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Spruce bark as an industrial source of condensed tannins and non-cellulosic sugars

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ABSTRACT

Norway spruce (*Picea abies*) is an important raw material for the forest industry in Nordic countries. The chemical composition and hot water extraction of spruce bark was studied to find out its potential as an industrial source of condensed tannins. Industrial bark was found to contain a high amount of wood (up to 21%), a sufficient amount of tannin for industrial extraction (10.7% of wood-free bark), and a high amount of non-cellulosic glucose, varying according to the felling season (7.7–11.5% of wood-free bark). Temperature had a major effect on the overall extraction yield. Selective extraction of only tannins or water-extractable carbohydrates was not possible. The extraction was scaled up to pilot-scale and an extract was produced having a promising 50% tannin content. Glycome profiling performed on bark and hot water extracts showed the presence of xyloglucan, pectic polysaccharides and arabinogalactan in bark. In addition the extracts were characterized using size exclusion chromatography and ^{31}P nuclear magnetic resonance spectroscopy. Spruce bark appears to be a promising new source of tannins, however the high content of free, glycosidic, and polymeric sugars in the raw extract may need to be tackled prior to use in applications.

1. Introduction

Increasing energy consumption, depletion of fossil fuel reservoirs, and mitigation of climate change motivate to seek alternatives for petroleum-based chemical industry and transport fuel production. Lignocellulose is the most abundant renewable biomass resource on earth and could offer a sustainable alternative for fuel and chemical production. Softwood bark, especially spruce bark, is regaining interest as a readily available source of valuable precursors and biochemicals. In the past softwood bark was actually used as a tanning agent in e.g. Russia and Poland (Surmiński, 2007). The Finnish forest industry uses on average 23 Mm³ spruce logs per year producing ca. 0.9–1.3 Mt/a of dry spruce bark calculated with bulk density of 380 kg/m³ and 10–15% volumetric bark content in logs (Anonymous, 2012). This volume of bark, now being combusted for energy, could provide components suitable for upgrading to higher value products, for instance adhesives, resins and plastics, before being combusted in the end of their life-cycle.

The availability and cost of biomass are of essence when designing feasible biorefinery concepts. The unique composition of the biomass utilized in the particular applications is also important.

Interesting opportunities arise when an existing industry is looking for new raw material sources to expand its market portfolio. The tannin industry is currently facing this situation. Tannins are polyphenolic compounds based either on flavan-3-ol monomers (condensed tannins, also called proanthocyanidins), or on gallic or hexahydroxydiphenic acid esters linked to a sugar moiety (hydrolysable tannins). Tannins have molecular weight from 500 to 3000 Da (Bate-Smith and Swain, 1962). Annual production of tannins is ca. 200,000 t out of which condensed tannins cover 90% (Pizzi, 2006). The main use for tannins through the past centuries and still today is leather production, where tannins are used to bind the collagen proteins in animal hides making the leather more flexible and less susceptible to microbial attack (Haslam, 1989). Because of their phenolic nature, tannins can be used to replace fossil-based phenol in many applications such as insulating foams and adhesives (Pizzi, 2006; Tondi et al., 2009). Current main industrial sources of tannin, acacia, quebracho, hemlock, tara, chestnut and sumach species are not abundant enough to provide tannin outside the current markets covering leather tanning, wine industry, animal nutrition, and some industrial uses such as mineral flotation, and oil drilling (Pizzi, 2006). The leather industry is not only looking for collagen binding, but also for the colour of the final tanned leather. On the other hand, the new expanding market of natural polymers is looking for optimal chemical reactivity and physical properties. The tannin industry in general, is looking for new

inexpensive feedstocks to produce tannin extracts of various qualities for the expanding markets.

The dominant industrial tannin production is based on hot water extraction. The method is also suitable for the extraction of spruce bark tannins, but unlike most current feedstocks, spruce bark has a high content of water soluble extractives other than condensed tannins (Roffael et al., 2000). Up to 33% of spruce bark solids may be extracted with sequential pressurized water extractions (Le Normand et al., 2012). The tannin-rich extract also contains considerable amounts of stilbenes, ash, and sugars in various forms. Optimizing the extraction procedure and understanding the effect of extraction parameters on the component yields is essential when developing applications for tannin. The analysis of the chemical composition of the extract is also highly important since this type of information is lacking in the current literature.

This study describes in detail the composition of spruce bark collected in winter and in summer from an industrially relevant source. We report the effect of the main parameters on the extraction yield, scale up the tannin extraction process from bench-scale to pilot-scale, and report the chemical composition and glycome profile of the barks and the extracts.

2. Materials and methods

2.1. Collection of spruce bark

Two batches of industrial Norway Spruce (*Picea abies*) bark were collected from the debarking unit of Metsä Wood Kertopuu plant (Lohja, Finland). The debarking unit processes fresh moist logs and employs dry debarking technology in the process. The first batch of bark termed as winter bark was collected in February 2012, and larger wood chips were removed manually. The typical felling time is only 1–3 months before debarking, thus the logs were felled between November 2011 and January 2012. Dry matter content of the bark was 39%. The average temperature in January–February 2012 was ca. −6 °C.

The second bark batch termed as summer bark was collected from the same place in August 2012 after a relatively cold summer (ca. 16 °C average temperature in June–August). Dry matter content of the bark was 51%. The trees were felled maximum of three weeks before debarking which was done in the morning of the collection day. No manual separation of wood was carried out except for a small amount (1 kg) for analytical purposes to analyze the composition of the wood-free part of the material.

2.2. Bench-scale extraction

A set of 10 extractions was performed for winter bark in a 15 L pressure cooker rotating 2.3 rpm. The total mass in the extraction was 8 kg out of which 5, 10 or 15% (w/w) was bark (on dry basis). Tap water was heated up to 60, 75 or 90 °C in the reactor, after which warm bark was added into the cooker and timing started. In one experiment 2% of sodium bisulfite and 0.5% sodium carbonate were dosed as percentage of bark dry weight. Extract samples were collected from the reactor after 10, 30, 60, 90 and 120 min and centrifuged for 10 min at 3000 rpm to remove solids. The centrifuged extract samples were stored at −18 °C.

2.3. Pilot-scale extractions

A total of 114 kg of summer bark (on dry basis) was extracted in six separate batches. Extraction was carried out in a 250 L vessel with forced circulation. The bark was placed in 10 μm polypropylene filter bags, which were closed with a cable tie, and the bags were placed in the reactor. The reactor was filled with hot tap water containing the extraction chemicals (2% of sodium bisulfite and 0.5%

sodium carbonate), and turbulent circulation with ca. 50 L/min flow rate was started together with heating. Extraction time of 120 min was started when the temperature of the circulation water reached 75 °C. The average solids content of bark in the extractions was 8.8%.

Primary extract was let out of the reactor and the wet extracted bark was washed with ca. 160 L hot (ca. 55 °C) tap water for 5 min. The washing water was let out of the reactor, combined with the primary extract, and concentrated by vacuum evaporation (150 mbar, 50 °C, 200 kg/h evaporation rate). The concentrated extract was spray-dried (210–220 mbar, 175 °C inlet and 75 °C outlet temperature) producing 10.0 kg crude tannin powder with a 6% moisture content. Crude tannin powder was stored in dry conditions in room temperature.

2.4. Yield calculations

Extraction yields related to bench-scale extraction experiments were calculated on mass basis by multiplying the concentration of the compound in the extract sample by the whole mass of water in the system consisting of added water and the moisture contained in the bark. Thus, we assumed that the concentration of dissolved compounds was the same everywhere in the system. The mass of the extracted compound was then divided either by the mass of the original dry bark (yield given as % of bark dry matter) or by the mass of the same compound in the original dry bark (yield given as % of theoretical).

Dry matter and tannin yields for pilot-scale extraction were calculated as above (theoretical extraction yields), but also actual yields were calculated from the amount of the extract that was recovered from the system. The actual yields take into account the losses of solubilized compounds that remain bound to the wet residual bark after extraction.

2.5. Chemical analysis

2.5.1. Extractives and lignin

The content of lipophilic extractives in bark was determined gravimetrically by Soxhlet extraction with heptane from 3 g milled dry bark (extraction time 5 h). The acid insoluble lignin content was determined after the removal of extractives using two-step sulfuric acid hydrolysis (NREL Laboratory Analytical Procedure #003) with minor modifications (60 min incubation in the first step). The acid soluble lignin content was determined according to Goldschmid (1971). The ash content of the samples was measured gravimetrically after combustion in a furnace at 550 °C.

2.5.2. Carbohydrates

The carbohydrate content of bark was analyzed using two methods. Neutral sugars were quantified after the previously described two-step acid hydrolysis using high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). HPAEC was run with Dionex ICS-3000 liquid chromatograph (Dionex Corp., Sunnyvale, CA) according to Tenkanen and Siika-aho (2000) with minor modifications (equilibration with 15 mM NaOH, isocratic elution with water). Because acidic sugars degrade in acid hydrolysis, they were quantified by gas chromatography after methanolysis of the sample and silylation of the sugar monomers according to Sundberg et al. (1996). Non-cellulosic glucose content was determined as the glucose released in methanolysis. Cellulosic glucose was determined as the total glucose released in the acid hydrolysis subtracted by the non-cellulosic glucose. Bark carbohydrate content was expressed as anhydrous polymeric carbohydrates.

Soluble free neutral and acidic monosaccharides in the extracts were quantified using the HPAEC-PAD method as described above. The total content of soluble neutral carbohydrates in the extracts