving a sample of 20 mg into 1 mL of distilled water. Suspension was mixed vigorously and centrifuged with 13 400 g for 2 min. Supernatant was removed and the amount of dried precipitate was measured.

2.5. HPLC-ELSD study of oxidized starch

An oven dried samples (5 mg) from the oxidation A (10 mass% of starch) or from the oxidation B (20 mass% of starch) were dissolved into 1 mL of distilled water. Products from the oxidation B were fully soluble as well as the 24 h product from the reaction A. In the oxidation A the products of the 2 or 5.5 h reaction were not equally soluble. A sample from each solution (10 or 30 μL) was injected to the HPLC equipment. The temperature of the injector and columns was kept at 40 °C by using a column heater (Shimadzu, CTO-10AS). The ELS detector was optimized for the analytes and following parameters were used: the evaporative temperature 80 °C, the temperature of the nebulizer 50 °C and the nitrogen gas flow 0.90 mL/min. The mobile phase was distilled deionized water passed through in-line membrane filters (0.45 μm Millipore, Bedford, MA) at the flow rate of 0.4 mL/min. The system was controlled and data was handled by using LC solution program from the same source.

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