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# Comparison of fatty and resin acid composition in boreal lodgepole pine and Scots pine for biorefinery applications

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ABSTRACT

To investigate the potential for Scots- and lodgepole pine for biorefinery applications such as e.g., biodiesel and glue production, wood samples from five different sites in northern Sweden were compared. 21 fatty and 10 resin acids were detected by extraction and GC–MS analysis. Total fatty- and resin acid contents of Scots pine varied between 2.4 and 41.4 mg/g. Corresponding concentrations for lodgepole pine were 2.3 and 26.0 mg/g of dry material. Multivariate models were made with principal component analysis to take advantage of the multivariate correlations between the individual acids. Wood tissue type explained most of the variation in fatty and resin acid content, with heartwood having up to five times the extractive concentration of sapwood. Resin acids were mainly associated with heartwood, while fatty acids were more associated with sapwood. A five-component PLSDA-model distinguished between the two species, mainly due to differences in their hexadecanoic and heptadecanoic acid contents. Heartwood from Scots pine is more suitable for resin extraction while lodgepole pine is a better option for fatty- and resin acid extraction because of the extractives' evenly distribution between wood types. Around 150 kg of fatty acids and 1 ton of resins can be harvested per hectare from a typical mature boreal lodgepole pine stand, for biorefinery use. Systematic fractionation and selection of heartwood and sapwood will likely optimize industrial applications (e.g. biodiesel production) of each fraction.



## 1. Introduction

### 1.1. Pine extractives for fuel and chemical production

Scots pine (*Pinus sylvestris* L.) and lodgepole pine (*Pinus contorta* var. *latifolia*), the two most common pine species in Sweden, are commercially interesting not only as sources of raw material for the pulp/paper and saw timber industries but also for industries that rely on the extractives produced by the trees. These include substances such as fatty and resin acids, waxes, sterols, terpenes and other phenolic compounds (Ekeberg et al., 2006; Hillis, 1987). Fatty and resin acids are generally regarded as problematic compounds in paper and board making (Farrell et al., 1997; Sun and Tomkinson, 2001). However, fats are valuable resources for producing fuels like biodiesel while resins are suitable for producing glues and inks (Demirbas, 2011). Pine extractives can also be processed in biorefineries to produce numerous other products including soaps, insect repellants, adhesives, medicines, and health-promoting agents (Cherubini, 2010; Demirbas, 2009; Taylor, 2008). For example, Ayrilmis et al. (2009) found that the addition of pine cone resin during panel- and board manufacture significantly reduced formaldehyde emissions and also improved the water resistance of the final product. SunPine, a company in Piteå, Sweden (http://www.sunpine.se), already produces 100 000 $m^3$ crude tall oil diesel per year from pine and is currently building an associated plant for an annual production of 20 000 tons of resins. Also, UPM-Kymmene Corporation in Lappeenranta, Finland (http://www.upm.com/en/Pages/default.aspx) is planning to produce wood-based biodiesel. Nevertheless, extractive production is currently not taken into consideration in economical calculations or silvicultural plans for pine stands, even though the usage of pine extractives is increasing and can be a valuable supplement to timber and pulp production.

### 1.2. Extractive production is dependent on species and wood tissue type

The quantity and relative abundance of the different extractives in any given tree depends on its species (Hillis and Inoue, 1968; Örså and Holmbom, 1994). While different pine species generally have quite similar extractive contents and composition (Uçar and Fengel, 1995), lodgepole pines are known to be richer in extractives than Scots pines (Koch, 1996; Sjöström, 1993). Lodgepole pine was introduced into northern Sweden on a large scale from

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Canada around 1970 to meet expected future demand for forest raw material, primarily pulpwood (Elfving et al., 2001; Engelmark et al., 2001). It is expected to contribute substantially to Sweden's wood supply during the coming decades because its growth rates are 30–40% greater than those of the domestic Scots pine (Elfving et al., 2001).

The heartwood of pines, i.e. the inner part of mature trees, usually contains more extractives such as fatty- and resin acids than the sapwood (Hillis, 1987; Uusitalo, 2004). Heartwood of Scots pine stumps may have very high contents of extractives (Eriksson et al., 2012). Campbell found that the average extractive content of the sapwood of lodgepole pine was 2.03% while that of the heartwood was 3.30%, based on a sample of 27 trees from the northwestern United States and Canada (Campbell et al., 1990). This result is consistent with a previous report (McMillin, 1970) in which it was stated that the extractive content of the heartwood of lodgepole pine is considerably higher than that of the sapwood. It should be pointed out that many literature references give only total amount of extractives and do not provide speciation information.

### 1.3. Objectives

Because many of the factors that affect the production of extractives are related to site conditions and tree age/height, a comparison of the extractive contents of mature Scots and lodgepole pines grown at the same geographical sites was crucial. If we can quantify the current extractive production of pines, we can also better plan and organize the outtake of extractives to biorefineries. There is a possibility to manage the forests to produce more of certain extractives, and to choose the most suitable stands for extraction. Because different extractives have different commercial uses, there is a need to determine the extractive content of each species at high resolution. The objective of this study was to compare the fatty- and resin acid composition in heartwood and sapwood of Scots pine and lodgepole pine at five different sites in northern Sweden, to determine the potential for large scale outtake of pine extractives to biorefineries.

## 2. Methods

### 2.1. Sampling

Between five and eight pairs of sample trees were selected from five old trial sites in northern Sweden that had been planted with both Scots pine and lodgepole pine (Tables 1 and 2). Some sites contained mixed stands of the two species while in others they were planted in separate neighboring plots. Only dominant healthy and undamaged trees were considered. The trees within each pair were growing in close proximity to one-another and would have experienced the same growth conditions. In total, 60 trees (30 of each species) aged between 57 and 82 years were sampled.

The height, diameter on bark at 1.3 m, bark thickness and height to living crown were measured for each sampled tree. In addition, two 5 mm increment cores were taken from each sampled tree at a height of 1.3 m using an increment borer. The border between sapwood and heartwood was marked on the fresh cores in the field based on their visual differences due to their differing moisture contents. The radius of the heartwood and sapwood and the number of growth rings in each were then measured in the laboratory. The cores were subsequently stored at low temperature pending chemical analysis.

Prior to analysis, the heartwood and sapwood fractions of the increment cores were separated based on the demarcations made in the field and the samples from the two cores for each tree were pooled into one heartwood and one sapwood sample in order to provide sufficient material for the extraction process.

### 2.2. Chemical analysis

The chemical analyses were performed in two steps – first the fatty- and resin acids were extracted and then the chemical components of the extractives were analyzed. Fatty- and resin acids in the samples were extracted using a Soxhlet apparatus (Universal Extraction System B-811 from Büchi Labortechnik AG, Flawil, Switzerland) with a mixture of petroleum ether (bp 40–60 °C) and acetone (90:10 v/v) as the solvent for 1 h (12 cycles). The extraction time was optimized for the material. The extract was weighed carefully after derivatization with exactly 80 μl of bis-(trimethylsilyl)-trifluoroacetamide (Fluka, Sigma–Aldrich, Buchs SG, Schweiz) and 40 μl of trimethylchlorosilane (TMCS) (Fluka, Sigma–Aldrich, Buchs SG, Schweiz) at 70 °C, according to a previously reported method (Arshadi et al., 2008, 2009; Arshadi and Gref, 2005). The derivate was analyzed by GC–MS using a Shimadzu (QP2010 Plus) GC–MS instrument (Tokyo, Japan) with an auto-sampler operating in electron-impact mode (EI 70 eV). The instrument was equipped with a 30 m × 0.25 mm i.d., 0.25 μm film HP-5 MS capillary column coated with cross-linked 5% phenyl methyl siloxane. The column was temperature programmed as follows: 100 °C isothermal for 0 min, rising to 220 °C at 10 °C/min then to 235 °C at 1 °C/min and finally to 260 °C at 10 °C/min. The system was then maintained at 260 °C for 5.5 min. One microliter aliquots of the silylated samples, prepared according to a previously published method (Arshadi et al., 2009; Arshadi and Gref, 2005), were injected. An internal standard (heptadecanoic acid) (Acros Organics, USA) was added to permit the quantitative analysis of fatty acids and resin acids. The internal standard gave a signal that was different from the heptadecanoic acid naturally found in the extracts. All samples (including references) were run directly after extraction to avoid possible changes of signals over time in GC–MS spectra.

### 2.3. Statistical analysis

Statistical calculations were performed using MINITAB 15 (Minitab Statistical Software 2007) in conjunction with analysis of variance (ANOVA) tables. To check the assumption of constant variance, plots of residuals against fitted values were studied. Studies of the residuals did not reveal any heteroscedasticity, distortion, or other type of bias that would require transformation of the data. A significance threshold of 0.05 was used.

GC–MS can produce concentration data for each fatty and resin acid. As a result, the data set obtained in this work was large and complex, and required sophisticated multivariate tools to facilitate data analysis. Principal component analysis (PCA) (Jackson, 1991) can reduce a data set with many variables to a few meaningful principal components. The components usually describe a high percentage of the sum of squares of all the data; a smaller percentage is considered to be noise and left in a residual (Beebe et al., 1998; Brereton, 2003). PCA results are usually visualized in terms of score plots, which are used to analyze the clustering of objects (in this case, individual samples), and loading plots that are used to study clustering, outliers and gradients in the variables (in this case, individual fatty and resin acids). In this work, the GC–MS data set contained 120 objects (5 sites, 2 species and 2 wood types, with approximately 10 samples for each combination) and 31 variables in the form of the concentrations of specific fatty and resin acids (Table 3). The measured concentrations of some analytes were below the limit of detection (0.002% for individual fatty and resin acids) and were therefore set to zero. Before the analysis, all variables were mean-centered and scaled against their own standard deviation. This preprocessing step eliminates the potential for components with large concentrations to dominate the analysis.

Partial least squares discriminant analysis (PLSDA) (Beebe et al., 1998; Brereton, 2003), was used to model discrete (0/1) variables in