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Extraction of Tannins from Birch Inner Bark

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MOTIVATION, GOAL OF THE STUDY

The aim of the study was the piloting and building a Nordic/Baltic value chain for natural tanning agents to replace imported vegetable tannins typically sourced from South America.

Based on previous studies, bark has shown promise as a tanning agent for leather. This research aimed to determine whether extracts from spruce and birch inner bark could be used as tanning agents. The objective was to optimize the extraction and enrichment of tannins for potential future industrial tanning applications.

Plant based condensed and hydrolysable tannins are non-toxic natural polyphenols that are a commercial commodity industrialized for tanning hides to obtain leather and for a growing number of other industrial applications mainly to substitute petroleum-based products (Pizzi et. al. 2024). They are a definite class of sustainable materials of the forestry industry. They have been in operation for hundreds of years to manufacture leather and now for a growing number of applications in a variety of other industries, such as wood adhesives, metal coating, pharmaceutical/ medical applications, and several others.

On average, amount of bark in birch round wood variates from 12 % (Southern Finland) to 16 % (North Finland). (Partanen 2017; Hautakangas 2021).

PICTURE 1. Birch bark in the Centria open event. Background leather is spruce bark tanned and coloured by Kokkolan Nahka.

ACTIVITIES AT CENTRIA

1 CHEMICAL COMPOSITION OF BIRCH BARK

The diagram below (figure 1) shows one view of the mass balance of birch bark (Korpinen 2023). Tannin content will be included in phenolic acids, and tannins can be found mainly from inner bark of the birch.

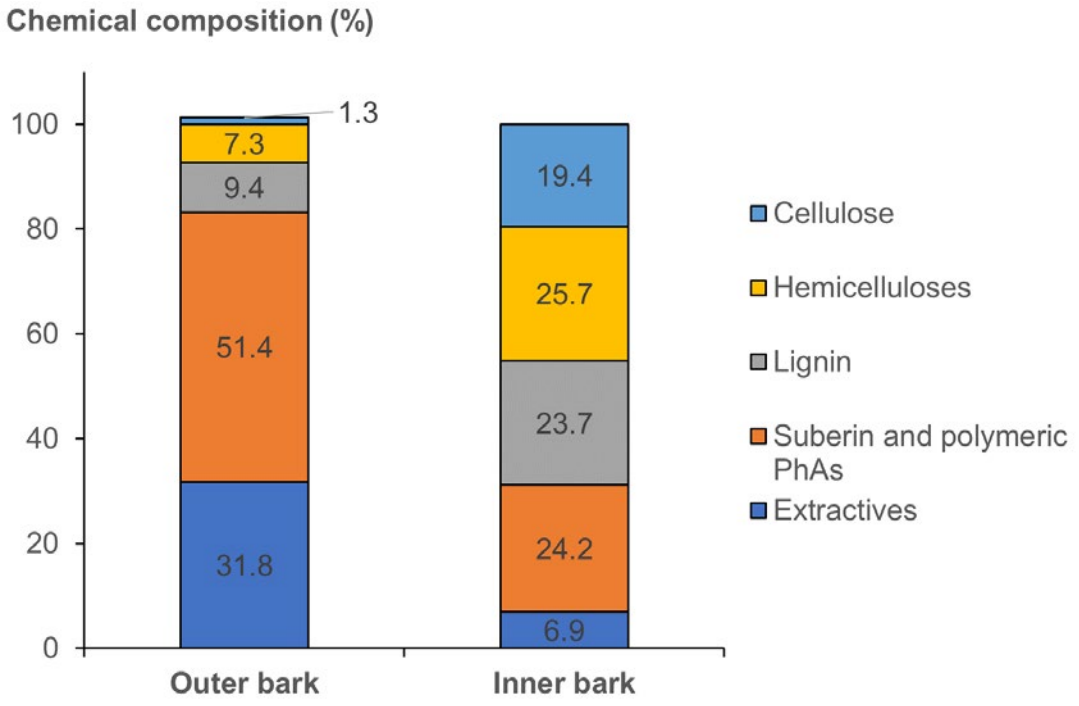


FIGURE 1. Gross chemical composition of birch outer and inner bark. Korpinen 2023.

Liimatainen (2013) provides a detailed analysis of the phenolic compounds found in the inner bark of silver birch (Betula pendula) in her thesis. Phenolic compounds are a prevalent class of plant secondary metabolites. The inner bark of birch is particularly rich in these compounds and exhibits one of the highest antioxidant activities among 92 Finnish plant materials. Condensed tannins (CTs), also known as proanthocyanidins (PAs), convert to anthocyanidins when exposed to hot acidic conditions.

2 OPTIMISATION OF EXTRACTION PROCESS

At Centria, the primary task was to optimize the extraction of tannins from birch inner bark, an industrial side stream. Utilizing forestry side streams in high value-added products is a key objective of the CEForestry project. Additionally, we conducted extraction trials on spruce bark to gain a realistic understanding of potential industrial extraction methods for other bark materials.

In the early stages of the project, a method for determining raspberry ketone was tested and developed. This quantitative method could serve as an indicator for the yield of hot water extractions of birch bark. Both HPLC and GC-MS methods were tested for raspberry ketone and found to be suitable, although the HPLC method may be challenging at low concentrations due to high noise in the chromatogram.

Optimization tests were conducted in the first year to better understand the conditions and plan the experimental design using MODDE software. Spruce bark was used as the raw material for these tests.

During the project, Marjo Puro completed a thesis titled “Optimization of Pressurized Hot Water Extraction: Spruce Bark Extraction with an ASE Device” (in Finnish) at Centria. The thesis focused on optimizing the separation of phenolic compounds from spruce bark using pressurized hot water extraction. The extraction was performed with an ASE device using ultra-pure water as the solvent at temperatures ranging from 90 to 140°C. The extraction time varied from 10 to 30 minutes, and the sample-to-solvent ratio was 1 g dry weight to 10–40 ml. Phenolic compounds were measured spectrophotometrically using the Folin-Ciocalteu method, and MODDE software was used for optimization. The results indicated that higher extraction temperatures were more effective in yielding phenolic compounds. Additionally, increasing the extraction time increased the total phenol content, but the solid-to-solvent ratio should not be too high.

The following figure (Figure 2) illustrates the results of optimizing tannin extraction from birch inner bark (sourced from Innomost). The variables tested were sodium hydroxide concentration and temperature. Total phenolic content (TPC) was measured to estimate tannin levels, while total reducing sugars were measured using the DNS method. For the tanning process, a high tannin content and low sugar content are desirable, as sugars are not beneficial.

According to MODDE, the optimal parameters for extracting tannins from birch inner bark are a sodium hydroxide concentration of 0.08–0.14 M and a temperature of 65–75°C. However, these experiments should be repeated, and the Divergan method should be used to determine tannin content.

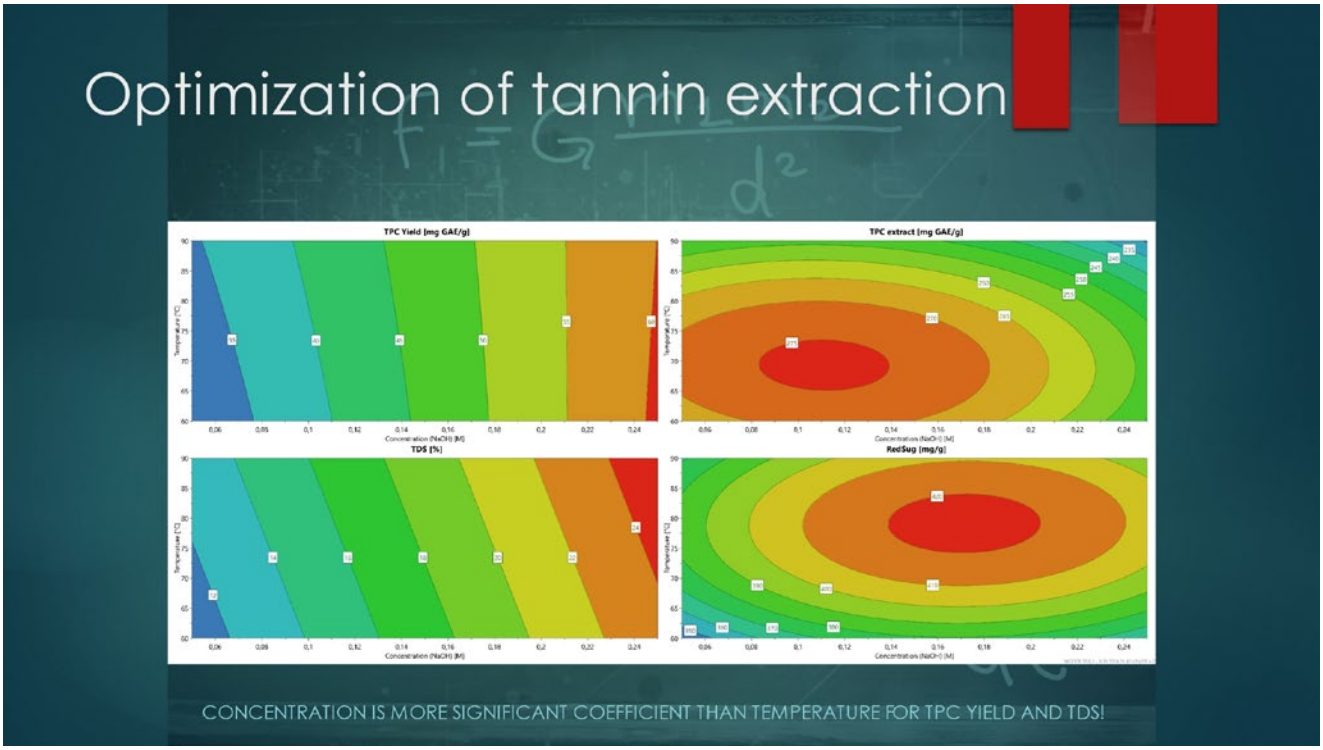


FIGURE 2. Optimization of tannin extraction. (Centria, Tatu Hiltunen)

3 DEVELOPMENT OF TANNIN CONTENT DETERMINATIONS

Given the current lack of a user-friendly and cost-effective method for determining tannin concentration in industrial applications, a reliable and consistent approach is essential. At Centria, both qualitative and quantitative methods were evaluated to determine tannin content and characteristics. The following methods were tested:

1. **ASTM D6401-99 (2020) - Hide Powder Method**: This standard test method is used to determine the quantity of soluble non-tannins and tannins in solutions of tannin extracts, water extracts of vegetable tanning materials, or tanning liquors. Tannins bind to hide powder when mixed as per this method.

1. **Divergan Method**: This method utilizes polyvinylpyrrolidone to adsorb tannins, and the total amount of tannins is then determined gravimetrically.

Pizzi (2024) compared the hide powder method and the Divergan method for testing the tanning power of tannins in leather manufacturing. The hide powder method involves the absorption of tannins on standardized dried powdered hide, which is still produced for gravimetric analysis of vegetable tanning agents and extracts. However, Pizzi (2024) notes that the hide powder method is now considered obsolete and has been replaced by the Divergan method (using polyvinylpyrrolidone*), due to its better reproducibility and more reliable standardization.

The Divergan titration method has thus superseded the hide powder method and is used to determine the percentage of tannins in an extract. Both methods are specific to leather tanning, measuring only the phenolic oligomers from tannin trimers to higher molecular weight oligomers, which are useful for leather tanning. They do not measure phenolic monomers and dimers, which, while not useful for tanning hides into leather, are valuable for adhesives, resins, and other applications. Therefore, these methods are not recommended for applications outside of leather tanning.

3.1 Characterisation of tannin by pyrolysis-GC-MS

Using pyrolysis-GC-MS, it is possible to identify pyrolytic fragments of commonly known condensed tannin structures (Figure 3). This method is fast for analyzing dry tannin samples and could serve as a straightforward approach for determining tannin content in plant-based products and extracts.

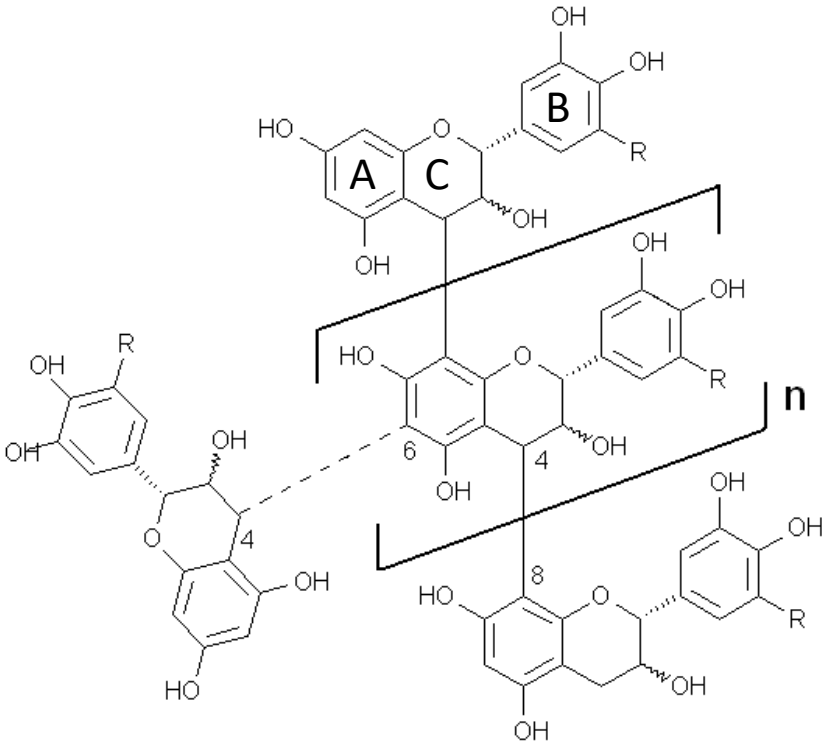


FIGURE 3. Common structure of condensed tannins. Bertaud, F., 2010. Possible pyrolytic fragments, ring A, B and C.

During pyrolytic fragmentation, tannin macromolecules typically produce specific fragments: resorcinol from ring A, catechol (R = H) from ring B, and pyrogallol from ring B (R = OH). These fragments help in identifying and analyzing the structure of tannins.

*[Polyvinylpolypyrrolidone Divergan RS 9003-39-8 - MilliporeSigma]

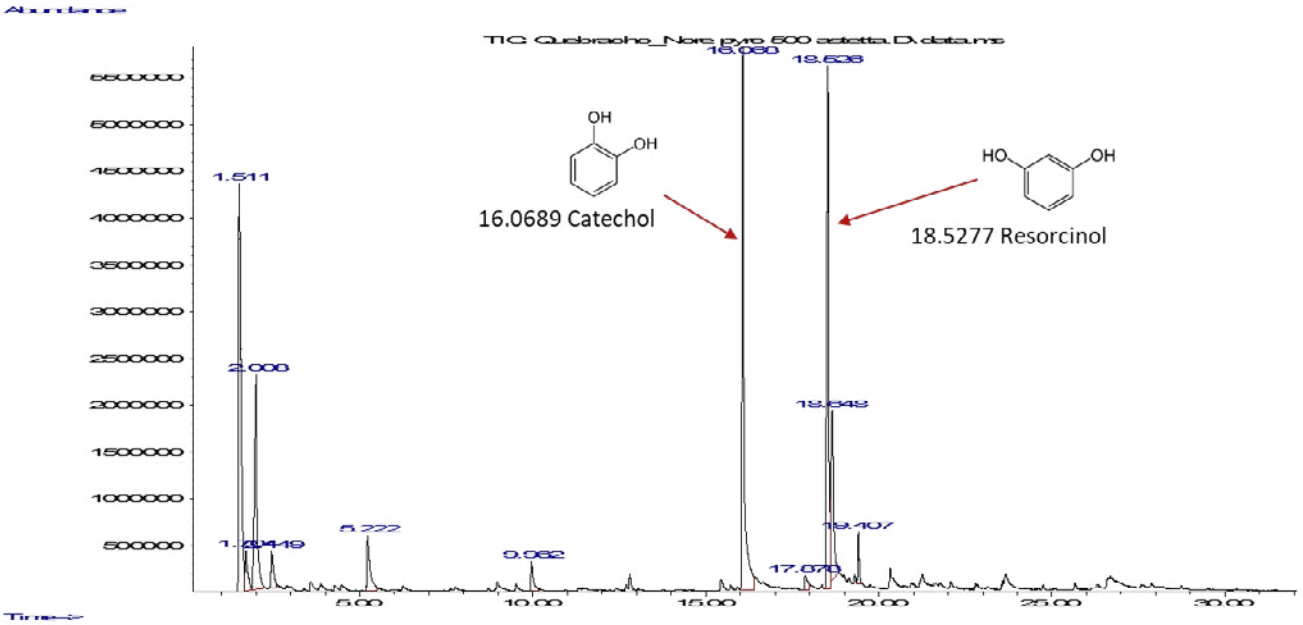


FIGURE 4. The pyrogram (py-GC-MS) of a Quebracho sample.

Quebracho sample (Figure 4) contains couple building blocks of condensed tannin structures. Therefore, pyrograms can be utilized to estimate the purity of tannins in these samples. This method helps in identifying and quantifying the various components, ensuring the quality and effectiveness of the tannins for their intended applications.

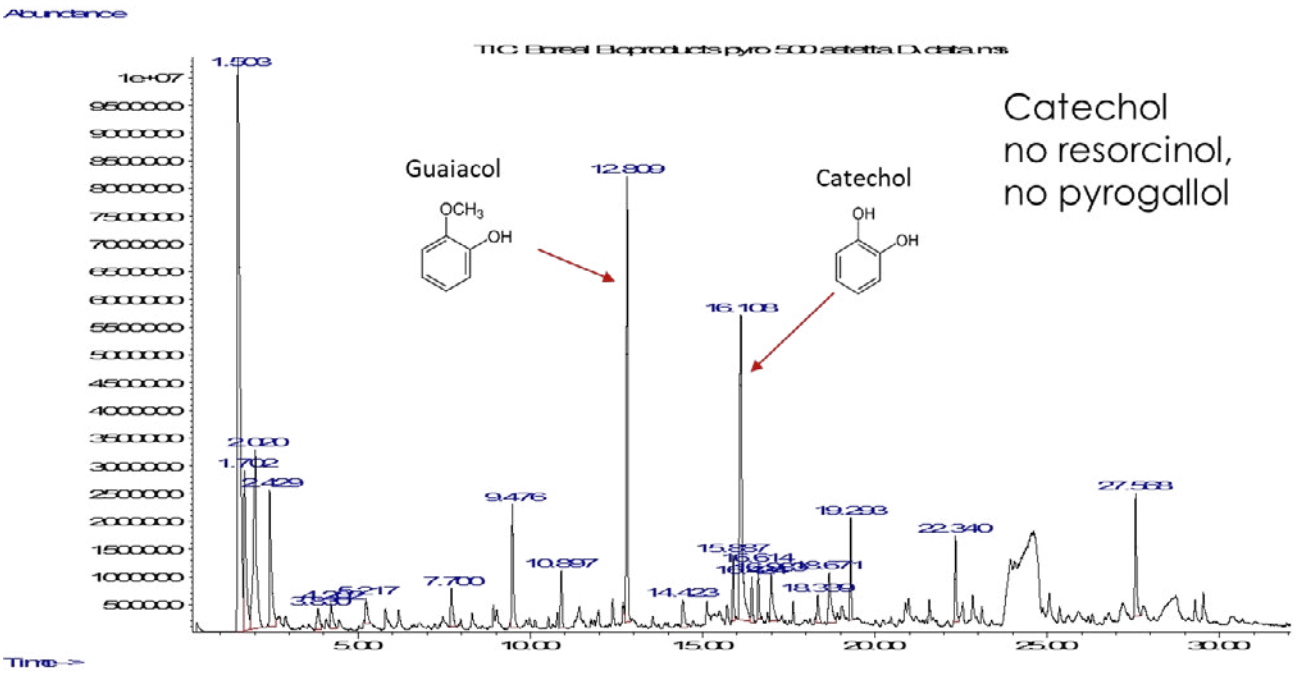


FIGURE 5. The pyrogram of a spruce bark extract sample.

Figure 5 indicates that spruce bark releases catechol moieties during pyrolysis, but there is no clear evidence of resorcinol or pyrogallol. Nevertheless, tanning experiments have demonstrated that spruce bark exhibits good tanning properties for deer hide.

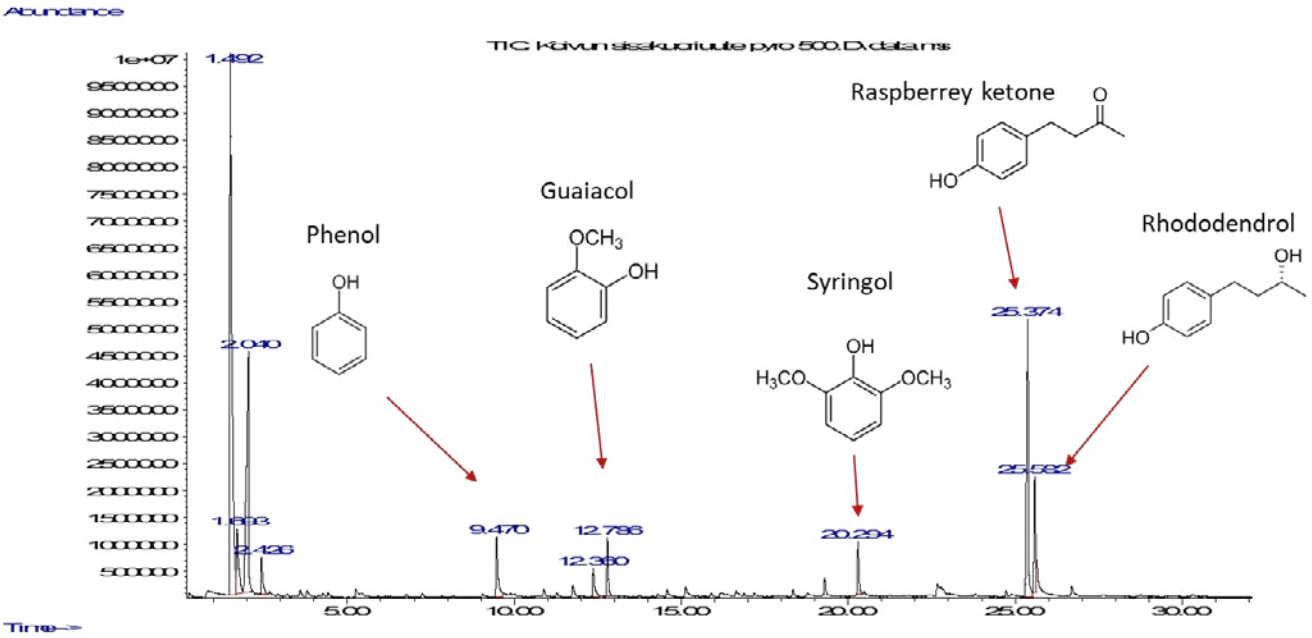


FIGURE 6. Pyrogram of birch inner bark extract.

Figure 6 shows that the sample contains numerous phenolic compounds but very few, if any, building blocks of the tannin structure. Only a small peak of catechol was observed at a retention time of approximately 16.1 minutes.

In summary, pyrolysis-GC-MS is an excellent tool for the qualitative assessment of tannins in wood biomasses. However, further testing with different samples is necessary to confirm its validity for determining tannins.

3.2 Comparison of the results between Luke (Natural Resources Institute Finland) and Centria

Centria and Luke compared the Divergan, ASTM, and UV methods to determine which are the most reliable and consistent for tannin analysis (Figure 7). Their goal was to identify methods that could be recommended for further development and utilization by enterprises.

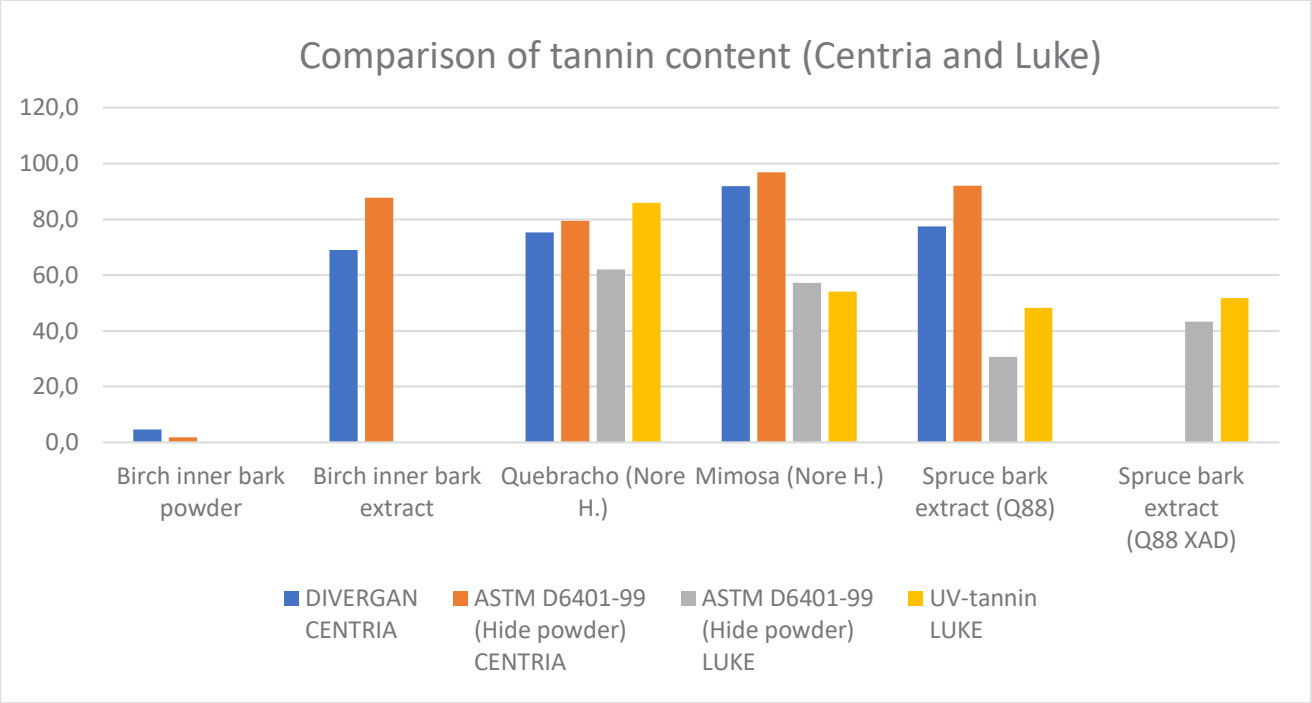


FIGURE 7. Comparison of tannin content by three different methods (Divergan, ASTM and UV) and between Centria and Luke.

Quebracho, mimosa, and spruce bark extracts (Q88) were analyzed at both Centria and Luke. Quebracho showed the most consistent results across the three different methods. However, the hide powder method result from Luke was somewhat lower than the other values. The results for mimosa and Q88 were somewhat confusing when compared between Centria and Luke, though internal results were more aligned. It's important to remember that the methods are different, and the reason for the significant differences remains unknown. More measurements and comparison work are needed.

Currently, the Divergan method appears to be the most promising for testing tannin content in various samples, showing good correlation when conditions and samples change. The study also indicates that birch inner bark and spruce bark are potential raw materials for tanning agents, as their tannin concentrations are almost equal to those of commercial tanning agents like Quebracho and Mimosa.

The UV-tannin method applied by Luke is responsive to changes in samples and is easy and fast to perform. However, a clean/pure standard is essential for accurate determinations and valid results.

Conca et al. (2024) utilized the ISO 14088:2020 standard method to determine the content of tannins and insoluble components. They measured a tannin content of 40.2% for chestnut tannin and 79.4% for quebracho tannin

TABLE 1. Comparison of determination methods of tannin content (%).

Sample	DIVERGAN CENTRIA	ASTM D6401-99 (Hide powder) CENTRIA	ASTM D6401-99 (Hide powder) LUKE	UV-tannin LUKE
Birch inner bark powder	4,6	1,9		
Birch inner bark extract	69,0	87,7		
Quebracho (Nore H.)	75,3	79,4	62,0	85,9
Mimosa (Nore H.)	91,9	96,8	57,2	54,0
Spruce bark extract (Q88)	77,4	92,0	30,7	48,2
Spruce bark extract (Q88 XAD)			43,2	51,7

Birch inner bark powder contains approximately 2–5% tannins. The extraction process significantly increases the tannin content, bringing it to levels comparable to those found in traditionally used tanning agents like Quebracho and Mimosa.

At Centria, the ASTM-method experiments generally yielded higher tannin content results, except for birch inner bark powder. The results between Centria and Luke were somewhat inconsistent. Nevertheless, all methods provided satisfactory tannin content levels for all measured bark extracts, including quebracho and mimosa.

In the original optimization test (Figure 3), the Divergan method was not yet applied, so determinations were made using TPC and DNS methods. These samples were later analyzed using the Divergan method. As shown in Table 2, there is a good correlation between extraction conditions and tannin content, indicating that the Divergan method responds well to changes in NaOH concentration and temperature. These results also confirm earlier findings from TPC analysis. The optimal NaOH concentration is around 0.08–0.12 M, and the optimal temperature is approximately 70°C.

TABLE 2. Optimization of birch bark extraction by NaOH solutions.

Sample	Tannins (Divergan) (%)	TPC (mg/GAE g)
Birch inner bark powder	4,6	35,2
Birch bark extract (opt. 0.25M NaOH, 60 °C)	41,9	58,7
Birch bark extract (opt. 0.15M NaOH, 75 °C)	96,7	48,3
Birch bark extract (0.25 M NaOH, 90 °C)	69,0	58,0
Mimosa H.Nore remeasurement	92,4	513,5

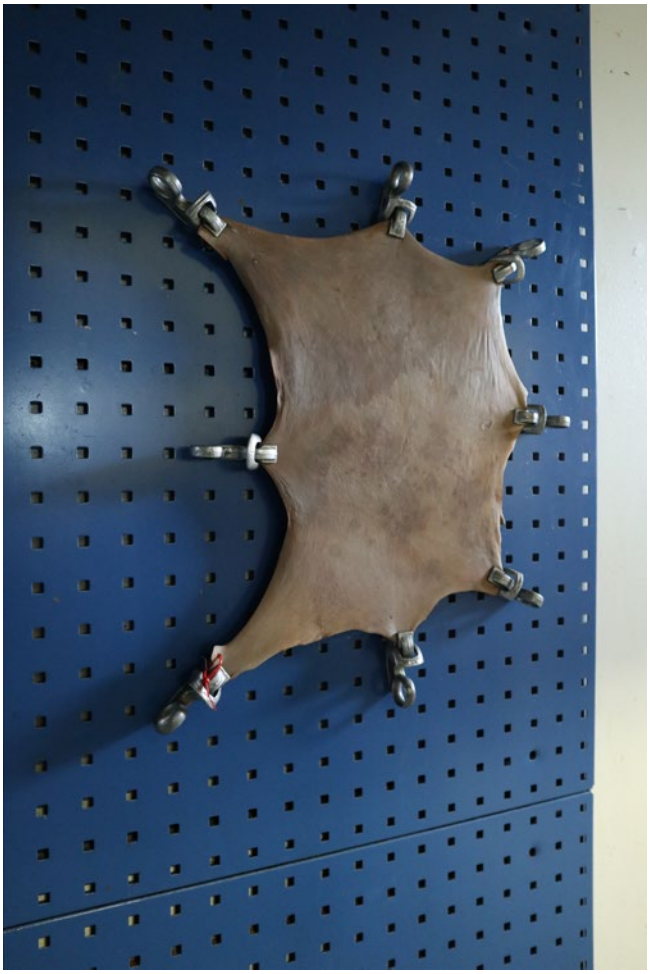
Table 2 shows that the highest measured tannin content was found at 0.15 M NaOH and a medium-high temperature using the Divergan method. Conversely, the TPC method yielded the best results with more concentrated NaOH. This suggests that the nature of tannins differs somewhat from the generic value of total phenolics. Further determinations and comparisons are needed to verify this. Overall, the Divergan method appears to be the preferred choice for determining tannins in leather tanning applications.

TANNING OF THE LEATHER

Preliminary leather tanning experiments were conducted by traditional tanning expert Hanna Nore at Kemiö Island in the Turku area. The final assessment of bark extract applicability for leather tanning can only be determined through lab-based tanning tests on real skin.

The initial tanning trials by Hanna Nore yielded very promising results, indicating significant potential to establish a national/Baltic value chain. This value chain would span from raw materials to bark extracts (intermediate products) and leather tanning, potentially replacing imported vegetable tannins from South America.

PICTURE 2. Raw deer skin, ready for tanning experiments. Photo Hanna Nore.



PICTURE 3. Tanned deer skin by plant origin natural tanning agent. Photo Hanna Nore.

PICTURE 4. Tanned deer leather by natural (originating from trees/plants) tanning agents and process. Photo Hanna Nore.

CONCLUSIONS

Birch bark has traditionally been used in plant-based tanning. At Centria, our goal was to enhance the tanning properties of birch bark by enriching its tannin content through extraction. Preliminary experiments showed that extracting birch inner bark with 0.15 M NaOH did not produce highly concentrated tanning agents, suggesting that this concentration might be too strong. Therefore, other extraction solvents should be tested for the inner bark fraction. Further work is needed to optimize and scale up the process, as well as to assess the feasibility of production.

Various methods were tested to measure the efficiency of tannin extraction. Natural tannins are chemically complex and heterogeneous, and the lack of standards complicates their straightforward determination. Our qualitative research indicated that birch bark tannins differ from those in spruce or pine bark. Total phenolic content (TPC) was used as an indicative method for tannin content, but preliminary results suggest that TPC does not accurately reflect the true tannin content.

The Hide Powder method, including ASTM standard methods ASTM D6401-99 (2020) and ASTM D6402-99 (2020), was tested for tannin determination. However, this method proved to be laborious and time-consuming. Consequently, the Divergan method (Pizzi et. al. 2024) was also tested and compared with other available methods. Meanwhile, LUKE has successfully applied the UV-tannin method in their research. The Divergan method proved to be much faster and less laborious than the Hide Powder method. Preliminary results were promising, showing a good correlation between tannin content and changes in extraction conditions.

RECOMMENDATIONS FOR FUTURE WORK

1. **Utilization of Birch Bark**: Birch bark is a high-volume side stream of the forest industry, making it readily available. There is a growing demand for sustainable tanning agents to replace environmentally hazardous chromium-based agents. Domestic needs could be met using native birch, spruce, and pine bark.

1. **Tannin Content Analysis**: Preliminary analyses using the Divergan method, Hide Powder method, and TPC showed that birch bark extract is comparable to exotic mimosa and quebracho. Although the NaOH extract of birch inner bark was not successful in tanning experiments, milder extraction conditions should be tested. Further verification is needed to confirm these results. Additionally, process scale-up and a techno-economic feasibility study are necessary.

1. **Divergan Method**: The Divergan method has shown promising results for tannin determination. It is faster and easier to use than the standard ASTM (Hide Powder) method. However, more data is needed to validate and improve the reliability of this method.

1. **Future Applications**: Purified tannin products have the potential for novel applications. Pizzi (2019) has compiled a comprehensive list of different industrial uses in a review article.

By focusing on these areas, we can enhance the utilization of birch bark and other native materials for sustainable tanning applications and explore new industrial uses for purified tannin products.

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Extraction of Tannins from Birch Inner Bark

Leather tanning has been practiced for centuries, even millennia, by immersing skins in water with special barks or woods containing tannins. This traditional method could take up to a year to produce leather. However, the modern tannin extraction industry is relatively new (Pizzi 2019).

Tannins are natural products found in most higher plants (Pizzi 2019). They are produced in almost all parts of the plant, including seeds, roots, bark, wood, and leaves, due to their fundamental role in defending the plant against insects, infections, fungi, and bacteria. This defense mechanism is based on tannins' ability to irreversibly complex proteins. There are two broad classes of tannins: hydrolysable tannins (such as gallo-tannins and ellagi-tannins) and condensed polyflavonoid tannins, the latter being stable and rarely subject to hydrolysis.

In this Interreg BSR-funded project, our research focused on the usability of birch bark applications, particularly for tanning leather. Preliminary tests indicated that birch inner bark has sufficient properties for tanning. Enriching the tannin fraction of birch inner bark through extraction can improve tanning properties and reduce logistic costs. However, further research is needed to verify results and improve the techno-economic feasibility of production. This includes further analysis of the extract, optimization of the extraction process, tanning experiments with hides of different origins, and larger-scale piloting.

During extraction optimization tests at Centria, there was a significant need to determine the tannin content in the extracts. We compared the traditional Hide Powder method, the Divergan method, and Total Phenolic Content (TPC) internally. The results were also compared with Luke's determinations using the Hide Powder method and the UV tannins method. Preliminary results suggest that the Divergan method is very suitable for determining tannins in tanning agent analysis. The Divergan method is fast, less laborious, and reliable enough to optimize both process development and product quality. The literature also supports the suitability of the Divergan method for leather tanning (Pizzi 2019; Pizzi, Laborie, Candan 2024).

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