

Analysis of the 10 samples with differing genera for mid infrared

Xanthorrhoea arborea (A)

Multiple transition energies around the C = O transition around 1600 cm^{-1} suggests that there could be more distribution of energetic transitions of this group within the molecule. It could also suggest that there are multiple C = O environments for within the material. There is a large distribution of weaker peaks around the $2850 - 3000\text{ cm}^{-1}$ which could be an indication of a high complexity surrounding the carbon backbone. There is a strong peak at around 1512 cm^{-1} , referring to substantial portions of the analysed mixture being aromatic which is absent in the other genera. This is also supported as there are absorption peaks at around $1350\text{--}1000\text{ cm}^{-1}$ which indicate aromatic skeletal vibrations and a peak at 1631 cm^{-1} indicating that there are C = C bonds present and are conjugated. There is a broader peak at 3327 cm^{-1} which corresponds with OH stretching and hence could indicate presence of an acid group in the samples, as there is the absence of peaks at around 1690 cm^{-1} to 1710 cm^{-1} , shows support for the absence of the polymerised communic acid related peaks in the far-IR spectra. Studies shown by Ghisalberti (Ghisalberti and Godfrey, 1998) have shown the resin from the *Xanthorrhoea* to contain mostly aromatic compounds which is what is suggested through the mid-IR experimentally.

Eucalyptus largiflorens (B)

The main differences these genera have from the visual inspection of the mid-IR is the larger peak at 1605 cm^{-1} in comparison to the peak at 2939 cm^{-1} which suggests that there is higher intensity of transitions of conjugated C = C (1605 cm^{-1}) in comparison to the C-H vibrational transitions which occur at 2939 cm^{-1} . This could indicate the presence of ring structures indicating a phenolic resin which would then further be suggested by peaks present at 1445 cm^{-1} (aromatic ring stretching), 1311 cm^{-1} (phenol), 1191 cm^{-1} (phenol stretching) and possibly 1096 cm^{-1} which indicates the presence of cyclic C-O stretching in the form of large ring structures and or cyclic ethers. The transition peak at 1694 cm^{-1} could indicate the presence of a carboxylic acid which is in conjugating considering the shift in wavenumber to a lower frequency from the non-conjugated carboxylic acids.

Stericula diversifolia (now *Brachychiton populneus*) (C)

The IR absorbance spectra for *Stericula diversifolia* showed a large broad peak at between 3100 cm^{-1} and 3500 cm^{-1} centring at around 3200 cm^{-1} . This suggests the presence of a hydroxyl group with a small peak for a carbonyl group at 1731 cm^{-1} which suggests the presence of an aldehyde group. There is a strong peak at around 1592 cm^{-1} which suggests a substantial portion of alkenes in the molecule, which also suggests the presence of C=C- in cyclisation, which suggests the presence of a high number of aromatic groups. There is also a large broad peak which centres at around 1034 cm^{-1} to 1012 cm^{-1} which has a range of peaks that are not well distinguishable from each other which also suggests a quite

complex aromatic and chain backbone structure in the molecules present. There is limited documented information regarding the chemical composition of this genus. The minor peak for the aldehyde functional group at 1731 cm^{-1} , suggests the presence of a small portion of COH (aldehyde) functionality which could be a result of the degradation via oxidation of a primary alcohol group which could have occurred with aging of the exudate.

***Acacia bakeri* (D)**

Previous studies by Granzotto (Granzotto, et al., 2019) using mass spectrometry of *Acacia senegal* have identified pent5 oligosaccharide which contains five pentose units being the main featuring structure in the gum *Senegal*, a species was analysed that demonstrated similar peaks between all species of *Acacia* exudates. The gum from *Acacia* is broadly suggested to contain highly branched polysaccharides. The IR spectra obtained experimentally shows a strong large OH peak centred at around 3300 cm^{-1} with peaks at 2918 cm^{-1} . A large broad peak at 1595 cm^{-1} (carboxylate ions), 1412 cm^{-1} (carboxylates) 1284 cm^{-1} (aromatic ketones) 1123 cm^{-1} (1,2 disubstituted aromatic) 1052 cm^{-1} 1017 cm^{-1} (1,2 disubstituted aromatic), 981 cm^{-1} (alkenes), 914 cm^{-1} (alkanes). This suggests that the resin is composed of aromatics and polysaccharides.

***Myoporum viscosum* (E)**

The mid-infrared spectrum of the sample of *Myoporum viscosum* contained a large absorption at which centres at 3270 cm^{-1} with an uneven distribution of transition energies around the centre, which is observed by an asymmetric band with uneven weak shoulder bands on either side of the main peak. This suggests that multiple OH groups were present within the molecular structure with multiple chemical environments. This along with the absence of bands for the assignment of a C = O group or aromatic groups, is a defining comparative feature of this genera. There is a large peak at around 2936 cm^{-1} (C-H asymmetric stretch) which suggested higher amounts of methylene groups which is further supported by a series of peaks at 1456 cm^{-1} (CH bend), 1020 cm^{-1} (cyclohexane ring vibrations), 967 cm^{-1} , 953 cm^{-1} , 929 cm^{-1} (cyclohexane ring vibrations), 714 cm^{-1} . The presence of bands at 1302 cm^{-1} (vinylidene C-H in plane bend) and 885 cm^{-1} (vinylidene C - H out of plane bend) further suggested the presence of a vinylidene group. There are a range of peaks from 1322 cm^{-1} and 1350 cm^{-1} (C - H bending) suggest a smaller relative portion of the structure to be made up a methyne C - H group. There is a band at 1081 cm^{-1} with a smaller band at approximately $1050 - 1060\text{ cm}^{-1}$ which can be assigned to C - O stretch for a combination of primary and secondary alcohols, with a higher portion secondary alcohol. The overall structure has a high relative amount of the alcohol functional groups.

***Grevillea striata* (F)**

The mid IR spectra for *Grevillea striata* was observed to be highly complex but with a few defining bands. Bands that suggested the presence of a carboxylate functional group such as 1575 cm^{-1} (C = O

carboxylate), 1326 cm^{-1} and the presence of a conjugated ketone as there are observed strong peaks at 1611 cm^{-1} . The peaks are less defined in this area suggesting that there are several types and environments for both functional groups which all overlap. There are minor peaks at slightly above 3000 cm^{-1} and 1650 cm^{-1} which could suggest a minor portion of the molecule showing some unsaturation around the skeletal carbon background. Peaks at 2925 cm^{-1} and 2853 cm^{-1} (methylene C - H asymmetric/symmetric stretching) suggested the presence of the major component to be a saturated carbon backbone which is further supported by the presence of bands at 1452 cm^{-1} and 1427 cm^{-1} which are attributed to methylene C-H bonds and multiple bands between 1195 cm^{-1} and 1000 cm^{-1} which suggests the presence of a branched cyclohexane ring system.

***Erythrophleum labonchorii* (G)**

The IR spectra of the of the *Erythrophleum* genus showed a broad peak with a low absorption value in comparison to the larger absorption values for the CH methyl and methylene stretching which occur at 2925 cm^{-1} and 2872 cm^{-1} with shoulders for each suggesting there are several different environments affecting the energy transition of the stretching. There is a large broad unsymmetric peak at 1705 cm^{-1} which indicates the presence of a carboxyl group, which due to the position indicates the presence of a ketone. There is also a broad peak at which spans toward the 1500 cm^{-1} region which along with the selection of peaks between 910 cm^{-1} and 1084 cm^{-1} and 1452 cm^{-1} which indicate aromatic ring functionality. There also seems to be a smaller peak at around 1162 which could indicate an aromatic phosphine group. A peak at 1380 cm^{-1} also suggests that there are phenol compounds present but in a lower amount in comparison to the carbonyl peak.

***Canarium australasicum* (H)**

The IR spectra for *Canarium* genus showed overall a similar spectrum to the previously mentioned *Erythrophleum* genus with a smaller broad peak at around 3100 cm^{-1} to 3500 cm^{-1} in relative proportion to the peaks for saturated carbon at 2929 cm^{-1} and 2868 cm^{-1} which are not symmetrical suggesting the presence of aromatic groups which was further supported by the presence of peaks as 1454 cm^{-1} (C = C - C aromatic vibrations) and a collection of overlapping peaks in the range of 1100 cm^{-1} to 656 cm^{-1} which are assigned to aromatic C-H in plane bending and out of plane bending. Peaks at 1379 cm^{-1} and 1368 cm^{-1} (OH bend, phenol) suggested the exudate to have a major chemical component as being a phenol compound. It differs from the *Erythrophleum* genus as aromatic ring bands at 1454 cm^{-1} and phenol band at 1379 cm^{-1} is greater relative to the absorbance of the ketone transition bands at 1705 cm^{-1} .

***Callitris calcarata* (I)**

The absorption spectra in the mid infrared range demonstrated peaks overall that suggested the presences of polycommenic acid and an absence of peaks relating to that of aromatic species. It has also

been suggested to previously contain a characteristic component, callitrisic acid (4-epidehydro-abietic acid) (Simoneit, et al., 2018). There is a broad peak at 3500cm^{-1} to 3000cm^{-1} with a centre toward the 3300cm^{-1} range which suggests a group of COOH acidic functional group in comparison to the an alcohol functional group, this is further suggested due to a major peak at 1692 cm^{-1} with a shoulder peak of 1652 cm^{-1} this suggests there are two different types of C=O bonds which could be in conjugation with each other or a alkene group. As it is below the 1700 cm^{-1} range this suggests that there is a carboxylate salt group rather than a ketone or simple carbonyl group. Absence of major peaks between 1470 cm^{-1} to 1650 cm^{-1} suggests that aromaticity is not present although as there are multiple peaks at 1466 cm^{-1} (CH), 1448 cm^{-1} (CH), 1029 (cyclohexane ring vibrations – out of plane), 887 cm^{-1} (CH) and 790 cm^{-1} (C-C vibrations) suggesting that there is the presence of a complex molecule involving cyclohexane rings with an carboxylic acid functional groups with the presence of some a minor but present amount of vinyl groups.

***Araucaria cunninghami* (J)**

The absorption spectra in the mid infrared of the *Araucaria* were similar to that of the *Callitris* genera, however some key differences arose at the position and shape of the absorption peaks at 1231 cm^{-1} and 1151 cm^{-1} suggesting that there are phenol components to the exudate and there is a tertiary alcohol present. The peaks in the mid- IR spectra for the *Araucaria* species were broad at around both 1231 cm^{-1} and 1151 cm^{-1} in comparison to the three distinguishable peaks starting at 1260 cm^{-1} and a larger asymmetric peak at 1176 cm^{-1} . The peak at 1028 cm^{-1} which is assigned to cyclohexane ring vibrations is much greater for the *Araucaria* species in comparison to its ratio against the other identifiable peaks and takes a much broader shape with shoulders each side of the main peak. There is also a broader extension of the peak at 1645 cm^{-1} which extends further into the 1500 cm^{-1} range which suggests that there is some aromatic functionality which further suggests the presence of phenolic compounds.

Analysis of the 10 samples with differing genera for far infrared

***Xanthorrhoea arborea* (A)**

The main intensity peaks in the recorded spectra were at 510-508 cm^{-1} (out of plane ring deformation) approximately 550 cm^{-1} , 439 cm^{-1} (in plane ring deformation(Graf, et al., 2020)) (δCO) (Prati, et al., 2011), 245 cm^{-1} (out of plane ring deformation CH_3 rotation(Graf, et al., 2020)), 619 cm^{-1} (out of plane ring deformation) and 633-635 cm^{-1} δ (CCC) across differing species, *Xanthorrhoea australia* has a peak at around 580 which is characteristic of triterpenic compounds. With the number of peaks present and the overall broadening of the peaks suggests a mixture of different phenol/benzene components.

***Eucalyptus largiflorens* (B)**

The recorded spectra had fewer distinguishable peaks in comparison to other samples. The peaks that were present had low absorbance values but were unique to that sample in the genera comparison, this however was not observed to be the case for all samples from the genera of *Eucalyptus*. A vast range of transition bands were found across the spectra for the differing species of *Eucalyptus*. In this species the main defining transitions were found at 330 cm^{-1} and 500 cm^{-1} which were not previously assigned to a transition through previous studies. There is a transition at 579 cm^{-1} which has been previously described as a transition common to the triterpenic resin compounds.

***Sterculia diversifolia* (C)**

The acquired spectrum showed a low change in absorption for the transition bands, with main differentiating bands at 382 cm^{-1} (δ CCC), 351 cm^{-1} 487 cm^{-1} (δ CCC) and 202 cm^{-1} and 164 cm^{-1} . Majority of the transitions found for this resin are not previously described and are not able to be assigned.

***Acacia bakeri* (D)**

The recorded spectrum was observed to show a limited number of distinguishable peaks. The mid-IR suggested the *Acacia* sample to be majorly comprised of highly branched polysaccharides which are suggested to have lower absorbance in the far-infrared region (Vahur, et al., 2016), suggesting it to not be a highly valuable interpretive tool for chemical analysis of this genera. In that scenario it would be more valuable to investigate the chemical structure either some type of mass spectrometry or NMR (nuclear magnetic resonance) techniques as a tool for further differentiation if the use of laboratory-based mid-IR cannot be used for distinction. There are broad peaks at 550 cm^{-1} and 360 cm^{-1} which in combination suggests the presence of some aromatic groups.

***Myoporium viscosum* (E)**

The recorded spectrum was observed to contain major peaks at wavenumbers of 620 cm^{-1} (out of plane ring deformation (Graf, et al., 2020)), 501 cm^{-1} (out of plane ring deformation (Graf, et al., 2020)), 472 cm^{-1} , 412 cm^{-1} , 319 cm^{-1} , 246 cm^{-1} (CH_3 rotation out of plane ring deformation) and 119 cm^{-1} which are not previously assigned to transitions in literature. This sample had larger range of absorbance than most other sample. The spectra also suggested an absence of CCO transitions and is difficult to observe the transitions of aromatics or conjugated carbon backbones as there are larger peaks. This suggested that there are components which have intense absorption in the far-IR range. There is limited published data on the exact assignment of these peaks which makes it difficult to properly characterise however it allows for distinction from other exudates.

***Grevillea striata* (F)**

The acquired spectrum was observed to contain major peaks at wavenumbers 639 cm^{-1} (ring out of plane bend, chair type deformation), 532 cm^{-1} (in plane ring deformation $\text{C}_{\text{ring}}-\text{C}-\text{C}-\text{CH}$ torsion (Graf, et al., 2020)), 437 cm^{-1} (in plane ring deformation), 405 cm^{-1} which are not previously assigned transitions. It was suggested to be more of a non-conjugated carbon skeleton as peaks in the spectra are associated with ring out of plane bending, with a broad peak at around 639 cm^{-1} which suggested an elevated level of variance in structure.

***Erythrophleum labonchorii* (G)**

The acquired spectrum showed distinguishable features from other genera as it showed transitions which confirm the mainly phenolic components to the resin. The peaks observed were 555 cm^{-1} (δ CCO), 513 cm^{-1} (not previously described), 453 cm^{-1} (aromatic), 440 cm^{-1} (small and could be a feature of all spectra), 392 cm^{-1} (attribution of benzene ring distortions), 364 cm^{-1} (δ CCC) and 260 cm^{-1} (COC torsional).

***Canarium australasicum* (H)**

Canarium Australasicum generated a recorded far-IR absorption spectrum that was difficult to interpret as seems to be oscillations at relatively low absorbance rather than peaks but there are broader heightened regions which centre at around 525 cm^{-1} and 297 cm^{-1} which is suggested to be associated with δ (CCO) transitions, however the 297 cm^{-1} is yet to be assigned to a logical transition for the organic sample material.

***Callitris calcarata* (I)**

Callitris Calcarata has main intensity peaks of 556 cm^{-1} (δ CCO), 444 cm^{-1} (δ CCO), 369 cm^{-1} broad with shoulder at 387 cm^{-1} (δ CCC t CC), 297 cm^{-1} (t CCO), 255 cm^{-1} (t CH₃ -CH₂) which were assigned based off previous studies(Prati, et al., 2011). The spectrum also has peaks that have not been previously assigned such as 517 cm^{-1} , 195 cm^{-1} , 144 cm^{-1} and 129 cm^{-1} . The spectrum showed some similar peaks to that of the far-IR spectra for pine resin provided through the database.(Vahur, et al., 2019)

***Araucaria cunninghami* (J)**

The species generated a recorded far-IR absorption spectrum that showed main absorption peaks of 558 cm^{-1} (δ CCO), 261 cm^{-1} (tCH₃) and unassigned peaks 607 cm^{-1} , 518 cm^{-1} , 383 cm^{-1} , 299 cm^{-1} (t CCO), 144 cm^{-1} and 129 cm^{-1} . These are similar to the spectral data for the sample of exudate from *Callitris calcarata* sharing most peaks, however there are some peaks that differentiate such as 261 cm^{-1} (tCH₃), 607 cm^{-1} , 383 cm^{-1} (shift from 387 cm^{-1} as seen in *Callitris*).

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