Industrial Crops & Products 173 (2021) 114090

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

The effect of thermal drying on the contents of condensed tannins and stilbenes in Norway spruce (*Picea abies* [L.] Karst.) sawmill bark

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ARTICLE INFO

Keywords:
Condensed tannins
Stilbenes
Gravimetric extractives
Thermal drying
Degradation

ABSTRACT

Norway spruce (*Picea abies* (L.) Karst.) bark contains marked amounts of polyphenolic compounds. Condensed tannins (CTs) and stilbenes show commercial potential as antioxidants, antimicrobials, preservatives in food and cosmetic applications, technochemical products, and pharmaceuticals. Storing of bark before the conversion process leads to substantial losses of extractives compounds. In the present study, the potential of thermal drying for maintaining extractives content was assessed based on an experiment in which bark samples were dried in convection kilns at 40, 50, 60, and 70 °C temperatures. The development of CTs and stilbene contents and CT degradation were followed for 28–34 h. CTs were analysed from bark samples with thiolysis. Quantities of stilbene glycosides and stilbene aglycones in water-acetone extracts were analysed applying gas chromatography with flame-ionization detection (GC-FID). Multilevel regression analysis was used to analyse the statistical differences in moisture content and extractives composition between the drying schemes.

The initial CT content of 35–36 mg g^{-1} in dry bark material declined to 25–31 mg g^{-1} in 28–34 h. The average degree of polymerisation (DP) decreased slightly, and the relative proportion of prodelphinidins in CTs increased significantly in the 60 and 70 °C schemes. The proportion of A-type linkages slightly increased with the increase in drying temperature. The initial mean stilbene contents varied from 19 mg g^{-1} to 22 mg g^{-1} in dry bark mass. Isorhapontin was the major stilbene constituent, with a proportion of 45–49 % of the total stilbenes. Stilbene losses of up to 60 % were detected during the drying processes. In 10 h, for example, 36–43 % of total stilbenes were lost. Degradation activities by enzymes released from the bark and oxidative reactions after crushing at the debarking phase were concluded to be the primary mode of degradation. The results indicate that bark CT content can be preserved at a moderate temperature not exceeding 50 °C, but the degradation of CTs may affect their suitability for various applications. Sufficient stilbene content for industrial processes is unlikely to be maintainable through thermal drying. The permanence of the post-drying extractives content should be assessed based on a practical-scale storage experiment using bark dried to varying moisture contents.

1. Introduction

In 2018, less than 10 % of the chemical industry's chemicals and raw materials were generated from biomass (Popa, 2018). Reducing dependence on non-renewable resources is considered crucial to meet the EU's energy and climate targets, to maintain and strengthen its industrial competitiveness, and to achieve a fully deployed circular economy (European Commission, 2018). Bark produced by the forest industry is a promising feedstock for biorefining due to its high extractives content. Bark also meets many criteria set for sustainable biorefining feedstocks (Popa, 2018) – it does not compete with food production and is a by-product with low value.

Bark constitutes 5–30 % of commercial tree species' stem volume (FAO et al., 2020). Between 2015 and 2019, the Finnish forest industry consumed an annual average of 67 million m^3 of roundwood (solid over bark; Natural Resources Institute Finland, 2020a), of which 7.5 million

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https://doi.org/10.1016/j.indcrop.2021.114090
Received 21 May 2021; Received in revised form 13 August 2021; Accepted 23 September 2021
Available online 28 September 2021

m^3 ended up in energy generation in the form of bark (Natural Resources Institute Finland, 2020b). Norway spruce (*Picea abies* [L.] Karst.) bark is among the most interesting feedstocks for biorefineries in the Nordic countries. In Finland, the pulp and paper industries generate approximately one million dry tons of spruce bark per year (Kemppainen, 2015). For Norway spruce stem bark, extractives concentrations from 22 % up to 28 % of dry mass have been reported (Miranda et al., 2012; Routa et al., 2017). Norway spruce bark contains high amounts of water-extractable, hydrophilic polyphenolic compounds such as condensed tannins (CTs), stilbenes, lignans, and flavonoids (Jyske et al., 2020). Water is considered a benign solvent suitable for green extraction due to its high solvency, high flash points with low toxicity and low environmental impacts, biodegradability, non-petrochemical basis, low price, and potential to be recycled without harmful effects on the environment (Chemat et al., 2019).

Research into the utilisation of Norway spruce bark extractives has focused on tannins and stilbenes. Total tannin contents of up to 15 % have been reported for Norway spruce (Kemppainen, 2015). Tree age, vertical position, and bark fraction (inner vs outer bark) affect extractives content (Krogell et al., 2012; Jyske et al., 2014). However, reported extractives contents are highly dependent on the methods used in the analyses, as shown by Jyske et al. (2020). CTs are oligomers formed from polyhydroxyflavan-3-ol units (Bianchi et al., 2014). The hydroxylation pattern and the degree of polymerisation (DP) are the most critical factors affecting CTs' chemical and physical properties, influencing their reactivity and suitability for different applications. In Norway spruce bark, CTs are mainly procyanidins; that is, they are composed of (epi)catechins (Matthews et al., 1997; Bianchi et al., 2014; Hammerbacher et al., 2014; Jyske et al., 2020; Raitanen et al., 2020). Small proportions of prodelphinidins composed of (epi)gallocatechins have also been detected. Tannins have traditionally been used in the leather tanning and wine industries, but they can also be utilised in wood adhesives, pharmaceutical and medical applications, fireproof and insulating foams, mining applications, and inhibitors of metal corrosion, for example. Cationised CTs have also been successfully tested as coagulant and flocculant in wastewater treatment, using products made from tree species grown in the Southern hemisphere (Beltran-Heredia and Sánchez-Martín, 2009; Sánchez-Martín et al., 2010; Grenda et al., 2020).

Norway spruce's inner bark typically contains 5–10 % stilbene glucosides (Holmbom, 2011; Krogell et al., 2012). Hydroxylated stilbene glucosides (*trans*-astringin and *trans*-isorhapontin) are the major compounds, while trihydroxystilbene *trans*-piceid is present as a minor compound (Krogell et al., 2012; Jyske et al., 2014). The corresponding aglycones (piceatannol, isorhapontigenin and resveratrol), and various dimers of stilbene glucosides (Li et al., 2008, 2012) have also been identified. Hydroxystilbene glucosides are also found to be incorporated into lignin structure, creating a complex system (Rencoret et al., 2019). Stilbenes could be valorised for commercial applications as antioxidants, antimicrobials, and preservatives in cosmetics, technochemical products, or pharmaceuticals (Välimaa et al., 2020).

The current supply chains of industrial roundwood are designed for processes utilising stemwood, and the year-round supply of fresh bark feedstock is limited due to seasonal variation in wood harvesting and changes in the production output of the forest industry. The moisture content of softwood bark typically exceeds 60 % (Alakangas et al., 2016). Storage of moist bark material can result in substantial losses and changes in chemical composition due to hydrolysis by plant enzymes (respiration by living cells), and microbial and thermochemical oxidative processes (Krigstin and Wetzel, 2016; Jyske et al., 2020). In addition, volatile compounds are prone to evaporation (Nielsen et al., 2009), and hydrophilic extractives are lost due to leaching (Routa et al., 2017). Moreover, photodegradation of phenolic compounds (e.g. stilbenes) can occur (Välimaa et al., 2020). Environmental conditions and the properties of stored biomass (e.g. biomass component, particle size) influence the changes (Jyske et al., 2020). The extractives content starts to decrease immediately after tree felling (Routa et al., 2017; Jyske et al., 2020), and this degradation continues during storage. In the case of Scots pine (*Pinus sylvestris* L.), as much as 60 % of CT and 26 % of the quantified lipophilic compounds were lost after two weeks' storage of sawlog bark in a pile in autumn (Routa et al., 2020a). In another experiment (Routa et al., 2020b), approximately one-third of acetone-soluble extractives of Norway spruce sawmill bark were lost within eight weeks, and the major losses occurred during the first two weeks. Furthermore, stilbenes are lost rapidly after debarking. In winter, a total stilbene (including stilbene glucosides and aglycones) content of 24 mg g^{-1} dry matter (DM) was detected in bark removed from freshly felled Norway spruce logs and 17 mg g^{-1} DM in bark collected immediately after debarking at a sawmill (Halmemies et al., 2018). In a study by Jyske et al. (2020), the initial stilbene content of bark from intact spruce logs harvested in winter was 2.4-fold compared to summer samples, and its decomposition rate was slower than that of the logs harvested in summer.

Extractives content could be maintained by delayed debarking, as comminution increases material losses (Jyske et al., 2020). In case a fast and constant supply of feedstock cannot be organised for the biorefining industry, treatments preserving material quality are needed. The processes resulting in material losses could be retarded by drying the biomass (Jirjis, 1995; Therasme et al., 2019). Drying inhibits enzymatic degradation of plant biomass and limits microbial growth. Ambient air-drying has traditionally been used to preserve medicinal herbs, because low temperatures have been considered to inhibit the degradation of the active ingredients. However, this is a slow method, and the continuation of metabolic processes in the beginning of drying may result in losses in material properties (Harbourne et al., 2009). Artificial drying experiments with bark or wood have typically been conducted at high temperatures (Fagernäs et al., 2010). These studies have been motivated by the requirements set by various biofuel conversion processes rather than the need to preserve the extractives fraction. Moreover, drying of bark may be required in extraction processes utilising solvents other than water. The behaviour of bark extractives in the thermal drying of softwood bark is not well understood.

The present study was aimed at analysing the effects of drying time and temperature on the extractives content in Norway spruce bark, with the focus on CTs and stilbenes. The hypothesis was that increases in drying time and temperature would promote extractives degradation.

2. Materials and methods

2.1. Drying experiment and sample preparation

The bark used in the experiment originated from Norway spruce sawlogs 258–264 mm (over bark) in top diameter. The logs were harvested from several locations in Central Finland in winter, at a maximum of two months prior to industrial debarking 12 March 2020 at a temperature of ca. 0 °C. The bark samples were collected from the bark storage of the debarking plant immediately after debarking. Due to their industrial origin, the bark samples also contained some sapwood. Composite bark samples were mixed in large containers, and the material was comminuted using a shredder with 25 mm × 25 mm mesh. Shredded bark was homogenised, and samples of ca. 2 l were packed into plastic bags that were immediately taken to the freezer (<−20 °C).

The drying experiment was conducted from 16 to 25 March 2020 with two convection ovens, applying 40, 50, 60, and 70 °C drying schemes. The ovens warmed up to the desired temperatures were loaded with frozen samples placed in 2-litre foils on perforated trays. In addition, three samples ("zero samples") from each scheme were halved prior to drying. In each case, one half was used to determine the initial moisture content, and the other was taken back to the freezer to await pre-treatment for the chemical analyses.

The experiment was started with the 50 and 70 °C schemes, in which the samples were kept undisturbed during the drying process. Due to

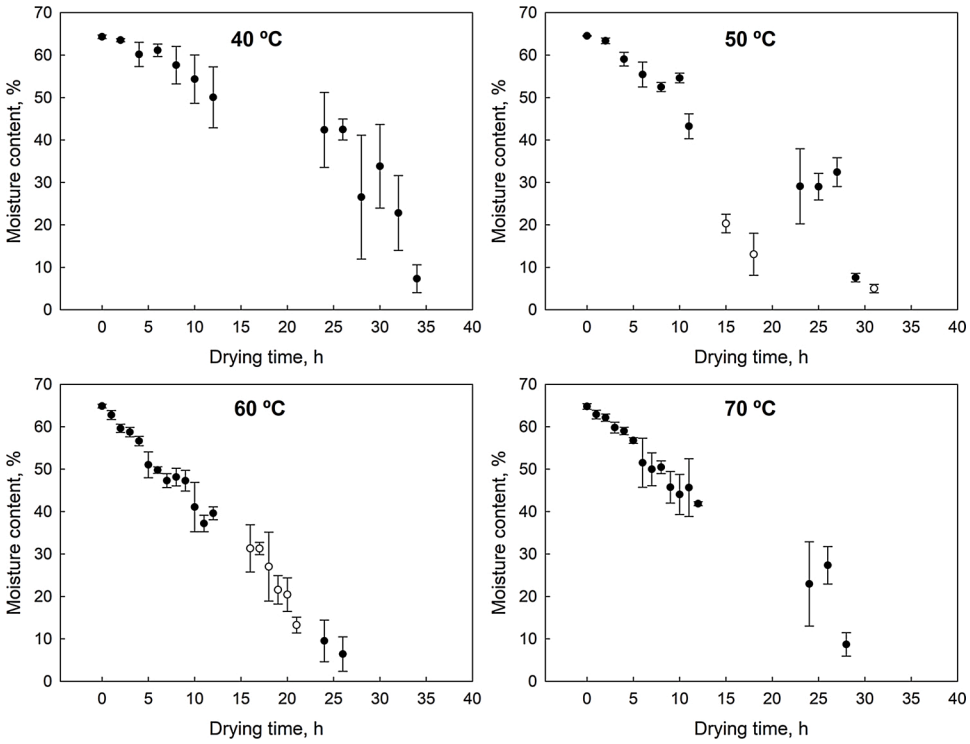

Fig. 1. Mean moisture contents (wet basis) of each set of bark samples ($n = 3$) removed from the ovens simultaneously, organised by drying scheme. Error bars indicate standard deviations of the moisture contents. The results from the complement drying series are denoted with open markers.

uneven drying of the bark during the first hours, the samples in the other schemes were lightly disintegrated at the thawing phase. Three samples at a time were removed from the ovens with a one- (60 and 70 °C schemes) or two-hour (40 and 50 °C schemes) interval. After removal from the ovens, the samples were homogenised and halved. One half of each sample was used for determining the post-drying moisture content. The other half was reserved for chemical analyses and packed into a plastic bag to be frozen. Due to the limitations in kiln capacity and night-time staff availability, complementing samples were dried in the 50 and 60 °C schemes. Initial moisture content and the bark samples' final moisture content were determined by applying the procedure described in ISO 18134-2:2015.

After the drying experiment, the samples allocated to the chemical analyses were stored in a freezer (< -20 °C) until they were freeze-dried for chemical analyses. A Retsch SM 100 cutting laboratory mill (Retsch GmbH, Haan, Germany) equipped with a bottom sieve with 0.5 mm perforation was used to grind the materials. The analytical moisture contents of the samples subjected to chemical analyses were determined according to SFS-EN 14774-3 by drying 1 g of bark powder at 105 °C overnight.

2.2. Analyses of condensed tannins

The zero samples and the samples removed 7–10 h after the beginning of the drying scheme were subjected to chemical analyses. CTs (proanthocyanidins) were determined from freeze-dried sub-samples as triplicates by ultra-high-performance liquid chromatography (UHPLC) after thiolytic degradation. On thiolysis, terminal units of CTs are released as free flavan-3-ols, and extension units are converted to corresponding thiol ethers. A-type linkages resist thiolytic degradation and produce A-type dimers (terminal units) and dimeric thiol ethers (extension units) as reaction products.

Samples were ground and weighed (20–30 mg) into 1.5 ml Eppendorf vials, and 1 ml of depolymerisation reagent (3 g cysteamine dissolved in 56 ml of methanol acidified with 4 ml of 13 M HCl) was added. After 60 min incubation at 65 C°, the samples were transferred into an ice bath, and cold samples were filtrated into high-performance liquid chromatography (HPLC) vials and analysed on an Agilent 1290 Infinity UHPLC device, as described by Korkalo et al. (2020). External standards of catechin, epicatechin, gallocatechin, epigallocatechin (Sigma Aldrich Oy, Espoo, Finland), and thiolysed procyanidin B2 and procyanidin A2 (Extrasynthese, Lyon, France) were used for quantification. The average DP was measured by calculating the molar ratio of all tannin units (terminal and extension) to terminal units.

2.3. Determination of total dissolved solids and stilbenes

The amounts of total dissolved solids were determined from the zero samples and the samples dried for at least 7–10 h. The bark samples were extracted with a Foss Soxtec™ 8000 as duplicates. The extractions were performed for 2 g of freeze-dried bark powder samples with 80 ml of acetone/water (95:5 v/v) mixture by keeping them in boiling solvent for 15 min. Thereafter, the thimbles were raised and kept in a rinsing position for 60 min. The acetone used for extractions was HPLC-grade (≥99.8 %) acetone (VWR Chemicals BDH®). The extracts were first concentrated by the extractor, after which the rest of the acetone was evaporated using a nitrogen stream. The remaining water was evaporated in the freeze-drier, and the contents of total dissolved solids were determined by weighing the dry extracts.

After determining the total dissolved solids, a stock solution of 50 ml was prepared for duplicated stilbene analyses by dissolving the extract in an acetone/water (95:5 v/v) mixture. For the qualitative and quantitative analyses, a volume of stock solution containing 3 mg DM of the extract was pipetted to a test tube, and acetone was evaporated under a nitrogen stream. For derivatization of the samples, 0.5 ml of pyridine and 0.3 ml of the silylation reagent N-trimethylsilyl imidazole (TMSI in pyridine, Sigma-Aldrich, Merck KGaA, Darmstadt, Germany) was added to the dry extract, and the sample was kept in an oven at 70 °C for 60 min. Gas chromatography–mass spectrometry (GC–MS; Hewlett-Packard 5973 MSD, EIMS 70 eV; Agilent, Santa Clara, CA, USA)

Table 1
The associations between oven temperature and drying of the samples.

	Moisture content, %	
Fixed effects		
Intercept	50.36***	(1.569)
Drying time	−1.347***	(0.124)
T (40 °C)		
T (50 °C)	−8.651***	(2.152)
T (60 °C)	−14.09***	(1.971)
T (70 °C)	−8.476**	(2.118)
T (40 °C) x Drying time, h		
T (50 °C) x Drying time, h	−0.425*	(0.188)
T (60 °C) x Drying time, h	−0.887***	(0.196)
T (70 °C) x Drying time, h	−0.400*	(0.201)
Random effects		
var_u	22.55	(5.188)
No. of observations	195	

Standard errors in parentheses, * $p<0.05$, ** $p<0.01$, *** $p<0.001$.

2.4. Statistical analyses

Multilevel regression analysis (multilevel modelling) was applied to analyse the statistical differences in moisture contents and extractives composition between the drying schemes. A multilevel modelling approach was chosen because three samples per removal from the ovens were analysed at a time and, thus, the observations are clustered within these three samples. Ignoring data clustering could lead to underestimated standard errors of regression coefficients and, thus, overly small *p*-values (Snijders and Bosker, 1999). Twelve random intercept models (1) were fitted to the data:

$$y_{ij} = beta_0 + beta_1 x_{1ij} + beta_2 x_{2ij} + beta_3\, x_{1ij}\, x_{2ij} + u_j + e_{ij} \quad (1)$$

Dependent variables (y) included post-drying moisture content, CT parameters (contents, DP, and the proportion of A-type bonds), and the contents of dissolved solids and stilbenes. Independent variables included one categorical variable (drying scheme), one continuous variable (drying time), and their interaction. The scheme with the lowest drying temperature (40 or 50 °C, depending on the experiment) was used as the reference group.[1] Stata/SE 16.1 software (StataCorp LLC, Texas, USA) and maximum-likelihood estimation were used.

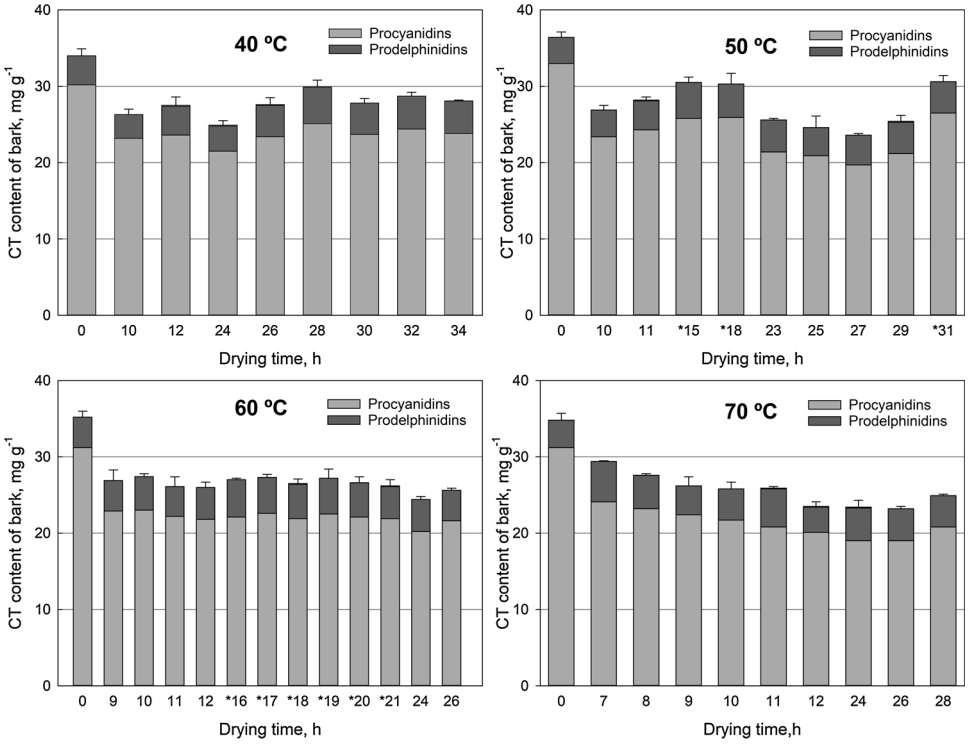

Fig. 2. The mean contents of condensed tannins (CTs; procyanidins and prodelphinidins) with the standard deviations for the total CTs. The results from the complementary drying samples are denoted with asterisks before drying hours on the *x*-axis.

equipped with a Zebron ZB-5MSi capillary GC column (30 m × 0.25 mm ×0.25 μm) was used for the qualitative analysis of silylated samples. Commercial (NIST14/Wiley11) libraries and other available MS libraries were utilised for peak identification. Quantitative analysis of stilbene glycosides and stilbene aglycones were carried out by GC-FID (Agilent Hewlett-Packard 6850) equipped with an Agilent HP-5 19091J-413 column (30 m × 0.32 mm ×0.25 μm) on silylated samples, using heneicosanoic acid (0.1 mg ml^{-1}; Sigma-Aldrich Chemie GmbH, Steinheim, Germany) and betulinol (0.1 mg ml^{-1}; Sigma-Aldrich, St. Louis, MO, USA) as internal standards. The GC injector and detector temperatures were 290 °C and 300 °C, respectively. The GC temperature program was set to 100 °C (1.5 min), 6 °C min^{-1} to 180 °C, 4 °C min^{-1} to 290 °C (13 min), 4 °C min^{-1} to 300 °C (20 min).

3. Results

3.1. Drying of the bark

The initial moisture content of the bark was 64–65 % (wet basis),

[1] In analyses, each drying scheme category is compared with the reference group. For example, a negative and statistically significant regression coefficient means that the parameter value is lower for the drying scheme in question than for the reference group. Similarly, a positive regression coefficient means that the value is higher.

Table 2
The associations among drying conditions, the content of condensed tannins (CTs), degree of polymerisation, and the proportion of A-type bonds.

	Condensed tannins, % of dry bark mass		Proportion of procyadinins, % of CT		Proportion of prodelphidins, % of CT		Degree of polymerisation		Proportion of A-type bonds, %	
Fixed effects										
Intercept	2.870***	(0.079)	86.474***	(0.511)	13.526***	(0.511)	10.096***	(0.068)	2.447***	(0.055)
Drying time	−0.009	(0.007)	−0.126**	(0.043)	0.126**	(0.043)	−0.013*	(0.006)	0.005	(0.005)
T (40 °C)										
T (50 °C)	−0.008	(0.106)	−0.583	(0.684)	0.583	(0.684)	−0.011	(0.094)	0.443***	(0.074)
T (60 °C)	−0.204*	(0.101)	−2.845***	(0.651)	2.845***	(0.651)	−0.223**	(0.086)	0.193**	(0.070)
T (70 °C)	−0.334**	(0.109)	−3.194***	(0.706)	3.194***	(0.706)	−0.232*	(0.094)	0.430***	(0.076)
T (40 °C) x Drying time, h										
T (50 °C) x Drying time, h	−0.017	(0.010)	−0.039	(0.064)	0.039	(0.064)	0.006	(0.009)	−0.003	(0.007)
T (60 °C) x Drying time, h	−0.019	(0.011)	−0.048	(0.072)	0.048	(0.072)	−0.021*	(0.010)	0.004	(0.008)
T (70 °C) x Drying time, h	−0.020*	(0.010)	−0.034	(0.067)	0.034	(0.067)	0.007	(0.009)	0.008	(0.007)
Random effects										
var_u	0.046	(0.011)	1.780	(0.439)	1.780	(0.439)	0.026	(0.008)	0.021	(0.005)
No. of observations	126		126		126		126		126	

Standard errors in parentheses, * $p<0.05$, ** $p<0.01$, *** $p<0.001$.

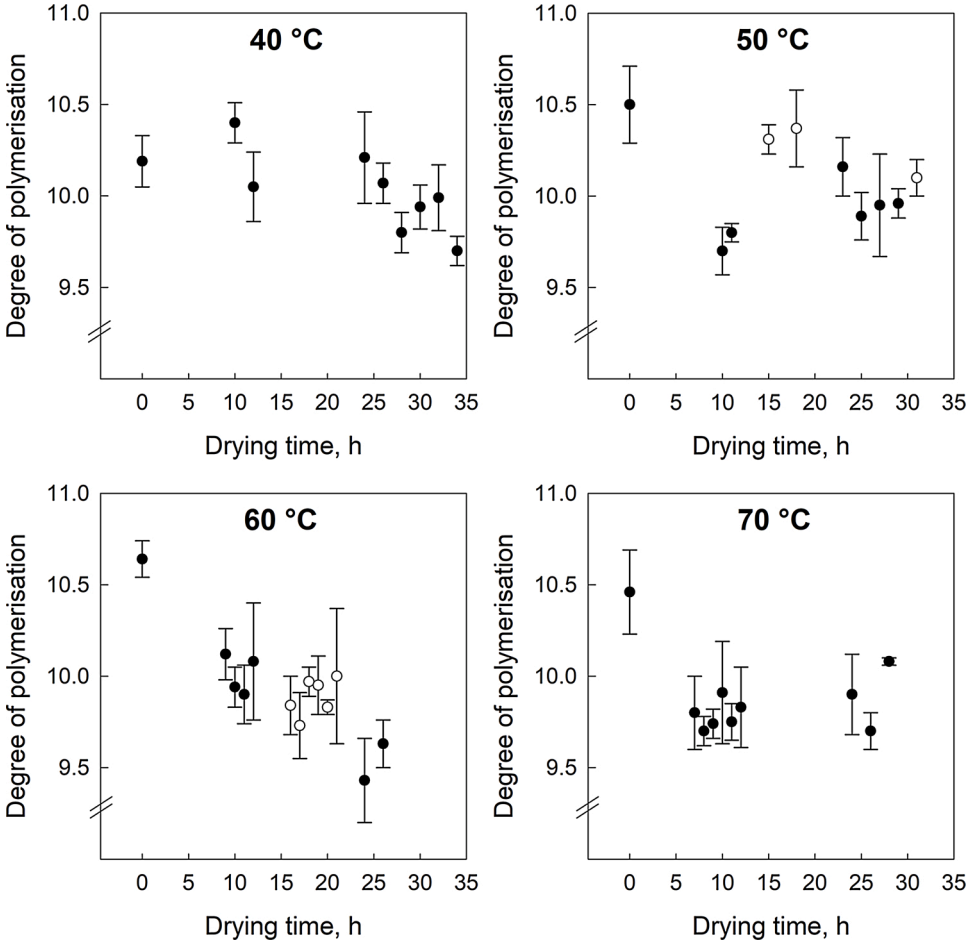

Fig. 3. Mean polymerisation degrees of condensed tannins (CTs) and their standard deviations by drying scheme. The results from the complementary drying series are denoted with open markers.

from which it declined below 10 % in all drying schemes (Fig. 1). Increases in drying time and temperature had a significant negative effect on the moisture content (Table 1). However, drying at 60 °C seems more efficient than at 70 °C. This inconsistency can be explained by the differences in the drying conditions – the samples were dried undisturbed at 70 °C, while the frozen bark clods were disintegrated at the thawing phase in the 60 °C scheme.

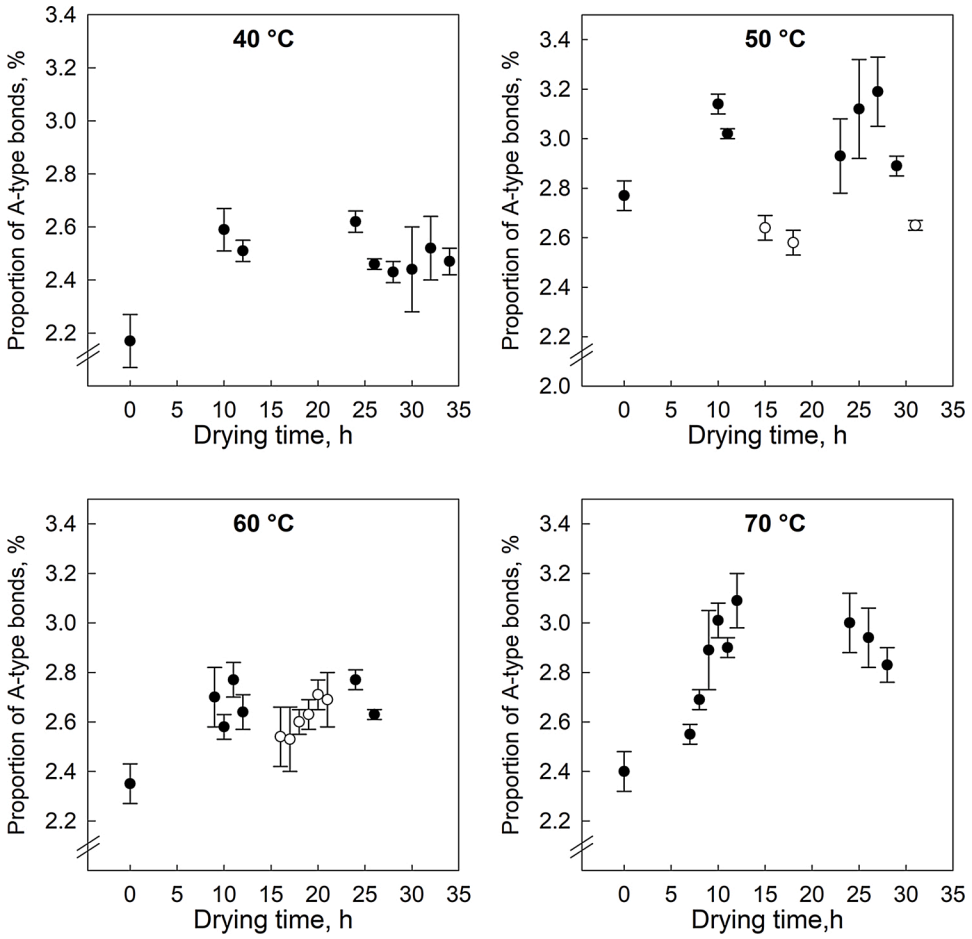

Fig. 4. The proportions of A-type bonds (%) in condensed tannins (CTs) of the bark and corresponding standard deviations (percentage points) by drying scheme. The results from the complementary drying series are denoted with open markers.

3.2. Condensed tannins

The initial CT content of 35–36 mg g^{-1} in dry bark material declined to 25–31 mg g^{-1} during the drying process (Fig. 2). The estimation results for the random intercept models (1) are provided in Table 2. Increase in temperature significantly ($p < 0.001$) decreased CT content at 60 and 70 °C when compared to the bark samples dried at the reference temperature of 40 °C. The average DP decreased slightly (Fig. 3), and the relative proportion of prodelphinidins in CT increased significantly in the 60 and 70 °C schemes. Generally, the proportion of A-type linkages was very low, but it slightly increased with increase in drying temperature (Fig. 4).

3.3. Total dissolved solids

The initial content of total dissolved solids in bark dry mass varied from 180 to 210 mg g^{-1} (Fig. 5). Extractive content decreased ca. 22–24 % from the original values in the 60 and 70 °C schemes, while the losses at 40 and 50 °C were lower (14 and 10 %, respectively). Increase in drying time increased the losses of extractives significantly ($p < 0.001$; Table 3). However, only the temperature of 60 °C reduced extractives content significantly when compared to the 40 °C scheme. Moreover, the interaction of drying time and the temperature of 70 °C was statistically significant.

3.4. Stilbenes

The initial mean stilbene contents varied from 19 to 22 mg g^{-1} in dry bark mass (Fig. 6). Isorhapontin was the major stilbene constituent with a proportion of 45–49 % of the total stilbenes, while astringin constituted 24–31 %, piceid 16–19 %. Stilbene losses up to 60 % were detected during the drying processes. In 10 h, for example, 36–43 % of total stilbenes were lost. Drying time significantly decreased the contents of all stilbenes ($p < 0.001$ or $p < 0.01$) while temperature had no effect with the present experimental setup (Table 4).

4. Discussion

The concentrations of all examined extractives declined rapidly with time. Increase in drying temperature promoted the loss of CTs. However, at least 70 % of the original CT content was left at the final stage of the drying scheme. The degradation of stilbenes was likely so quick that the effect of temperature was not possible to analyse with the present experimental design. Conducting a complete series of extractive analyses also covering the early drying hours and all temperatures was not possible due to limited resources, and the post-drying chemical analyses were started from moisture contents typical of forest chips received by large-scale heat and power plants (40–50 %; Hakkila, 2003). A moisture content of 30–50 % is considered favourable for microbial degradation activities (Hakkila, 1989). The moisture content reached with drying affects the bark material's storability prior to the conversion process. With moisture contents below 20 %, water is found only in the cell walls and no microbial growth is expected (Andersson et al., 2002). This moisture content was reached in all drying schemes.

Industrial Norway spruce bark has been found to contain marked amounts of wood (Kemppainen et al., 2014) and varying wood content

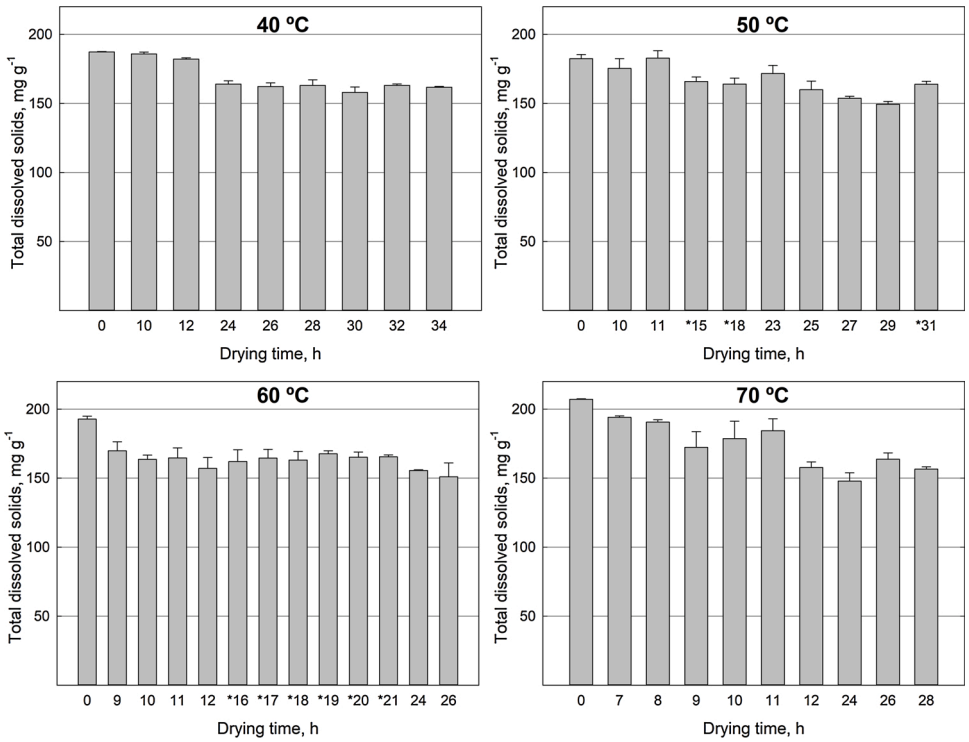

Fig. 5. Mean contents of total dissolved solids (mg g^{-1}) in bark dry mass with standard deviations by drying scheme. The results from the complementary drying samples are denoted with asterisks before drying hours on the *x*-axis.

Table 3
The associations between drying conditions and total dissolved solids.

	Gravimetric extractives, % of dry bark mass	
Fixed effects		
Intercept	17.400***	(0.240)
Drying time	−0.095***	(0.020)
T (40 °C)		
T (50 °C)	−0.561	(0.322)
T (60 °C)	−1.102***	(0.306)
T (70 °C)	−0.518	(0.332)
T (40 °C) x Drying time, h		
T (50 °C) x Drying time, h	0.000	(0.030)
T (60 °C) x Drying time, h	−0.013	(0.034)
T (70 °C) x Drying time, h	−0.078*	(0.031)
Random effects		
var_u	0.352	(0.098)
No. of observations	125	

Standard errors in parentheses, * $p<0.05$, ** $p<0.01$, *** $p<0.001$.

may have increased the material's heterogeneity, thus affecting the chemical composition of the samples. The bark used in the present study originated from logs harvested in dormant season (winter) when the bond between bark and sapwood is high, resulting in increased wood content in the bark (Ressel, 2006). The loss of extractive compounds in winter is slow (Jyske et al., 2020), but minor losses could have occurred prior to debarking. In a storage experiment with Norway spruce logs, bark stilbenes degraded more rapidly than tannins (Jyske et al., 2020).

In the present study, the bark samples were stored and dried in the dark. Consequently, the photodegradation pathway typical of stilbenes (Välimaa et al., 2020) may not be feasible explanation for the extractives losses. Losses of volatile compounds, in particular monoterpenes, are known to occur due to evaporation in the drying process (Granström, 2005).

In debarking, the structure of bark is disintegrated, which releases oxidative enzymes from cellular structures and increases diffusion of oxygen within the cells. Debarking also increases the surface area of the material, which promotes microbial growth and chemical reactions that damage plant cells. It is likely that various decomposition processes were already ongoing when the samples were placed in the freezer and restarted at the thawing phase in the kilns. However, biological activities likely had only a minor effect on the extractives degradation during relatively short drying times.

In wood fuel chip piles, temperature and moisture gradients are formed during storage (Hakkila, 1989). Similar temperature-dependent phenomena can occur in thermal drying of material that contains inner bark and sapwood. The main degradation pathways in chip piles are respiration reactions in living parenchyma and cambial cells of wood biomass, microbial reactions by fungi, and chemical reactions. Respiration consumes rapidly the microbes' nutrient reserves. Cell respiration increases when the temperature reaches 40 °C and ceases for the most part at 60 °C. For fungi, the optimum temperature range lies between 20 and 30 °C at a moisture content of 25–60 % (Hakkila, 1989). Oxidative reactions occur already at ambient temperatures (Aritomi and Donnelly, 1976). In microorganism-free wood biomass, they have been found at 40 °C, and at 50 °C they have become the major reaction consuming oxygen after the termination of cell respiration (Krigstin and Wetzel, 2016). In the present study, the environmental conditions for microbial degradation were favourable only for a short time, and therefore the role oxidation may have emphasised.

Wood enzymes and oxidative reactions can modify various compounds, for example by polymerising stilbenes and thereby reducing the amount of stilbene glucosides. Stilbene glucosides can also act as antioxidants, and therefore oxidative reaction (Reitberger et al., 2001) would decrease the amounts of these compounds. For example, stilbenes resveratrol, pinosylvin, and 5-hydroxystilbene react with hydroxyl radicals (Stojanovíc and Brede, 2002). Stilbene glucosides may have been available on the bark surfaces after debarking. Stilbene glucosides

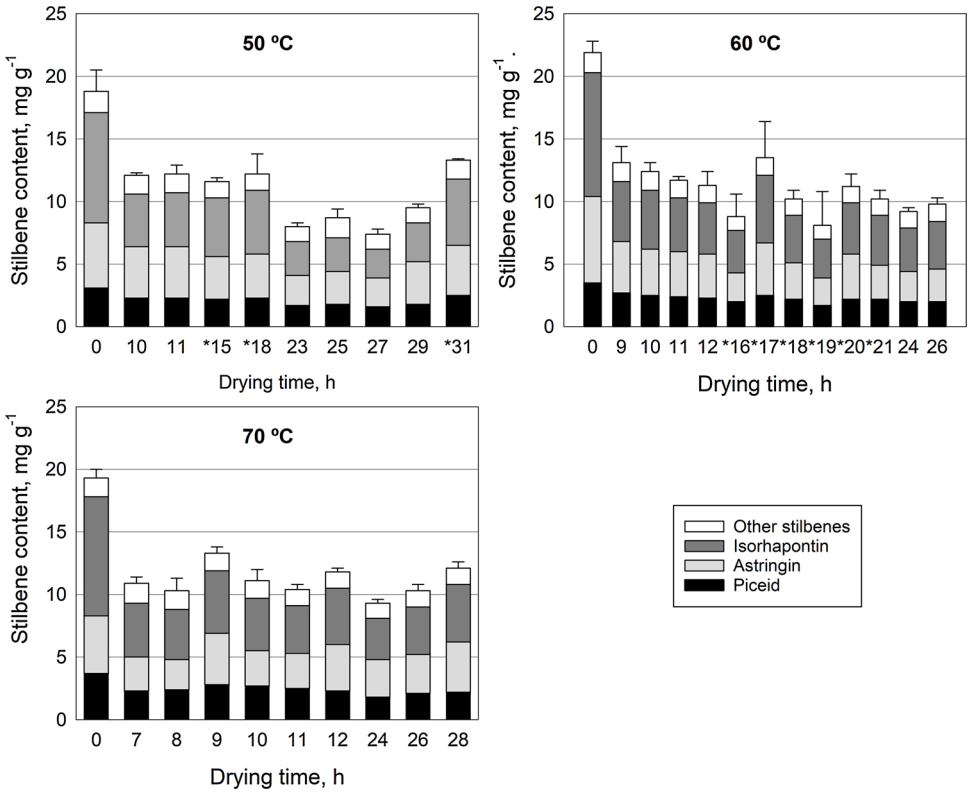

Fig. 6. Mean stilbene contents (mg g^{-1}) in dry bark mass. Error bars indicate standard deviations for the total stilbene contents in the drying experiment. The results from the complementary drying samples are denoted with asterisks before drying hours on the *x*-axis.

Table 4
The associations between drying conditions and stilbenes.

	Total stilbenes, mg g^{-1}		Piceid, mg g^{-1}		Astringin, mg g^{-1}		Isorhapontin, mg g^{-1}		Other stilbenes, mg g^{-1}	
Fixed effects										
Constant	1.174***	(0.068)	0.221***	(0.009)	0.361***	(0.021)	0.454***	(0.040)	0.138***	(0.003)
Drying time, h	−0.025***	(0.007)	−0.003***	(0.001)	−0.007**	(0.002)	−0.014**	(0.004)	−0.001**	(0.000)
T (50 °C)										
T (60 °C)	−0.073	(0.091)	0.003	(0.012)	−0.0380	(0.028)	−0.032	(0.053)	−0.005	(0.004)
T (70 °C)	−0.046	(0.100)	0.010	(0.013)	−0.032	(0.031)	−0.022	(0.058)	−0.003	(0.004)
T (50 °C) x Drying time, h										
T (60 °C) x Drying time, h	−0.015	(0.011)	−0.002	(0.001)	−0.007*	(0.003)	−0.005	(0.007)	−0.000	(0.001)
T (70 °C) x Drying time, h		(0.011)	−0.001	(0.001)	0.006	(0.003)	0.003	(0.006)	−0.000	(0.000)
Random effects										
var_u	0.042	(0.011)	0.001	(0.000)	0.004	(0.001)	0.014	(0.004)	0.000	(0.000)
var_e	0.011	(0.002)	0.000	(0.000)	0.002	(0.000)	0.002	(0.000)	0.000	(0.000)
No. of observations	98		98		98		98		98	

Standard errors in parentheses, * $p<0.05$, ** $p<0.01$, *** $p<0.001$.

in mature trees are mostly found in inner bark (Jyske et al., 2014), and enzymes and oxidative reactions could have modified these easily available compounds. Degradation of polyphenols would have slowed down after the first 10 h, since remaining stilbene glucosides would still have been compartmentalised inside the bark, inaccessible to enzymatic degradation or oxidation. Accordingly, the amounts of stilbene glucosides would have remained relatively stable after 10 h of drying when moisture contents were still too high (above 40 %) to maintain bark quality.

In a typical drying process, unbound water on the lignocellulosic surface of material is removed first, and thereafter mass transfer of internal water controls drying rate (Yi et al., 2020). If water is evaporated from bark surfaces, it could limit microbial activities and prevent the degradation of stilbenes. The behaviour of complementary samples in the 50 °C scheme supports this theory. The samples in the main series had been dried undisturbed, while the complementary samples removed from the oven after 15, 18, and 31 h had been disintegrated at the thawing phase, which had promoted drying. The moisture content may have had an effect on extractives degradation. Using frozen samples probably prolonged the time with favourable conditions for degradation processes requiring adequate moisture content. Stilbene aglycone solubility in water is relatively poor compared to stilbene glucosides, so it could have precipitated on surfaces during drying when water was evaporated. The CT content and polymerisation degree of the

complementary samples seemed higher and the proportion of A-type bonds lower than in the other samples. Moreover, more efficient drying may have promoted the loss of total dissolved solids. However, the data was inadequate to confirm the suppositions above.

Thermal lability of plant polyphenols is well known, and many studies on different plant materials have indicated that external heat induces loss in CT content (Hong et al., 2004; Khanal et al., 2010; Di Mattia et al., 2013; de Paepe et al., 2014; Cardoso et al., 2015). The results indicate that bark CT content can be maintained quite well with moderate temperatures not exceeding 50 °C. However, regardless of the drying temperature some loss of CT seems unavoidable. Likely the first hours are critical as after 10 h of drying CT content in all samples had declined distinctly. Further decline was noticed only in the samples dried at 60 and 70 °C. A slight decrease in the average DP during drying may indicate that highly polymerised CTs were more prone to degradation than the smaller ones. Another possibility is that the composition of CT is partly modified e.g. by oxidation during the drying process resulting chemical structures that cannot be detected by the thiolysis method applied in the current study. Consequently, this would have effect not only on the measured DP but also on the determined content of CT which would then be somewhat underestimated. A similar shift in CT size distribution (i.e. from polymers towards oligo- and monomers) has been noticed in sorghum, peach, apple, and blueberry products after heat treatments (Hong et al., 2004; Khanal et al., 2010; de Paepe et al., 2014; Cardoso et al., 2015). However, in cocoa beans, the smallest flavan-3-ols, monomers, were the most susceptible to degradation (Di Mattia et al., 2013). The heat-induced alteration in CT profile is probably a complicated process depending strongly on surrounding conditions, such as humidity, sample matrix, and nature of CT. Yet, though statistically significant, the decrease in DP during drying was negligible.

The CTs detected in the spruce bark mainly consisted of (epi)catechin units, but a moderate portion was found to be (epi)gallocatechins; in other words, the CTs were a mixture of procyanidins and prodelphinidins. The same structural units have been detected in spruce bark CTs in previous studies (Matthews et al., 1997; Bianchi et al., 2014; Hammerbacher et al., 2014; Jyske et al., 2020). The proportion of PDs increased slightly during the drying process, indicating that the PCs of spruce bark CTs are less stable than PDs. The proportion of PDs in spruce bark CTs also increased during summer storage of spruce logs in the study by Jyske et al. (2020). A-type linkages were detected to a small extent, and their proportion increased slightly during the process, except at the lowest drying temperature. Heat-induced oxidation can convert B-type linkages to A-type, as shown in previous studies (Kondo et al., 2000; Osman and Wong, 2007). The type of monomeric units and the DP greatly affect the chemical and physical properties of CTs. Better antioxidant properties, enhanced heavy metal chelation, and higher viscosities have been observed with increasing tannin DP (Bianchi, 2016).

5. Conclusions

Increase in drying time and temperature promoted the degradation of acetone-water soluble extractives in Norway spruce bark. These changes affect yields in the extraction processes. However, the profitability of a production system is trade-off between feedstock quality and resources consumption, including the cost of raw material's pretreatment.

Of the examined drying temperatures, the total content of CTs started to decrease from 60 °C onwards, while A-type bonds began to increase already at 50 °C. Besides extraction yields, these changes may also affect their suitability for various applications. However, the final CT losses remained moderate (16–28 %). Stilbene losses up to 60 % were recorded. This indicates that thermal drying may not be a feasible method for preserving stilbene content of Norway spruce bark. Besides alternative bark pre-treatment methods (e.g. freeze drying), unsustainable stilbene losses could be avoided through fast supply chains without intermediate storing. Preservability of extractives content of bark dried into varying moisture contents is an additional consideration when assessing the viability of bark supply chain based on intermediate storing.

CRediT authorship contribution statement

Paula Jylhä: Conceptualization, Visualization, Project administration, Resources (provision of study materials), Investigation (drying experiment), Writing of the original draft, editing. **Eelis Halmemies:** Investigation (stilbene analyses). **Jarkko Hellström:** Investigation (tannin analyses), Validation, Writing and review. **Maija Hujala:** Formal analysis (statistics). **Petri Kilpeläinen:** Supervision, Writing - review. **Hanna Brännström:** Funding acquisition, Conceptualization, Validation, Writing and review, Supervision.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

The authors thank Jaakko Miettinen, Reetta Kolppanen, and Satu Örling for skilful technical assistance. UPM-Kymmene Oyj Pietarsaari is acknowledged for providing bark materials for the experiments. The authors gratefully acknowledge the financial support received from EU/Interreg/Botnia-Atlantica, the Regional Council of Ostrobothnia, and Region Västerbotten within the framework of the Tannins for Wastewater Treatment (TanWat) project (20201484).

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