# Understanding the Effects of Ionic Liquids and Antisolvent Addition on the Extraction and Recovery of *Pinus Radiata* Bark Components

N. K. Brar,[a, b] W. Grigsby,[c, 1] S. J. Hill,[c] L. Raymond[c] and C. C. Weber[a, b*]

[a] *School of Chemical Sciences, University of Auckland, Auckland, New Zealand.*

[b] *MacDiarmid Institute for Advanced Materials and Nanotechnology, Wellington, New Zealand.*

[c] *Scion, Rotorua, New Zealand*

Corresponding author Cameron C. Weber: cameron.weber@auckland.ac.nz

---

[1] Present address: Henkel NZ Ltd, Auckland, New Zealand

# Understanding the Effects of Ionic Liquids and Antisolvent Addition on the Extraction and Recovery of *Pinus Radiata* Bark Components

Ionic liquids (ILs) are being increasingly explored as extraction solvents due to their tunable properties, which can control their ability to dissolve an array of solutes. IL selection requires an in-depth understanding of the consequences of IL structure on extraction outcomes for different substrates. Here, 14 ILs containing cations and anions that have been systematically modified to examine key structural effects have been explored for the extraction of chemical components from *Pinus radiata* bark. The extraction efficiency relative to the mass of bark ranged from 4 to 70%, and the isolation of bark components was evaluated using antisolvent addition. Extraction outcomes highlighted the importance of the IL anion in affecting extraction efficiency and selectivity, with a secondary role from the IL cation, and point towards a simple route for improving the overall selectivity of biomass extractions through control of the antisolvent addition process.

Keywords: ionic liquids, bark, solvent extraction, antisolvent, biorefinery

## Introduction

One of humanity's most significant challenges is the transition to sustainable energy sources in light of the need to combat climate change. Accompanying this transition is the need to identify renewable chemical feedstocks to replace existing petrochemical sources. Biomass has the potential to make a significant contribution toward sustainably meeting future chemical needs.[1] Bark, in particular, is a promising biological resource for this use as it is currently a widely available forestry waste product. *Pinus radiata* is one of the most utilised woods in New Zealand, accounting for ca. 90% of New Zealand's plantation forests.[2] It is a medium-dense softwood renowned for fast growth and applicable to a wide variety of traditional and emerging forestry product uses.[3] *Pinus radiata* bark, like most barks, contains four main classes of substances: suberin, lignin, carbohydrates (including hemicellulose and cellulose) and polyphenols together with other extractives. Many bark extractives show bioactivity such as antifungal, anti-tumour, anti-carcinogenic, anti-diabetic and anti-inflammatory activity and hence, are gaining attention from researchers as therapeutic agents.[4] The structural biopolymers of bark are of emerging interest for the production of bio-based chemicals and materials.[5-7] *Pinus radiata* bark represents a significant and growing waste product within New Zealand and, other than boiler fuel, has limited high value applications at present. Moreover, very few studies examine possible routes for the separation and isolation of key structural components such as cellulose, lignin and suberin in these barks alongside the fractionation and isolation of traditional bark extractives. Therefore, further research is needed to explore novel alternatives for the extraction and fractionation of *Pinus radiata* bark to more effectively utilise the components of this bark as part of future biorefineries.

Bark extraction processes have traditionally utilised organic solvents and water to separate the extractives from the structural biopolymers of bark.[4, 8] For example, an extractive content of loblolly pine (*Pinus taeda*) bark of up to 27.5% was observed by performing sequential and exhaustive extractions using hexane, benzene, ethyl ether, ethanol, water and 1% NaOH.[4] The issue of exhaustive extractions following this approach is the need for volatile and often flammable solvents and energy intensive distillation processes for the subsequent isolation of the extracts.

Ionic liquids (ILs) are salts often defined as having melting temperatures below 100 °C and have been proposed as non-volatile alternatives to conventional organic solvents due to their unique solvation properties.[9, 10] ILs can be considered “designer” solvents with tunable physicochemical properties that can be adjusted by selecting appropriate ions to suit the requirements of a particular process.[11] For example, the choice of anion and the length of the cation alkyl chain play an important role in the solubility of ILs in water.[12] IL ion selection is often supported by empirical polarity parameters, particularly Kamlet-Taft parameters, which can relate the polarity of IL ions to their performance in specific applications. These parameters are α (hydrogen bond donating ability), β (hydrogen bond accepting ability) and $\pi^*$(dipolarity/polarisability).[13] The α parameter is typically affected by the cation, the β parameter by the anion and $\pi^*$ values tend to be close to 1 and change only slightly with ion composition.[14, 15]

The composition of bark differs from that of wood due to a greater abundance of polyphenols, suberin, extractives, ash and lignin with a reduced quantity of carbohydrates.[4, 16] Although considerable work has been done exploring the extraction of wood and biopolymers abundant in woody biomass using ILs,[17-19] little is known about the ability of ILs to act as solvents for the selective extraction of bark components. Much of the interest in ILs for biomass extraction originates from the discovery that some ILs can solubilise traditionally poorly soluble biopolymers such as lignin, cellulose and hemicellulose without the need for derivatising agents or harsh conditions.[20-23] The dissolution of cellulose is favoured in ILs that incorporate strong hydrogen bond acceptor anions, i.e., those with large β values, due to strong hydrogen bonding interactions between hydroxyl functionalities of the cellulose and the IL anion.[20, 21, 23, 24] In contrast, the dissolution of lignin does not increase with increasing β value, although a minimum β is required to enable lignin dissolution. Instead, lignin dissolution tends to be affected by the α parameter of the IL.[25]

In addition to the biopolymers commonly found in other types of woody biomass, bark contains significant amounts of suberin. Suberin is a waxy substance found in cork and bark that is difficult to extract intact from these sources due to its complex hydrophobic structure. Isolation and depolymerisation of suberin is traditionally a laborious process requiring harsh chemical processes involving ester bond hydrolysis, normally attained by alkaline treatment.[26] While there have not been any studies performed on the extraction of suberin from *Pinus radiata* bark using ILs, the extraction of suberinic material from cork has been examined.[27] It was identified that choline-based ILs performed better than imidazolium ILs to extract suberinic material with minimal impact of the anion, albeit only similar carboxylate anions were investigated. These examples demonstrate that structural features of IL cations and anions are of substantial importance for determining the solubility of key structural biopolymers in biomass and hence will likely affect the selectivity of *Pinus radiata* bark extraction and the recovery of these compounds.

As illustrated by the preceding discussion, ILs are promising solvents for biomass extraction, although, to the best of our knowledge, there are no reported studies using these novel solvents for *Pinus radiata* bark extraction. Therefore, a major goal of this research is to understand the relationship between IL structure and the extraction of key components from *Pinus radiata* bark. Hydrogen-bonding interactions in ILs are likely to play a pivotal role in fractionating different chemical compounds found in the bark. Moreover, the amphiphilic nanostructure of ILs may affect the separation of bark components due to their greater affinity for hydrophobic compounds. To examine the effect of these factors, the ILs used were systematically varied to explore the relationships between hydrogen bonding and amphiphilic nanostructure on the extraction of the bark. Three different cation types: 1-alkyl-1-methylpyrrolidinium ($[C_nC_1pyrr]^+$), 1-alkyl-3-methylimidazolium ($[C_nC_1im]^+$) and 1-alkylguanidinium ($[C_ngun]^+$) were selected based on their increasing hydrogen bond donating strength with n = 4 and 8 to assess the influence of the alkyl chain on bark extraction. Similarly, the anions explored included bis(trifluoromethanesulfonyl)imide ($[NTf_2]^-$), dicyanamide ($[N(CN)_2]^-$), and dimethylphosphate ($[Me_2PO_4]^-$) in increasing order of their hydrogen bond accepting strength. The $[C_4gun]$ ILs, apart from $[C_4gun][NTf_2]$, were found to be solid at room temperature and were not used for bark extractions. Only $[C_8gun][NTf_2]$ was prepared of the $[C_8gun]$ IL series. The Kamlet-Taft parameters ($\alpha$, $\beta$, and $\pi^*$) of the ILs chosen, where they have been reported, are summarised in Table 1 to illustrate the variation in their hydrogen bonding abilities. The structures of the cations and anions selected are shown in Figure 1.

[Table 1 near here]

[Figure 1 near here]

The recovery of the bark extracts was also explored as this is an important but often-overlooked area when using non-volatile solvents such as ILs. Antisolvent additions were examined as the main route for recovery as this approach is one of the more practical methods for separating solutes under ambient conditions, both for biopolymers such as cellulose and for small molecules.[28-30] Similar to the use of ILs, antisolvents of varying polarity (water, acetonitrile (MeCN), dimethyl sulfoxide (DMSO)) were used to examine the relationship between the use of antisolvent and the nature of the recovered bark components. Antisolvents were added sequentially to explore the selectivity of the recovered extract with added antisolvent volume.

## Materials and Methods

### *Pre-drying of bark*

*Pinus radiata* bark was recovered from the lower stem (0 - 6 m) of freshly harvested 25-

28 year old trees and then air-dried before milling to 2-4 mm particle size. Prior to extractions being performed, the bark was pre-dried by heating under nitrogen flow at 50 °C for 2-3 hours and then in *vacuo* at 50 °C for 16 h. The drying procedure was performed in 10 g batches, and each time resulted in a reduction in mass of 20-23% compared to the air-dried bark. IR spectra were obtained before and after this procedure to confirm there were no significant structural changes due to the drying process. These are included in the ESI.

### *Synthesis of ILs*

The synthesis of ILs and the source of chemicals used is given in the ESI.

### *Extraction of bark by ionic liquids*

IL was added to a pre-weighed bark sample to produce a 5 w/v% suspension, which was then stirred at 100 °C for 24 h. The IL supernatant was removed and passed through a syringe filter to remove any suspended bark particles. The residual bark was collected by Buchner filtration. Residual bark was washed using an appropriate solvent (water or dichloromethane (DCM)) to remove residual IL. The bark residue was analysed using IR and solid-state NMR. The IL extracts were analysed by NMR, although the complexity of the IL extracts and the low concentration of individual components in these extracts limited the usefulness of this analysis. Moreover, the overall extraction yield was determined from the mass of recovered bark.

### *$^{13}$C Solid-State NMR*

$^{13}$C solid-state NMR was obtained using an AVIII 200 MHz spectrometer equipped with a 4 mm MAS probe. Samples were ground in a mortar and pestle to form a fine powder and were inserted into 4 mm ZrO rotors fitted with Kel-F caps and then analysed. The standard CP-MAS experiments had a 3.5 µs proton preparation pulse followed by 1 ms contact time. A total of 10k transients were collected for each sample, and the resulting data were Fourier transformed, applying 25 Hz Gaussian line broadening. Non-quaternary suppressed experiments were collected with a 70 µs (total) dephasing delay. NMR spectra were analysed using MestReNova software, applying a Savitzky-Golay smoothing followed by GSD deconvolution of peaks refined using 20 fitting cycles. Peak areas assigned to each of the key components were summed and normalised to the peak area of the lignan OMe peak at 56 ppm, with values compared to bark subjected to an identical washing procedure but not subjected to IL extraction.

### *Antisolvent addition to ionic liquid extracts*

To test the effect of antisolvent addition, small amounts of antisolvent were added sequentially, with any solid formed isolated and characterised separately to see if the quantity of antisolvent added influenced selectivity. The first step was the addition of 0.5 mL of antisolvent to 1 mL of the IL extract. Any suspended solids formed in the first sample were settled by centrifugation for 5 – 10 min. The supernatant was separated from the solids, and the solids were washed with the antisolvent used for their separation. Further antisolvent (0.5 mL) was added to the supernatant after the solids had been removed and the same process followed as for the first sample. This process continued with increasing amounts of antisolvent with any solids formed separated and characterised. The solids formed were characterised using IR. Based on the initial IR outcomes, the antisolvent addition process was further refined and scaled up (5 mL or 10 mL of IL extract) based on the optimal antisolvent addition volumes for the selective recovery of fractions, with the solids from the scaled-up samples further characterised by IR and pyrolysis GC-MS.

### *FT-IR analysis*

FTIR analysis was performed on a Bruker Vertex 70v FT-IR Spectrometer. Solid samples were dried at 50 °C, firstly under a nitrogen purge for 1 – 2 hours and then under high vacuum overnight to remove residual water. Before analysis, samples were ground into a powder using a mortar and pestle. Data were recorded at room temperature, in the range of 400 – 4000 $cm^{-1}$, by accumulating 256 scans with a resolution of 8 $cm^{-1}$.

### *Tetramethylammonium hydroxide pyrolysis gas chromatography mass spectrometry (TMA-OH-Py-GC/MS) analysis*

The Py-GCMS instrument was composed of a Lab Frontier pyrolysis furnace with an auto-shot sampler (Pyrolysis), an Agilent 7890A gas chromatograph (GC) and Agilent 5973 single quadrupole mass spectrometer (MS). Samples (0.5 mg ± 0.1) were weighed directly into a pyrolysis cup, and 10 µL of 25 wt% tetramethylammonium hydroxide (TMAH) in methanol was added to each to enable their derivatisation during pyrolysis. Samples were pyrolysed at 500 °C for 12 seconds before the gas/vapour products were injected into the GC/MS with a 20:1 split ratio. Analyte separation took place on a 30 m HP-5MS column (Agilent) with 0.25 mm inner diameter and 0.25 µm film thickness. The pyrolyser interface and the GC injection temperature were both set at 250 °C, the transfer line temperature was 280 °C, and the ion source temperature was 230 °C. The carrier gas was helium at a 1.0 mL/min constant flow rate. The oven temperature program was set at 1 min isothermal heating at 40 °C, followed by a ramp of 6 °C/min to 300 °C, then held at this temperature for 10 min. The mass spectra were obtained in electron impact (EI) mode at 70 eV by scanning m/z 35 – 800 amu at 2.6 scans/s.

The relative proportion of each structural component in the bark was determined as the sum of the total ion count of several characteristic pyrolysis products divided by the total ion count of all products. For suberin/waxes, the compounds used were the methyl esters of tetracosanoic acid, hexadecanoic acid, dodecanoic acid, docosanoic acid and the dimethyl ester of octadecanedioic acid. 2-Methoxy-5-methylphenol, 2,3,5,6-tetramethylphenol, 2,6-dimethoxyphenol, 2,5-dimethylanisole, and 2,4,6-trimethoxytoluene were selected as representative compounds corresponding to the lignin/tannin component. Finally, 3-methylfuran and 2-(methoxymethyl)furan were chosen as the carbohydrate components.

## Results and Discussion

### *Bark Extraction Yields*

The extraction efficiency of the ILs prepared was explored at a biomass loading of 5 w/v% at 100 °C for 24 h. A temperature of 100 °C was selected as this corresponds to the temperature where the maximum solubility of key biopolymers such as cellulose have been observed in ILs.[31] After their synthesis, it was discovered that the proposed [$C_n$gun][$Me_2PO_4$] and [$C_n$gun][$N(CN)_2$] ILs were solid at room temperature and therefore unsuitable for the extraction and recovery process, so these were excluded from the extraction studies. The extraction yield was quantified based on the mass loss of the washed and dried bark residue recovered after the extraction process compared to the initial mass of the dried bark (Table 2). Extraction yield experiments were repeated for ILs that demonstrated an ability to extract significant proportions of the bark, except for some [$N(CN)_2$]$^-$ ILs. Only individual runs were performed for [$N(CN)_2$]$^-$ ILs apart from [$C_4C_1$im][$N(CN)_2$] due to issues observed in their analysis highlighting potential side reactions in the bark, which will be discussed later. While most ILs displayed reliable extraction results, [$C_8C_1$im][$Me_2PO_4$] provided not readily reproducible outcomes. [$C_8C_1$im][$Me_2PO_4$] was the most viscous of the ILs explored and formed a gel following the bark extraction process. This affected the separation of bark from the IL and likely caused mass transfer limitations during the extraction process itself, leading to inconsistent outcomes.

[Table 2 near here]

Table 2 highlights that the extraction yield is strongly affected by the IL anion, with the yield typically decreasing in the order $[Me_2PO_4]^-$ > $[N(CN)_2]^-$ > $[NTf_2]^-$ (e.g. 70% to 4% for the $[C_4C_1pyrr]$ series). This order is consistent with the observed colour change of these ILs after extractions, with darker solutions observed following extraction for ILs containing the $[Me_2PO_4]^-$ anion compared to the weakly hydrogen bond accepting $[NTf_2]^-$ anion. This general order similarly agrees with prior studies on biomass extraction, where the β value of an IL is a key determinant in its ability to solubilise key compounds, particularly with respect to the solubility of structural biopolymers such as cellulose and lignin.[20, 21, 23, 25]

The effect of the cation on the extraction yield was also examined. Table 2 demonstrates that the $[C_4C_1pyrr]^+$ cation tends to lead to the most efficient bark extraction, with $[C_4C_1pyrr][Me_2PO_4]$ leading to the highest extraction yield observed (70%). In the case of the $[NTf_2]^-$ anion, $[C_4gun]^+$ led to the highest (14%) extraction yields of the $C_4$ cations, although all of these values are relatively small. The greater extraction yields observed for $[C_4C_1pyrr][Me_2PO_4]$ (70%) compared to $[C_4C_1im][Me_2PO_4]$ (33%) may arise from reduced cation-anion interactions, which will assist the solvation of bark components by the IL anion. It has also been found that pyrrolidinium ILs are capable of solvating aromatic solutes through the intercalation of alkyl chains between the localised charge on the cation and the aromatic substrate, which compensates for reduced cation-π interactions compared to imidazolium ILs.[32]

The localised charge also leads to a larger relative hydrophobic surface area of the cation, which may assist the extraction of the hydrophobic components of the bark, such as suberin and lower molecular weight waxes.

Increasing the alkyl chain of the cations typically led to a decrease in extraction yield. The large uncertainty in the extraction yield of $[C_8C_1im][Me_2PO_4]$ makes specific trends difficult to determine; however, it appears that smaller, more polar ILs tend to be more favourable for extracting bark components.

The extraction yields obtained compare favourably with extraction using conventional solvent systems. For example, the use of maceration led to extraction yields ranging from 2.0-23.4% for *Pinus radiata* bark using water, aqueous methanol and aqueous acetone.[33, 34] The highest yield of 23.4% was obtained using water at 100°C and a biomass loading of 2 w/v% and so is comparable to the extractions performed here.[34] This highlights that the ILs that display the most effective extraction efficiencies can outperform conventional solvent systems in terms of their absolute ability to extract components from *Pinus radiata* bark.

While extraction yield is an important measure, the selectivity of the extraction is in many ways more important given the ultimate aim of the fractionation of the bark. While attempts were made to characterise the IL extracts directly using NMR and IR, the complexity of the extracts and the low concentration of individual components meant that these attempts were unsuccessful. Instead, the residual solid was investigated to identify the chemical components removed during the extraction procedure.

### *Solid-State NMR analysis of bark residues*

$^{13}C$ solid-state NMR was used to characterise the solid residue remaining after the extraction of the bark with different ILs to gain insight into the selectivity of the extraction process. The assignment of the solid-state NMR peaks were made based on previous reports of similar biomass substrates.[35-38] The peaks at 144 ppm and 154 ppm were assigned to aromatic carbons from tannins and lignin, the peak at 56 ppm to the $OCH_3$ of lignans and methoxylated lignin, the peaks at 72 – 75 ppm to ring carbons of cellulose excluding those that form glycosidic bonds and the peaks at 20-40 ppm were assigned to the methylene groups of aliphatic constituents. While some overlap within these regions between structural components has been noted, changes in these spectral regions will provide a semi-quantitative guide to the components extracted from the bark. Figure 2 depicts the assignment of key solid state NMR peaks to the bark's lignin, tannin, suberin, and carbohydrate components.

[Figure 2 near here]

The recovered solid residues collected for solid-state NMR were washed with hot water for samples extracted with $[Me_2PO_4]$- and $[N(CN)_2]$-based ILs, whereas samples extracted with $[NTf_2]$-based ILs were DCM washed. These washing solvents were selected based on the solubility of the ILs. To account for any extraction that may occur during these washing steps, dried bark not subjected to extraction was similarly washed and analysed by $^{13}C$ NMR for comparison. It was found that washing with hot water and DCM proportionally increased the relative integral of peaks of all 3 components. As peak areas are normalised to the OMe peak at 56 ppm from lignin, this can be attributed to the preferential extraction of methoxylated aromatics in the washing step.[33]

To easily compare trends in the solid-state NMR data, the relative areas obtained for each spectral region were normalised to the area of the peak at 56 ppm. These relative peak areas were then divided by the corresponding area for the bark subjected only to the washing procedure. These proportions are summarised in Figure 3 for all ILs with NMR spectra and raw values provided in the ESI. A lower proportion implies the preferential extraction of that compound relative to the OMe peak at 56 ppm compared to bark subjected only to the washing procedure.

[Figure 3 near here]

Figure 3 reveals several notable trends. Firstly, most ILs containing the $[NTf_2]^-$ anion led to very small or insignificant changes in the proportion of lignin/tannins and carbohydrates present. This is to be expected given the low extraction yields for these ILs and the use of a weakly interacting anion. However, some aliphatic extraction was observed for these ILs, particularly $[C_4C_1im][NTf_2]$, $[C_4C_1pyrr][NTf_2]$, $[C_8C_1pyrr][NTf_2]$ and $[C_8gun][NTf_2]$.

Conversely, the extraction of bark by ILs containing the $[Me_2PO_4]^-$ anion led to notable decreases in the proportion of lignin/tannin remaining relative to the water washed bark, with proportions $< 0.7$ for all of these ILs and as low as 0.38 for $[C_4C_1pyrr][Me_2PO_4]$. Given the normalisation of the spectrum to the $OCH_3$ group of lignin, this shows greater extraction efficiency of non-methoxylated lignin and tannins by these ILs regardless of the cation present. These ILs also demonstrated the greatest preferential extraction of carbohydrates compared to the ILs containing other anions, consistent with the known ability of these solvents to dissolve cellulose.[39] However, the proportion of carbohydrates in the solid residue remained around 0.7 for these ILs, apart from $[C_8C_1pyrr][Me_2PO_4]$, where no preferential extraction could be observed, highlighting that the extent of carbohydrate extraction by these ILs likely remains small. The extent of aliphatic extraction by the $[Me_2PO_4]$-ILs appeared to be less than the $[NTf_2]$-ILs, with no clear evidence of preferential extraction at all by $[C_4C_1pyrr][Me_2PO_4]$, although the broad peaks observed in this region of the solid state NMR spectrum for bark extracted by $[C_4C_1pyrr][Me_2PO_4]$ may have led to an overestimation of the proportion of aliphatics (ESI).

The residues obtained following extraction by $[N(CN)_2]^-$ containing ILs did not show any notable preferential extraction of components. Moreover, residues obtained following extraction by $[N(CN)_2]^-$ ILs had additional peaks at chemical shifts of 21 ppm and 13 ppm not present for bark extracted by ILs containing different anions. This is despite the solid residue being washed with hot water to remove residual IL using the same conditions as for the $[Me_2PO_4]^-$ ILs. These additional peaks were present regardless of the cation used. This suggests that there is potentially a side reaction occurring between the bark and the $[N(CN)_2]^-$ anion. Further evidence for such a side reaction was observed due to unusual IR spectra observed, significant changes in the colour of the bark residue from brown to black after the extraction and elemental analysis results which are discussed in greater detail in the ESI.

### *Recovery and isolation of Pinus radiata bark extracts*

It has been determined that among the three IL anions that were explored, the $[Me_2PO_4]^-$ anion appeared to be the most effective for the extraction of a wider range of components than the $[N(CN)_2]^-$ and $[NTf_2]^-$ anions. Additionally, ILs generally appear to be more successful at extracting aromatics and aliphatics than carbohydrates.

Many investigations have been performed exploring the regeneration, purification, and separation of compounds from ILs using antisolvents.[21, 40, 41] For these extracts to be useful for the fractionation of the bark, it is necessary to explore if the components solubilised within these ILs can be selectively recovered. While multiple approaches could be used to isolate the extracts, one of the most feasible to perform on a larger scale is fractional precipitation by antisolvent addition. By controlling the quantity of antisolvent addition and the identity of the antisolvent, this approach could be useful in improving the selectivity of the extracted compounds within the recovery and isolation step, allowing for the separation of specific subclasses of compounds from the bark extract.

*Identification of recovered components*

Antisolvent addition was used on solutions obtained after employing the standard extraction conditions (Table 2). The $[NTf_2]^-$ ILs were excluded from this approach as they were determined to have negligible efficacy as extraction solvents. IR spectroscopy was used to initially characterise fractionated precipitates. From this analysis, the specific components that had been isolated could be classified by functional group, with key absorptions for aliphatics (suberin and waxes where waxes refers to smaller molecular weight aliphatic components such as fatty acids and resin acids) being 2919 $cm^{-1}$ and 2850 $cm^{-1}$, lignin 1604 $cm^{-1}$, tannins 1512 $cm^{-1}$ and carbohydrates 1033 $cm^{-1}$.[27, 42] To verify this assignment and gain insight into the relative absorbance of each of these components, IR spectra were obtained for model compounds. These included lignin (kraft lignin), tannins (tannic acid), suberin/waxes (decanoic acid), and carbohydrates (microcrystalline cellulose) (further details in ESI).

To gain insight into changes in the proportions of components within the recovered precipitates, the relative absorbances of the IR peaks were obtained, referenced to the lignin peak (1605 $cm^{-1}$). Underlying these absorptions from structural subclasses such as suberin/waxes, carbohydrates and lignin, there will be overlapping peaks that cannot be easily distinguished. For example, aliphatic hydrocarbon components other than suberin/waxes cannot be distinguished as they all contain significant C-H stretching absorbances around 2919 $cm^{-1}$ and 2850 $cm^{-1}$. Other polyphenols such as monomeric flavonoids also show aromatic ring-breathing absorptions similar to lignin and tannins,[43] although these tend to be at slightly lower wavenumbers (1448 $cm^{-1}$).

Water, MeCN and DMSO were selected as antisolvents to explore the effect of antisolvent polarity and the nature of their interactions with ILs. Initial experiments involved the addition of 0.5 mL of antisolvent to 1 mL of IL extract, followed by measuring both the yield and IR spectrum of any solid recovered and then sequentially adding more antisolvent until no further solid or limited additional amounts of solid could be isolated. Based on these initial experiments, it was revealed that MeCN and DMSO led to mixed fractions with limited evidence of preferential precipitation and low solid recovery yields (ESI). However, water led to evidence of preferential precipitation and good recovery yields in many cases, so these antisolvent additions were scaled up to enable the more detailed characterisation of the products formed.

Table 3 depicts the results of the scaled-up water antisolvent addition, which was performed on either 5 or 10 mL of IL extract. The IR spectra are given in the ESI. Table 3 includes the composition of the recovered solid as determined by IR spectroscopy, the mass of the recovered solid, and the recovery yield based on the bark extraction yield observed for the IL. The volume of antisolvent added in these experiments was determined by grouping together additions with similar selectivity based on the smaller scale experiments. These results showed that for many ILs, the addition of a small amount of water as an antisolvent facilitated the selective precipitation of suberin/wax and carbohydrate components, whereas further addition of water led to the isolation of purely or predominantly aromatic fractions. There was significant variation between the different ILs, highlighting both differences in the nature of the extracts and the interactions between the IL and antisolvent.

In terms of trends based on the IL anion, it was found that antisolvent addition to $[C_4C_1im][N(CN)_2]$ led to the recovery of suberin/waxes, tannin, and lignin, whereas no carbohydrates could be observed, consistent with the poor extraction of carbohydrates by this IL. However, there was evidence of potential side reactions between the $[N(CN)_2]^-$ anion and bark due to the complexity of the IR spectra obtained, which accords with the earlier observations relating to this IL anion. In contrast, all of the $[Me_2PO_4]$ ILs displayed the presence of at least some carbohydrates in the recovered precipitates alongside the other structural subclasses.

Another notable effect was the influence of the alkyl chain on the cation. While ILs with butyl chains led to suberin/wax and carbohydrate components being exclusively isolated in the first fraction, this was not the case for the ILs containing octyl chains. These ILs led to mixed fractions containing all components even with the extensive addition of water. This is most likely due to the increased solubility of hydrophobic compounds in the presence of water due to the formation of amphiphilic nanostructures within $[C_8C_1im][Me_2PO_4]$ and $[C_8C_1pyrr][Me_2PO_4]$. This would lead to the solubility of aliphatic/carbohydrate components even after adding large amounts of water. It has been recently shown that these and similar ILs retain their nanostructures even on dilution with appreciable concentrations of cosolvents.[44]

From the relative IR absorbances, it can be seen that fractions with much higher concentrations of aliphatics and carbohydrates than the original bark can be observed from all of the $[Me_2PO_4]^-$ containing ILs. This is despite the extraction results suggesting these ILs did not lead to extensive carbohydrate extraction compared to other bark components, which means this antisolvent approach can effectively concentrate the different bark components following the extraction process. Using the IR absorption values as a rough guide, it appears that $[C_4C_1pyrr][Me_2PO_4]$ achieved the highest selectivity towards aliphatic compounds, increasing their concentration by ~4 fold compared to the original bark. This may be due to the more hydrophobic nature of this cation combined with the ability of the structure of the IL to be more easily disrupted by the addition of water than ILs with longer alkyl chains. The other $[Me_2PO_4]^-$ ILs displayed high selectivity for the aliphatic components involving a 2-3 fold increase but were also effective in concentrating the carbohydrates with an increase of ~ 2 fold compared to the original bark. These results indicate that although pure suberin/wax or carbohydrate fractions were not achieved, their concentration could be substantially increased using the combination of the ILs and water as an antisolvent. Further to the concentration of the suberin/wax and carbohydrate components, both $[C_4C_1im][Me_2PO_4]$ and $[C_4C_1pyrr][Me_2PO_4]$ led to the isolation of purely aromatic fractions containing only lignin/tannin components on further addition of water.

A key consideration of the antisolvent addition process is not just the selectivity of the precipitates isolated but their yields. Table 3 reports the mass of each extract obtained, the relative proportion of each fraction isolated and the total yield of solid recovered relative to the extraction yield. The recovery ranged from 22% for $[C_4C_1pyrr][Me_2PO_4]$ through to 97% for $[C_4C_1im][Me_2PO_4]$ with the mass of recovered extracts ranging from 5.5 mg solid $mL^{-1}$ IL for $[C_4C_1im][N(CN)_2]$ up to 17.6 mg solid $mL^{-1}$ IL for $[C_8C_1im][Me_2PO_4]$. Given its good extraction efficiency, it is unclear why the proportional recovery was so low for $[C_4C_1pyrr][Me_2PO_4]$. Other ILs gave moderate to excellent proportional recoveries, apart from $[C_4C_1im][N(CN)_2]$, which is likely less efficient due to the reactivity of the IL with the bark discussed previously. In terms of the absolute recovery of the mass of solid per mL of IL, this is most strongly affected by the extraction yield, which favours the $[C_nC_1im][Me_2PO_4]$ ILs which can solubilise lignin, tannins, carbohydrates and other extractives due to the strong hydrogen bond donating and accepting nature of its constituent ions.

[Table 3 near here]

In terms of the recovered yield of the different fractions, only mixed fractions could be observed for the ILs with $C_8$ alkyl chains. For the other 3 ILs with $C_4$ alkyl chains, the pure aromatic lignin/tannin fractions comprise 35.9%, 55% and 38.8% of the recovered solid for $[C_4C_1im][Me_2PO_4]$, $[C_4C_1im][N(CN)_2]$ and $[C_4C_1pyrr][Me_2PO_4]$, respectively. Based on the extraction yield of bark using $[C_4C_1im][Me_2PO_4]$, this indicates that 12% of the bark mass can be isolated as lignin or tannins free of contamination by other structural biopolymers. While other approaches exist to produce higher yields of polyphenols, such as extraction using hot alkali solutions,[45] these often damage the remaining bark components. The antisolvent approach in conjunction with ILs explored here highlights the ability to separate and isolate carbohydrates and waxes from these aromatic constituents without leading to their degradation. The overall proportion of pure aromatic fractions and the purity of the recovered aliphatic/carbohydrate fractions can potentially be improved by optimisation of the initial bark extraction process and fine-tuning of the antisolvent addition, for example, by control of temperature.

While the cause of the low recovery yield from $[C_4C_1pyrr][Me_2PO_4]$ is not immediately apparent, it is clear from the solid recovered from this IL that it led to the highest proportion of waxes in the initial fraction recovered. This implies that the $[C_4C_1pyrr]^+$ cation improves the recovery of suberin monomers and other waxes. The selection of a less strongly hydrogen-bonding anion that retains water miscibility could improve this selectivity by further reducing the proportion of carbohydrates and aromatics extracted while retaining the ability of water to be used as an antisolvent.

These results demonstrate that carbohydrates tend to be recovered selectively with only small amounts of added antisolvent. The reasonably high initial concentrations of these are due to the $[Me_2PO_4]^-$ anion facilitating the dissolution of cellulose and other carbohydrates,[39] which is readily disrupted by the addition of water which competes for hydrogen-bonding interactions with the anion. In comparison, the precipitation of hydrophobic compounds (waxes, suberins) on the addition of small amounts of water is due to their poor solubility in aqueous media. Meanwhile, tannins and lignin are more soluble in water and tend to interact more strongly with the IL cation, which is an interaction that is not as readily disrupted by the addition of water. This accounts for their gradual precipitation on the addition of significant amounts of added antisolvent. The analysis of the recovered solid here was based on IR spectroscopy which is less comprehensive than other analytical tools. To gain greater insight into the composition of the extracts, pyrolysis GC-MS (Py-GC-MS) was used alongside solid state NMR when sufficient sample was obtained to enable their use.

### *Further analysis of recovered precipitates*

Pyrolysis GCMS (Py-GCMS) is a widely used method to characterise carboxylic acid and phenolic components from lignocellulosic biomass samples and was used to gain further insights into the compositions of isolated bark extracts.[46] These samples were analysed following tetramethylammonium hydroxide (TMA-OH) derivatisation to methylate fatty acid and phenolic compounds and improve their detection.[47]

Figures 4, 5, and 6 depict the proportional sum of these representative compounds observed using TMA-OH Py-GCMS in the recovered solids, with the dried bark source provided for reference. These compounds are broken into subclasses of suberin/waxes, lignin/tannins and carbohydrates. Only precipitates recovered from $[C_4C_1im][Me_2PO_4]$ and $[C_4C_1im][N(CN)_2]$ extracts were obtained in high enough yield for this analysis.

[Figure 4 near here]

It was observed that the proportion of products obtained from suberin was substantially greater for the samples recovered from the small initial addition of antisolvent for both ILs. This is in agreement with the IR results. The relative proportion of suberin/wax compounds appears to be higher for $[C_4C_1im][N(CN)_2]$ than $[C_4C_1im][Me_2PO_4]$ based on the Py-GCMS results, although this may be due to the reduced concentration of carbohydrates in the $[C_4C_1im][N(CN)_2]$ sample rather than a higher inherent recovery of waxes. Moreover, the amount of the fatty acid methyl esters (FAME) observed decreased for samples obtained on further addition of water which reiterates that these suberin/wax components are preferentially precipitated on the addition of small amounts of water as an antisolvent. The proportion of these compounds is much higher in the initial precipitate formed than in the pure bark, emphasising this preferential precipitation. Complementary solid-state NMR analysis of the $C_4$IMMP1 sample revealed a strong aliphatic $CH_2$ peak at 33 ppm, and a strong carbohydrate peak at 70 ppm with virtually no aromatic peaks observed (see ESI), consistent with the IR and the Py-GCMS results.

Figure 5 depicts the relative proportion of highly substituted phenolic derivatives assigned to lignin or tannins observed by Py-GCMS.[48] The trend for lignin/tannin products is the opposite of the suberin products previously discussed, with an increase in the proportion of these compounds for samples obtained when large amounts of antisolvent were added. The proportion of lignin/tannin related pyrolysis products within the solids obtained following the final antisolvent addition for both ILs are greater than the proportions in pure bark. This is consistent with the IR results indicating that these fractions predominantly contain aromatics.

[Figure 5 near here]

Lastly, Figure 6 represents the proportion of compounds detected by Py-GCMS, which correspond to the pyrolysis of carbohydrate components.[49] It was evaluated that the carbohydrates were recovered in greater amounts from $[C_4C_1im][Me_2PO_4]$ IL extracts on the addition of water than $[C_4C_1im][N(CN)_2]$ IL extracts, although the difference between these is less than is implied by the IR results. The proportion of carbohydrates in the isolated solid decreased with the further addition of water as an antisolvent, in agreement with the trends observed by IR. All samples show a reduction in carbohydrate content relative to pure dried bark, emphasising that ILs preferentially extract components other than carbohydrates from the bark, even when ILs shown to dissolve cellulose and related carbohydrates such as $[C_4C_1im][Me_2PO_4]$ are used.[39, 50]

[Figure 6 near here]

The combination of IR, solid-state NMR data and pyrolysis GC-MS results illustrate that the quantity of antisolvent addition can be used to control the composition of products recovered from the extraction of *Pinus radiata* bark. The addition of small amounts of water as an antisolvent (1-1.5 equivalents by volume) can yield selective separation of carbohydrate and suberin/wax rich fractions. After these are separated, further addition of water lead to the isolation of purely aromatic fractions.

## Conclusion

The extraction of *Pinus radiata* bark was explored using a range of ILs that vary systematically in terms of their hydrogen-bonding capabilities and the presence of amphiphilic nanostructures. The IL anion was found to govern the extraction yield, with $[Me_2PO_4]^-$ generally the most effective anion of those explored. The cation had a secondary effect on extraction yield and selectivity with $[C_nC_1pyrr]^+$ cations typically resulting in greater suberin/wax components extraction, whereas ILs with $[C_nC_1im]^+$

cations tended to lead to a higher proportion of aromatic components. Longer alkyl chains on the cation reduced the extraction efficiency of carbohydrates while increasing the extraction of aliphatic components.

Water was determined to be the most effective antisolvent for recovering components from the IL extracts, in contrast to DMSO and MeCN. The addition of small amounts of water led to precipitates with higher concentrations of aliphatic components and carbohydrates. Further addition of water to the supernatant led to predominantly aromatic fractions. The cation played a significant role in the recovery process, with ILs featuring longer alkyl chains reducing the selectivity of the recovered fractions, with mixed aliphatic and aromatic fractions present even after substantial antisolvent addition. The use of the $[C_4C_1pyrr]^+$ cation led to the greatest selectivity for recovered aliphatic components, whereas the $[C_4C_1im]^+$ cation led proportionally to more carbohydrate recovery, while both also led to the recovery of pure aromatic fractions. This highlights that IL-solute-antisolvent interactions can be used to improve the selectivity of biomass fractionation from *Pinus radiata* bark using ILs. These outcomes demonstrate the potential to tailor such interactions to formulate ILs and recovery processes that target the extraction and recovery of different *Pinus radiata* bark fractions.

## Acknowledgements

The authors would like to thank Beatrix Theobald for assistance with processing TMA-OH-Py-GC/MS samples. Funding for this work was obtained from the NZ Ministry of Business, Innovation, and Employment under Contract CO4X1802 Bark Biorefinery: Unlocking New Hydrophobic Polymers.

## Declaration of interest statement

The authors report there are no competing interests to declare.

## References

[1] Bauen, A.; Berndes, G.; Junginger, M.; Londo, M.; Vuille, F.; Ball, R.; Bole, T.; Chudziak, C.; Faaij, A.; Mozaffarian, H. *Bioenergy – a sustainable and reliable energy source. A review of status and prospects.*; 2009.

[2] Mead, D. J. *Sustainable management of Pinus radiata plantations*; Food and Agriculture Organization of the United Nations: Rome, Italy, 2013; p FAO Forestry Paper No. 170.

[3] Pásztory, Z.; Mohácsiné, I. R.; Gorbacheva, G.; Börcsök, Z., The Utilization of Tree Bark. *BioResources* **2016,** *11* (3), 7859-7888.

[4] Fengel, D.; Wegener, G., Constituents of Bark. In *Wood: Chemistry, ultrastructure, reactions*, Fengel, D.; Wegener, G., Eds. De Gruyter: 2011; pp 240-267.

[5] Graça, J., Suberin: the biopolyester at the frontier of plants. *Front. Chem.* **2015,** *3*, 62.

[6] Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J., Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem. Soc. Rev.* **2011,** *40* (7), 3941-3994.

[7] Upton, B. M.; Kasko, A. M., Strategies for the Conversion of Lignin to High-Value Polymeric Materials: Review and Perspective. *Chem. Rev.* **2016,** *116* (4), 2275-2306.

[8] Md Salim, R.; Asik, J.; Sarjadi, M. S., Chemical functional groups of extractives, cellulose and lignin extracted from native Leucaena leucocephala bark. *Wood Science and Technology* **2021,** *55* (2), 295-313.

[9] Passos, H.; Freire, M. G.; Coutinho, J. A. P., Ionic liquid solutions as extractive solvents for value-added compounds from biomass. *Green Chem.* **2014,** *16* (12), 4786-4815.

[10] Rogers, R. D.; Seddon, K. R., Ionic Liquids - Solvents of the Future. *Science* **2003,** *302*, 792-793.

[11] Madeira, P. P.; Passos, H.; Gomes, J.; Coutinho, J. A. P.; Freire, M. G., Alternative probe for the determination of the hydrogen-bond acidity of ionic liquids and their aqueous solutions. *Phys. Chem. Chem. Phys.* **2017,** *19* (18), 11011-11016.

[12] Brennecke, J. F.; Maginn, E. J., Ionic liquids: Innovative fluids for chemical processing. *AIChE Journal* **2001,** *47* (11), 2384-2389.

[13] Pandey, A.; Rai, R.; Pal, M.; Pandey, S., How polar are choline chloride-based deep eutectic solvents? *Phys. Chem. Chem. Phys.* **2014,** *16* (4), 1559-1568.

[14] Ab Rani, M. A.; Brant, A.; Crowhurst, L.; Dolan, A.; Lui, M.; Hassan, N. H.; Hallett, J. P.; Hunt, P. A.; Niedermeyer, H.; Perez-Arlandis, J. M.; Schrems, M.; Welton, T.; Wilding, R., Understanding the polarity of ionic liquids. *Phys. Chem. Chem. Phys.* **2011,** *13* (37), 16831-16840.

[15] Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, J. M.; Salter, P. A.; Welton, T., Solvent - solute interactions in ionic liquids. *Phys. Chem. Chem. Phys.* **2003,** *5*, 2790-2794.

[16] Kurth, E. F., The Chemical Composition of Barks. *Chem. Rev.* **1947,** *40* (1), 33-49.

[17] George, A.; Brandt, A.; Tran, K.; Zahari, S. M. S. N. S.; Klein-Marcuschamer, D.; Sun, N.; Sathitsuksanoh, N.; Shi, J.; Stavila, V.; Parthasarathi, R.; Singh, S.; Holmes, B. M.; Welton, T.; Simmons, B. A.; Hallett, J. P., Design of low-cost ionic liquids for lignocellulosic biomass pretreatment. *Green Chem.* **2015,** *17* (3), 1728-1734.

[18] Vo, H. T.; Kim, C. S.; Ahn, B. S.; Kim, H. S.; Lee, H., Study on Dissolution and Regeneration of Poplar Wood in Imidazolium-Based Ionic Liquids. *J. Wood Chem. Technol.* **2011,** *31* (2), 89-102.

[19] Haykir, N. I.; Soysal, K.; Yaglikci, S.; Gokce, Y., Assessing the effect of protic ionic liquid pretreatment of Pinus radiata from different perspectives including solvent-water ratio. *J. Wood Chem. Technol.* **2021,** *41* (6), 236-248.

[20] Brandt, A.; Hallett, J. P.; Leak, D. J.; Murphy, R. J.; Welton, T., The effect of the ionic liquid anion in the pretreatment of pine wood chips. *Green Chem.* **2010,** *12* (4), 672-679.

[21] Kunov-Kruse, A. J.; Weber, C. C.; Rogers, R. D.; Myerson, A. S., The A Priori Design and Selection of Ionic Liquids as Solvents for Active Pharmaceutical Ingredients. *Chem. Eur. J.* **2017,** *23* (23), 5498-5508.

[22] Qiu, F.; He, T.-Z.; Zhang, Y.-Q., The isolation and the characterization of two polysaccharides from the branch bark of mulberry (Morus alba L.). *Arch. Pharm. Res.* **2016,** *39* (7), 887-896.

[23] Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D., Dissolution of Cellose with Ionic Liquids. *J. Am. Chem. Soc.* **2002,** *124*, 4974-4975.

[24] Clough, M. T.; Geyer, K.; Hunt, P. A.; Son, S.; Vagt, U.; Welton, T., Ionic liquids: not always innocent solvents for cellulose. *Green Chem.* **2015,** *17* (1), 231-243.

[25] Hart, W. E. S.; Harper, J. B.; Aldous, L., The effect of changing the components of an ionic liquid upon the solubility of lignin. *Green Chem.* **2015,** *17* (1), 214-218.

[26] Gandini, A.; Pascoal Neto, C.; Silvestre, A. J. D., Suberin: A promising renewable resource for novel macromolecular materials. *Prog. Polym. Sci.* **2006,** *31* (10), 878-892.

[27] Ferreira, R.; Garcia, H.; Sousa, A. F.; Petkovic, M.; Lamosa, P.; Freire, C. S. R.; Silvestre, A. J. D.; Rebelo, L. P. N.; Pereira, C. S., Suberin isolation from cork using ionic liquids: characterisation of ensuing products. *New J. Chem.* **2012,** *36* (10), 2014-2024.

[28] Zhu, S.; Wu, Y.; Chen, Q.; Yu, Z.; Wang, C.; Jin, S.; Ding, Y.; Wu, G., Dissolution of cellulose with ionic liquids and its application: a mini-review. *Green Chem.* **2006,** *8* (4), 325-327.

[29] Weber, C. C.; Kunov-Kruse, A. J.; Rogers, R. D.; Myerson, A. S., Manipulation of ionic liquid anion-solute-antisolvent interactions for the purification of acetaminophen. *Chem. Commun.* **2015,** *51*, 4294-4297.

[30] An, J.-H.; Kim, W.-S., Antisolvent Crystallization Using Ionic Liquids As Solvent and Antisolvent for Polymorphic Design of Active Pharmaceutical Ingredients. *Cryst. Growth Des.* **2013,** *13*, 31-39.

[31] Minnick, D. L.; Flores, R. A.; DeStefano, M. R.; Scurto, A. M., Cellulose Solubility in Ionic Liquid Mixtures: Temperature, Cosolvent, and Antisolvent Effects. *J. Phys. Chem. B* **2016,** *120* (32), 7906-7919.

[32] Bordes, É.; Costa, A. J. L.; Szala-Bilnik, J.; Andanson, J.-M.; Esperança, J. M. S. S.; Gomes, M. F. C.; Lopes, J. N. C.; Pádua, A. A. H., Polycyclic aromatic hydrocarbons as model solutes for carbon nanomaterials in ionic liquids. *Phys. Chem. Chem. Phys.* **2017,** *19* (40), 27694-27703.

[33] Aspé, E.; Fernández, K., The effect of different extraction techniques on extraction yield, total phenolic, and anti-radical capacity of extracts from Pinus radiata Bark. *Industrial Crops and Products* **2011,** *34* (1), 838-844.

[34] Ku, C. S.; Jang, J. P.; Mun, S. P., Exploitation of polyphenol-rich pine barks for potent antioxidant activity. *J. Wood Sci.* **2007,** *53* (6), 524-528.

[35] Cordeiro, N.; Belgacem, M. N.; Silvestre, A. J. D.; Pascoal Neto, C.; Gandini, A., Cork suberin as a new source of chemicals.: 1. Isolation and chemical characterization of its composition. *Int. J. Biol. Macromol.* **1998,** *22* (2), 71-80.

[36] Lopes, M. H.; Gil, A. M.; Silvestre, A. J. D.; Neto, C. P., Composition of Suberin Extracted upon Gradual Alkaline Methanolysis of Quercus suber L. Cork. *J. Agric. Food Chem.* **2000,** *48* (2), 383-391.

[37] Perra, B.; Haluk, J. P.; Metche, M., IR, 1H and 13C NMR Spectroscopic Studies of Suberin from Beech Barks (Fagus sylvatica L.). *Holzforschung* **1995,** *49* (2), 99-103.

[38] Raymond, L. G.; Hill, S. J.; Grigsby, W. J.; Bogun, B. R., A chemometric approach for the segregation of bark biomass based on tree height and geographic location. *J. Wood Chem. Technol.* **2020,** *40* (6), 361-369.

[39] Zicmanis, A.; Zeltkalne, S., Ionic liquids with Dimethyl Phosphate Anion as Highly Efficient Materials for Technological Processes: A Review. *Int. J. Petrochem. Res.* **2018,** *2* (1), 116-125.

[40] Berga, L.; Bruce, I.; Nicol, T. W. J.; Holding, A. J.; Isobe, N.; Shimizu, S.; Walker, A. J.; Reid, J. E. S. J., Cellulose dissolution and regeneration using a non-aqueous, non-stoichiometric protic ionic liquid system. *Cellulose* **2020,** *27* (16), 9593-9603.

[41] Huo, F.; Liu, Z.; Wang, W., Cosolvent or Antisolvent? A Molecular View of the Interface between Ionic Liquids and Cellulose upon Addition of Another Molecular Solvent. *J. Phys. Chem. B* **2013,** *117* (39), 11780-11792.

[42] Neto, C. P.; Rocha, J.; Gil, A.; Cordeiro, N.; Esculcas, A. P.; Rocha, S.; Delgadillo, I.; De Jesus, J. D. P.; Correia, A. J. F., 13C solid-state nuclear magnetic resonance and Fourier transform infrared studies of the thermal decomposition of cork. *Solid State Nucl. Magn. Reson.* **1995,** *4* (3), 143-151.

[43] Heneczkowski, M.; Kopacz, M.; Nowak, D.; Kuźniar, A., Infrared spectrum analysis of some flavonoids. *Acta Pol Pharm* **2001,** *58* (6), 415-420.

[44] Yalcin, D.; Welsh, I. D.; Matthewman, E. L.; Jun, S. P.; McKeever-Willis, M.; Gritcan, I.; Greaves, T. L.; Weber, C. C., Structural investigations of molecular solutes within nanostructured ionic liquids. *Phys. Chem. Chem. Phys.* **2020,** *22* (20), 11593-11608.

[45] Sun, M. U. N. J.; Chul, K. I. M. H.; Phil, M. U. N. S., Chemical Characterization of Neutral Extracts Prepared by Treating Pinus radiata Bark with Sodium Bicarbonate. *J. Korean Wood Sci. Technol.* **2020,** *48* (6), 878-887.

[46] Klingberg, A.; Odermatt, J.; Meier, D., Influence of parameters on pyrolysis-GC/MS of lignin in the presence of tetramethylammonium hydroxide. *J. Anal. Appl. Pyrolysis* **2005,** *74* (1), 104-109.

[47] Challinor, J. M., A pyrolysis-derivatisation-gas chromatography technique for the structural elucidation of some synthetic polymers. *J. Anal. Appl. Pyrolysis* **1989,** *16* (4), 323-333.

[48] Fabbri, D.; Helleur, R., Characterization of the tetramethylammonium hydroxide thermochemolysis products of carbohydrates. *J. Anal. Appl. Pyrolysis* **1999,** *49* (1), 277-293.

[49] Paine, J. B.; Pithawalla, Y. B.; Naworal, J. D., Carbohydrate pyrolysis mechanisms from isotopic labeling: Part 4. The pyrolysis of d-glucose: The formation of furans. *J. Anal. Appl. Pyrolysis* **2008,** *83* (1), 37-63.

[50] Lall-Ramnarine, S. I.; Thomas, M. F.; Jalees, M.; Payen, F.; Boursiquot, S.; Ramati, S.; Ewko, D.; Zmich, N. V.; Wishart, J. F., Probing the Physical Properties, Synthesis and Cellulose Dissolution Ability of Dialkyl Phosphate Ionic Liquids. *Phosphorus Sulfur Silicon Relat. Elem.* **2015,** *190* (5-6), 891-895.

[51] Spange, S.; Lungwitz, R.; Schade, A., Correlation of molecular structure and polarity of ionic liquids. *J. Mol. Liq.* **2014,** *192*, 137-143.

# Tables

**Table 1** Kamlet-Taft parameters of selected ILs used.

| **ILs** | **Abbreviation** | **α** | **β** | **$\pi^*$** | **Ref** |
|---|---|---|---|---|---|
| 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide | $[C_4C_1im][NTf_2]$ | 0.72 | 0.24 | 0.90 | [14] |
| 1-butyl-3-methylimidazolium dicyanamide | $[C_4C_1im][N(CN)_2]$ | 0.54 | 0.60 | 1.05 | [14, 20] |
| 1-butyl-3-methylimidazolium dimethyl phosphate | $[C_4C_1im][Me_2PO_4]$ | 0.45 | 1.13 | 0.98 | [14, 20] |
| 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide | $[C_4C_1pyrr][NTf_2]$ | 0.57 | 0.23 | 0.87 | [14] |
| 1-butyl-1-methylpyrrolidinium dimethyl phosphate | $[C_4C_1pyrr][Me_2PO_4]$ | 0.24 | 1.14 | 1.02 | [14] |
| 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl) imide | $[C_8C_1im][NTf_2]$ | 0.60 | 0.29 | 0.96 | [14] |
| 1-methyl-3-octylimidazolium dicyanamide | $[C_8C_1im][N(CN)_2]$ | 0.43 | 0.71 | 0.97 | [51] |
| 1-methyl-1-octylpyrrolidinium bis(trifluoromethanesulfonyl) imide | $[C_8C_1pyrr][NTf_2]$ | 0.80 | 0.08 | 0.73 | [14] |

**Table 2** Extraction yields from bark with ILs *at* 5 w/v% bark loading for 24 h at 100 °C.

| **ILs used** | **Yield (%)**[a] |
|---|---|
| $[C_4C_1im][NTf_2]$ | 4 |
| $[C_4C_1im][N(CN)_2]$ | 28 ± 2 |
| $[C_4C_1im][Me_2PO_4]$ | 33 ± 2 |
| $[C_4C_1pyrr][NTf_2]$ | 4 |
| $[C_4C_1pyrr][N(CN)_2]$ | 37 |
| $[C_4C_1pyrr][Me_2PO_4]$ | 70 ± 3 |
| $[C_8C_1im][NTf_2]$ | 4 |
| $[C_8C_1im][N(CN)_2]$ | 32 |
| $[C_8C_1im][Me_2PO_4]$ | 48 ± 19 |
| $[C_8C_1pyrr][NTf_2]$ | - |
| $[C_8C_1pyrr][N(CN)_2]$ | 10 |
| $[C_8C_1pyrr][Me_2PO_4]$ | 39 ± 4 |
| $[C_4gun][NTf_2]$ | 14 |
| $[C_8gun][NTf_2]$ | 7 |

[a] Reported errors are standard deviations of replicate experiments where replicates were performed (see text for details).

**Table 3** The fractions of bark components isolated from IL extracts using water as an antisolvent. Total yield % is calculated with respect to the extraction yield of each IL.

| IL/DES Extract used (mL) | Sample Name | Vol. (mL) | Absorbance | | | Solid recovered (mg) | Proportion of Fraction (%) | Total Yield (mg) |
|---|---|---|---|---|---|---|---|---|
| | | | A : L$^a$ | C : L$^a$ | T : L$^a$ | | | |
| - | Bark | - | 0.3,0.2 | 1.54 | 0.45 | - | - | - |
| $[C_4C_1im][Me_2PO_4]$ (10 mL) | $C_4$IMMP1 | 15 | 0.6,0.4 | 2.67 | 0.46 | 103 | 64 | 161 (97%) |
| | $C_4$IMMP2 | 10 | $0^b$ | $0^b$ | 0.56 | 15 | 9 | |
| | $C_4$IMMP3 | 75 | $0^b$ | $0^b$ | 0.52 | 43 | 27 | |
| $[C_4C_1im][N(CN)_2]$ (10 mL) | $C_4$IMNCN1 | 10 | 0.3,0.2 | $0^b$ | 0.78 | 24 | 45 | 55 (40%) |
| | $C_4$IMNCN2 | 10 | $0^b$ | $0^b$ | 0.86 | 13 | 24 | |
| | $C_4$IMNCN3 | 5 | $-^c$ | $-^c$ | $-^c$ | 9 | 15 | |
| | $C_4$IMNCN4 | 75 | $0^b$ | $0^b$ | 0.89 | 9 | 16 | |
| $[C_4C_1pyrr][Me_2PO_4]$ (5 mL) | $C_4$PYMP1 | 10 | 1.1,0.7 | 1.54 | 0.67 | 24 | 61 | 39 (22%) |
| | $C_4$PYMP2 | 90 | $0^b$ | $0^b$ | 0.49 | 15 | 39 | |
| $[C_8C_1im][Me_2PO_4]$ (5 mL) | $C_8$IMMP1 | 7.5 | 0.9,0.5 | $-^d$ | 0.67 | 45 | 51 | 88 (73%) |
| | $C_8$IMMP2 | 5 | 1.0,0.6 | 3.11 | 0.60 | 8 | 9 | |
| | $C_8$IMMP3 | 87.5 | 0.6,0.4 | 1.40 | 0.55 | 36 | 41 | |
| $[C_8C_1pyrr][Me_2PO_4]$ (5 mL) | $C_8$PYMP1 | 5 | 0.9,0.6 | 3.19 | 0.36 | 21 | 42 | 49 (50%) |
| | $C_8$PYMP2 | 30 | $-^c$ | $-^c$ | $-^c$ | 24 | 49 | |
| | $C_8$PYMP3 | 65 | 0.2,0.1 | $0^b$ | 0.55 | 4 | 9 | |

[a] A = aliphatic (suberin/wax), L = lignin, T = tannin, C = carbohydrate. Ratios calculated with respect to the absorbance of the lignin peak at 1605 cm$^{-1}$. [b] Peaks not present in the IR spectrum. [c] Insufficient sample or sample powder was too fine to be isolated for IR analysis. [d] Peak obscured.

## Figures

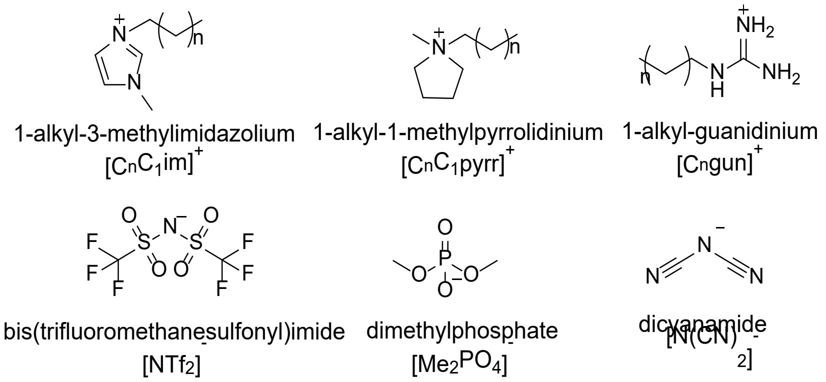

**Figure 1** The structures and abbreviations of cations (top) and anions (bottom) used for the ILs explored for bark extraction.

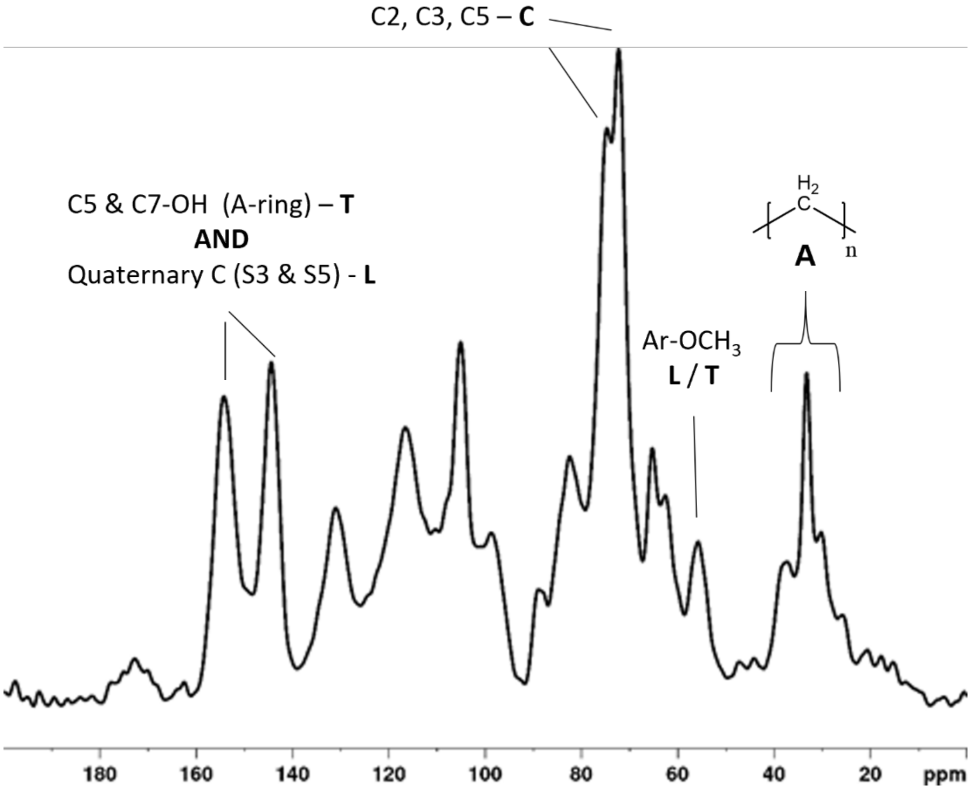

**Figure 2** Carbon peaks of the $^{13}$C solid-state NMR of the initial bark used assigned to tannins (T), lignin (L), carbohydrates (C) and aliphatics (A) which include suberin and waxes.

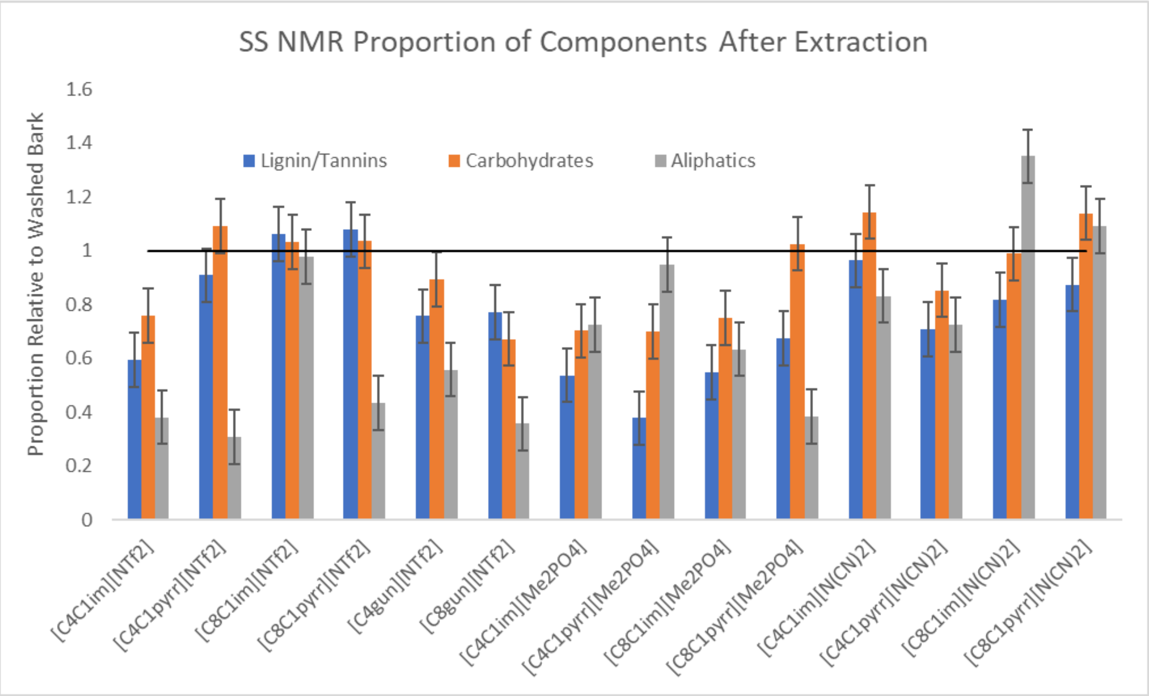

**Figure 3** Proportion of identified components in bark after extraction compared to bark subjected only to the washing procedure based on $^{13}$C solid-state NMR integration. Black line at a proportion of 1 provided as a guide for the eye. Errors are estimated based on reproducibility of deconvolution procedure.

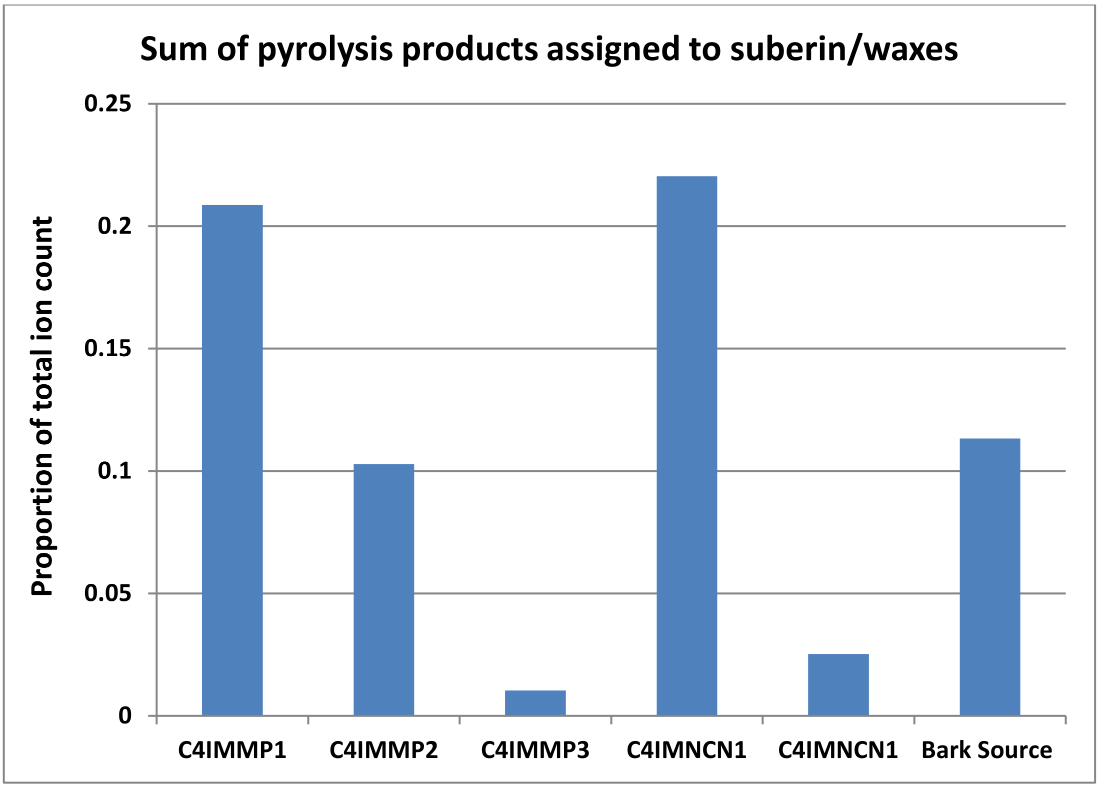

**Figure 4** Observed relative TIC areas for the sum of compounds assigned to suberin/waxes following TMA-OH-Py-GCMS analysis. Sample names are from Table 3.

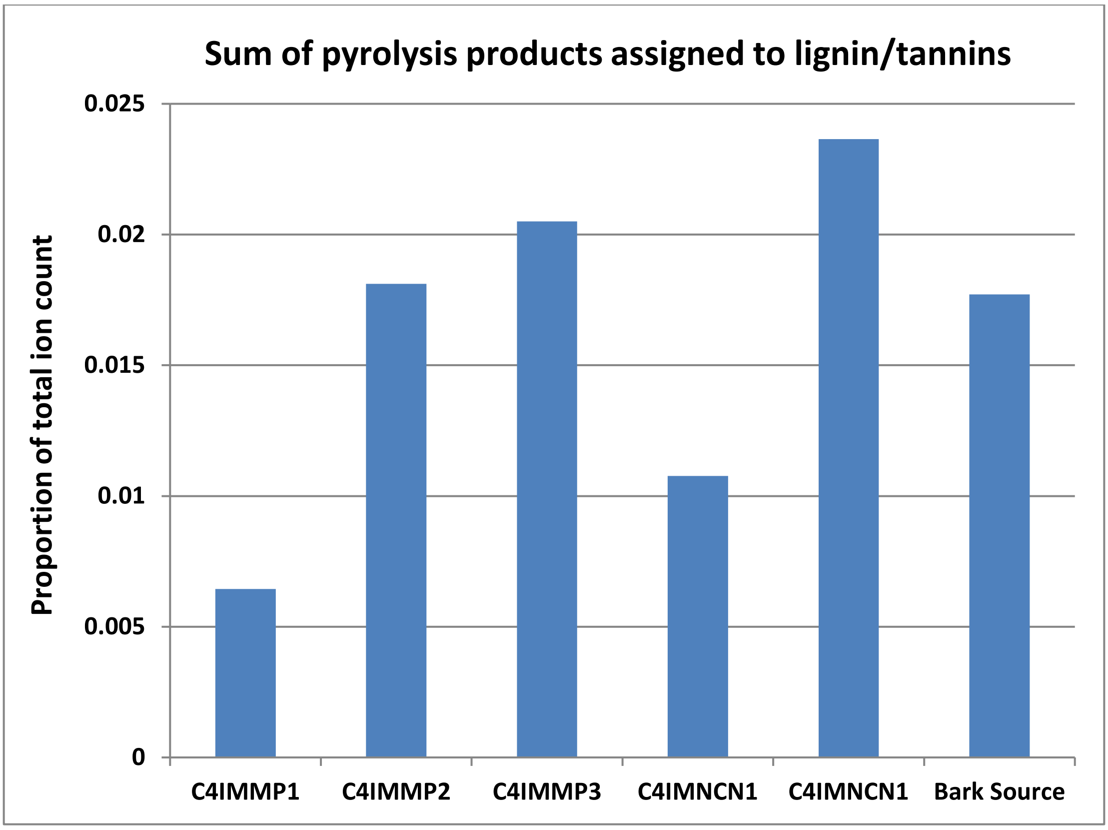

**Figure 5** Observed relative TIC areas for the sum of compounds assigned to lignin/tannins following TMA-OH-Py-GC/MS analysis. Sample names are from Table 3.

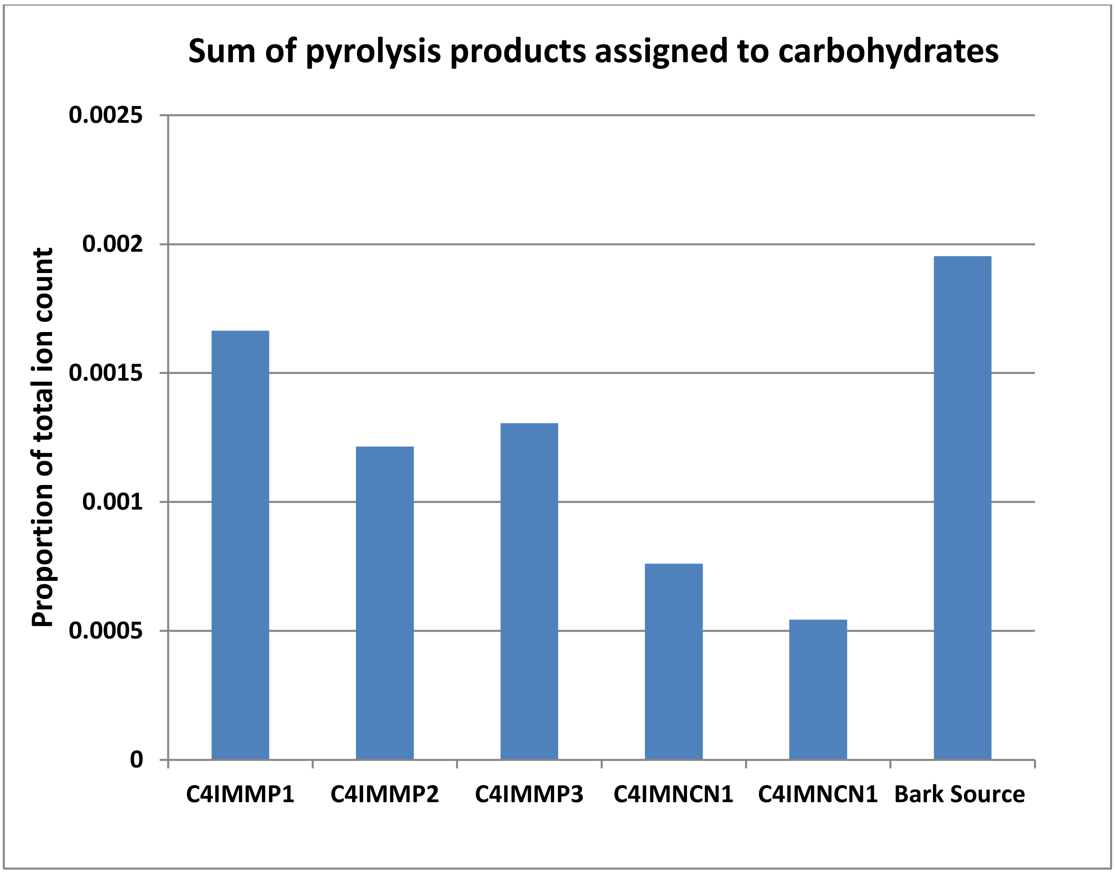

**Figure 6** Observed relative TIC areas for the sum of compounds assigned to carbohydrates following TMA-OH-Py-GCMS analysis. Sample names are from Table 3.

## Figure captions

**Figure 2** The structures and abbreviations of cations (top) and anions (bottom) used for the ILs explored for bark extraction.

**Figure 2** Carbon peaks of the $^{13}$C solid-state NMR assigned to tannins (T), lignin (L), carbohydrates (C) and aliphatics including aliphatics (A) such as suberin and waxes.

**Figure 3** Proportion of identified components in bark after extraction compared to bark subjected only to the washing procedure based on $^{13}$C solid-state NMR integration. Black line at a proportion of 1 provided as a guide for the eye. Errors are estimated based on reproducibility of deconvolution procedure.

**Figure 4** Observed relative TIC areas for the sum of compounds assigned to suberin/waxes following TMA-OH-Py-GCMS analysis. Sample names are from Table 3.

**Figure 5** Observed relative TIC areas for the sum of compounds assigned to lignin/tannins following TMA-OH-Py-GC/MS analysis. Sample names are from Table 3.

**Figure 6** Observed relative TIC areas for the sum of compounds assigned to carbohydrates following TMA-OH-Py-GCMS analysis. Sample names are from Table 3.