

Fourier Transform Infrared characterization of Pai wood (*Afzelia africana* Smith) extractives

E.-M. A. Ajuong, M. C. Breese

The major functional groups of the various extractive components recovered from Pai wood using organic solvents and hot water have been identified and assigned by means of Fourier transform infrared analyses. The analyses revealed that the components removed by toluene, found mainly in cell lumina and/or lumina surfaces, were predominantly of non-polar, aliphatic compounds such as fatty acids and their monohydric esters. Gummy substances were also evident as well as minor amounts of materials of aromatic nature. The extract fractions recovered using ethanol and hot water, derived principally from within cell walls, consisted of cyclized aromatic components of increased polarity. It has been demonstrated that these components are tannins.

FTIR-Charakterisierung der Extraktstoffe von Apa-Holz (*Afzelia africana* Smith)

Extraktstoffe von Apa-Holz wurden mit organischen Lösemitteln und Heißwasser isoliert. Die funktionellen Gruppen der verschiedenen Komponenten wurden mittels FTIR bestimmt. Die Toluol-löslichen Bestandteile, die vor allem aus den Zell-Lumina bzw. von der Oberfläche der Lumina stammen, enthielten vor allem unpolare aliphatische Substanzen wie Fettsäuren und deren Ester. Gummyartige Substanzen waren ebenso vorhanden wie geringe Mengen aromatischer Komponenten. Die in Ethanol und Heißwasser löslichen Fraktionen stammen vorwiegend aus der Zellwand und bestehen aus aromatischen Substanzen höherer Polarität. Es handelt sich dabei überwiegend um Tannine.

1

Introduction

The contribution of extractive compounds to the overall infrared spectrum of wood has long been recognised (Chow 1972), but research workers have usually regarded such contributions as contaminants of the absorption patterns produced by the structural constituents of wood (Chow 1972; Obst 1982; Owen and Thomas 1989). Nevertheless Manville and Tracey (1989) used spectroscopic methods, including infrared (IR) to differentiate between Alpine firs of British Columbia on the basis of differences

in their extractive chemical composition. More recently the ability of diffuse and reflectance infrared Fourier transform (DRIFT) in detecting differences amongst similar species has been demonstrated by Nault and Manville (1992). This facility has made it possible to differentiate between mixed species commonly found in lumber producing mills of British Columbia.

In contrast to softwoods, little information is available relating to tropical hardwoods (including popular species such as *afzelia*) and as a consequence attempts to investigate the features of these species are of interest. The objective of this study was to gain information on the chemical nature of extractive components in Pai wood. Towards this purpose infrared characterization of the different extractive fractions has been undertaken.

2

Materials and methods

The specimens for infrared studies were obtained from wood flour using a sequential extraction procedure described by Ajuong and Breese (1997). Details of specimen preparation for infrared analyses have also been published (Ajuong 1994). The samples to be analysed were taken from each stage of extraction. However because the toluene and ethanol-toluene extracted fractions tended to become sticky when dried, components removed by organic solvents were analysed in liquid form whilst the water soluble components were characterized using a KBr pellet technique.

The fluid specimens from each extraction stage were concentrated to 7.5 mg/ml by evaporation of solvent. Using a pipette a drop or two of this solute was then placed on sodium chloride discs (Specac Ltd, Orpington, Kent), allowed to evaporate and analysed using a "Perkin Elmer" double beam spectrophotometer. The traces produced were then compared to charts of group frequencies for the assignment of the major functional groups for each extract components as described by Silverstein et al. (1991). In the case of the water soluble extracts 5 mg of dry, powdered extract were thoroughly mixed with 0.5 g of dry, powdered potassium bromide (KBr) (approximately 1% w/w) by grinding the powders in a smooth, agate mortar. As reported elsewhere (Silverstein et al. 1991) the quality of the spectrum depended on the intimacy of mixing and the reduction of extract particle size in the potassium bromide powder. Using a micro spatula transparent KBr based dies were prepared by placing 60–70 mg of the dry, powdered potassium bromide/extract mixture in a small press under vacuum. In a manner similar to their fluid counterparts the dies so produced were subjected to IR analyses to identify the major functional groups present.

For comparison both liquid and die samples were also subjected to Fourier transform infrared (FTIR) analyses. Because FTIR was found to be more accurate in the as-

Elijah-M. A. Ajuong, Martin C. Breese
School of Agricultural and Forest Sciences, University of Wales,
Bangor, Gwynedd LL57 2UW, UK

Correspondence to: E.-M. A. Ajuong

The senior author wishes to thank professor J.F. Levy (Emmeritus Professor of Wood Science, Imperial College of Science, Technology and Medicine, London) for suggesting the need for a Postdoctoral work in order to publish the findings of this research and the Society for the Protection of Science and Learning for partially funding the preparation of the series for publication.

signment of peaks and sharper in spectrum resolution compared to the infrared (IR) its spectra are used in this report.

3 Results and discussion

An FTIR spectrum of substances removed by toluene is shown in Fig. 1. Toluene is a non-polar solvent and is traditionally believed to be incapable of opening up and penetrating wood cell walls. Thus when used for extraction it would be expected to merely recover the extractable materials located within the cell lumina. Previous reports indicate such substances as consisting largely of long-chain fatty acids, fats, resins, waxes, terpenes and phytoosterols (Anon 1988; Laks 1991) – materials known for their relatively high molecular weight.

Peak assignment for toluene extracted material revealed a weak, broad stretching band of the intermolecular bonded hydroxyl group at 3350 cm^{-1} , with very strong methylene and methyl stretching frequencies appearing at 2914 and 2870 cm^{-1} respectively. A very weak aromatic “shoulder” was apparent at 3050 cm^{-1} . In association with the observed intermolecular hydroxyl group band at the short wavelength an ester carbonyl peak was produced at 1735 cm^{-1} as a “shoulder” to a strong carboxylic carbonyl stretching peak seen at 1713 cm^{-1} . These bands may be arising from the carbonyl of dimerized saturated aliphatic acids which absorb at $1720\text{--}1706\text{ cm}^{-1}$ and their saturated esters which frequently absorb at $1750\text{--}1735\text{ cm}^{-1}$. Close to this carbonyl functionality can be seen a medium intensity olefinic double bond (or an aromatic ring breathing mode) stretching at 1640 cm^{-1} . A series of weak within-ring skeletal carbon to carbon single bonded stretching peaks are registered at 1585 , 1500 and 1400 cm^{-1} respectively. These bands involve stretching and contraction of all the bonds in the ring together with the interactions between the modes of response.

In the middle of the spectrum appears a strong methylene “scissoring” and methyl asymmetrical bending band at 1462 cm^{-1} , coupled with methyl symmetrical bending at 1372 cm^{-1} . A broad, strong carbon single bonded oxygen stretching vibration appears at 1260 cm^{-1} . This band could be an interaction band between carbon single bonded oxygen stretching and in-plane carbon single bonded hydroxyl bending in carboxylic acids, since in carboxylic carbonyl the carbon single bonded hydroxyl group functionality is masked by the methylene scissoring

arising from the methylene group adjacent to the carbonyl. The strong, broad band appearing at 1166 cm^{-1} , may be arising from saturated esters in conformity with ester carbonyl stretching, which usually absorbs in the $1210\text{--}1163\text{ cm}^{-1}$ region of the spectrum. The weak shoulder appearing at 1120 cm^{-1} , may arise from aliphatic ether stretching.

In the “finger print region” the band appearing at 1070 cm^{-1} may be produced by symmetrical stretching of an aryl alkyl ether, which absorbs usually between $1070\text{--}1020\text{ cm}^{-1}$, whilst the weak shoulder at 1030 cm^{-1} is probably due to carbon to oxygen single bonded stretching in acetates of primary alcohols. These frequently vibrate at $1061\text{--}1031\text{ cm}^{-1}$. They could also be caused by an interaction between non-conjugated, straight chain carbon to oxygen stretching and acidic anhydride groups, whose absorption occurs at 1047 cm^{-1} .

Finally, the far peaks at low frequencies of 835 and 720 cm^{-1} are arising from ring out-of-plane carbon single bonded hydrogen bending vibrations associated with two adjacent hydrogen atoms and in-plane methylene rocking absorptions in straight chain paraffins respectively.

3.1 Extractives removed by ethanol

Ethanol is a good bulking agent (Gardner et al. 1967) and can swell wood structure by 83% of that caused by water (Morgan and Orsler 1969). Thus ethanol would be expected to recover materials from within the wall structure and these include, among others, condensed tannins, flavonoids and phenolics (Laks 1991). An FTIR spectrum of the substances, removed by ethanol is presented in Fig. 2.

These substances unlike toluene soluble components have strong, intermolecular bonded hydroxyl groups stretching at 3328 cm^{-1} coupled to weak bands of stretching methylene and methyl groups at 2942 and 2920 cm^{-1} respectively. Similarly, in contrast to that for toluene extracted material the spectrum shows there is a weak carbonyl functionality stretching at 1713 cm^{-1} , possibly from dimerized saturated aliphatic acids. In addition, and in contrast to the weak carbonyl functionality is a sharp, intense band at 1613 cm^{-1} . This may be due to a carbon to carbon double bond stretching at a lower than usual frequency, but with increased intensity because of conjugation with a carbonyl group. However, it is more likely that this band may be arising from a strong ring breathing mode in conformity with the strong, sharp and

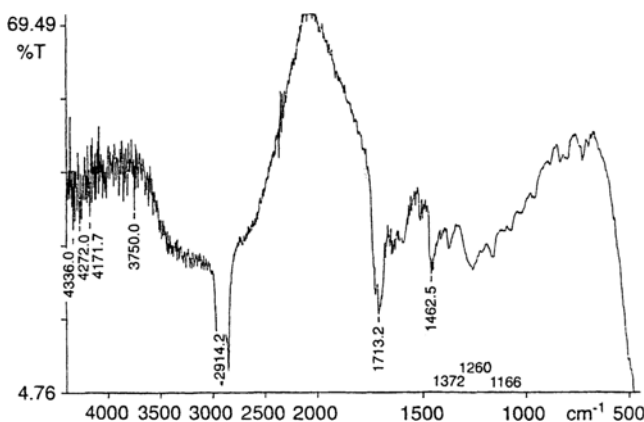


Fig. 1. FTIR spectrum of the extractives removed by toluene
Bild 1. FTIR-Spektrum der Toluol-Extrakte

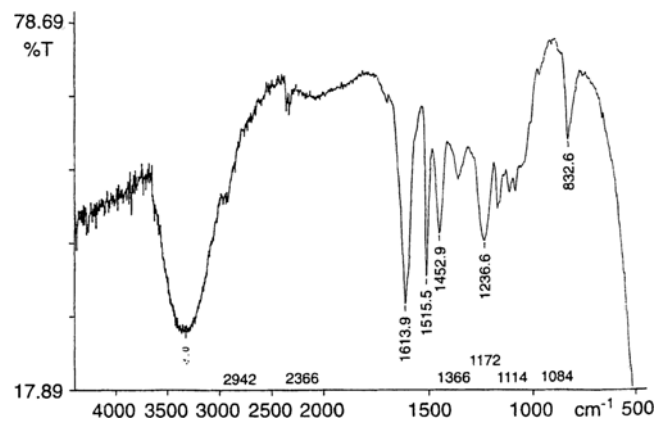


Fig. 2. FTIR spectrum of ethanol soluble extractives
Bild 2. FTIR-Spektrum der Ethanol-Extrakte

intense within-ring carbon to carbon single bonded skeletal stretching vibration at 1515 cm^{-1} .

Methylene scissoring and methyl asymmetrical bending absorptions appear at 1452 cm^{-1} , whilst methyl symmetrical bending of medium intensity at 1366 cm^{-1} . Meanwhile, a broad strong carbon to oxygen single bonded band, unrecorded in the spectrum of extracted toluene extractives appears at 1236 cm^{-1} . This peak may be attributable to an asymmetrical stretching vibrations of an aryl alkyl ether and the band registered at 1172 cm^{-1} may be caused by the ethanol counterparts of saturated ester carbon to oxygen single bonded stretching. In a similar manner, the peak registered at 1114 cm^{-1} may be arising from carbon to oxygen single bonded stretching of aromatic esters of primary alcohols. Finally an aryl alkyl ether symmetrical stretching absorptions appears at 1084 cm^{-1} , and the far strong absorption at 832 cm^{-1} is from an out-of-plane ring bending vibration associated with two hydrogen atoms in the α -ring.

Comparing the spectra of the compounds recovered by the two solvents toluene and ethanol revealed the disappearance in the spectrum of ethanol soluble fractions of the strong carbonyl functionality band observed in toluene extract at $1735\text{--}1710$. Instead the traces show a weak band, indicative, perhaps, of the limited contribution of this type of chemical grouping to the total amount of ethanol soluble components for the species. Besides, the weak ring absorptions appearing in the spectrum of toluene extracted fractions at 1585 , 1500 and 1400 cm^{-1} were consolidated into sharp, strong ring absorptions at 1613 and 1515 cm^{-1} respectively. Similarly, the lower frequency vibrations appearing at 1236 , 1114 , and 832 cm^{-1} in the spectrum of ethanol extract components, all displayed strong ring bands in contrast to that of toluene.

Observations of the two solutes indicated that toluene extracted components consisted of clear coloured, waxy substances with a slight yellow taint which shows their aliphatic nature, whilst the material removed by ethanol was dark brown, thus qualitatively showing them as tannins (Hathway 1962). When ethanol was evaporated from the extract solution and the extracts residue re-taken up in a solvent mixture consisting of acetone and water (50:50% v/v), the extract dissolved completely, therefore, agreeing with the suggestion by Laks (1991) that ethanol recovers condensed tannins. Previous reports (ASTM D1105-56, TAPPI T 204 om-88) indicate that non-polar solvents like toluene remove such extract materials as fats, resins, waxes and non-volatile hydrocarbons. Thus, it may be concluded that the components recovered by toluene from the lumina surfaces of cell walls are largely high molecular aliphatic compounds consisting of fatty acids and their monohydric esters with little contribution from the aromatic compounds, whereas the ethanol solubles were predominantly aromatic substances of polar nature. These have been demonstrated to be tannins by the acetone-water solvent mixture tests.

3.2 Ethanol-toluene mixture extractives

An FTIR spectrum for the components extracted by this solvent mixture is presented in Fig. 3. Essentially this spectrum is very similar to that produced by the ethanol soluble components except for minor differences. These include the appearance of a medium intensity carboxylic and/or α - β -unsaturated aliphatic and aryl ester carbonyl functionality at 1725 cm^{-1} , and the presence of an ali-

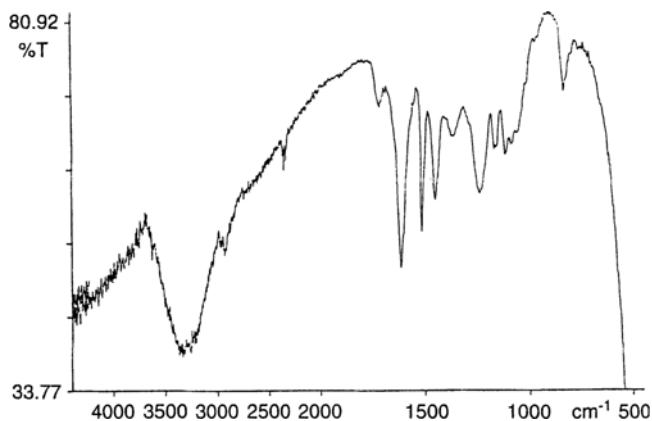


Fig. 3. FTIR spectrum of the ethanol-toluene extractives
Bild 3. FTIR-Spektrum der Ethanol/Toluol-Extrakte

phatic ether stretching at 1119 cm^{-1} (at lower than usual position) due to determination in a polar medium (Silverstein et al. 1991). The above small differences were to be expected, partly because of the dominance of ethanol in the solvent mixture (i.e. 2:1 v/v) and partly because of the limited amount contributed to the total extractive content by the low-molecular weight, non-polar compounds present within the cell walls of this wood. Experiments showed this fraction to constitute merely 1.5% of the dry, extractive-free weight of wood. It has been reported that this solvent mixture recovers such compounds as low-molecular carbohydrates and water solubles, besides some fats, resins, and waxes (Anon. 1988).

3.3 Water soluble extractive components

Hot water extraction when applied recovers from wood condensed tannins and water-soluble, low-molecular weight carbohydrates. The spectrum produced by this extract material is given as Fig. 4. Following the successive depletion of the extraneous substances from the wood by the preceding solvents it would be expected that fewer peaks would appear in this spectrum. In fact only those substances difficult to remove by the organic liquids due to their high polarity and/or strong attachment to the cell wall polymeric structures through chemical bonding (Bates-Smith 1962; Hillis 1962; Hillis and Carle 1959; Sarkanen et al. 1967; Sinclair et al. 1960; Swanson and Cordingly 1959) would be expected to remain this far. The

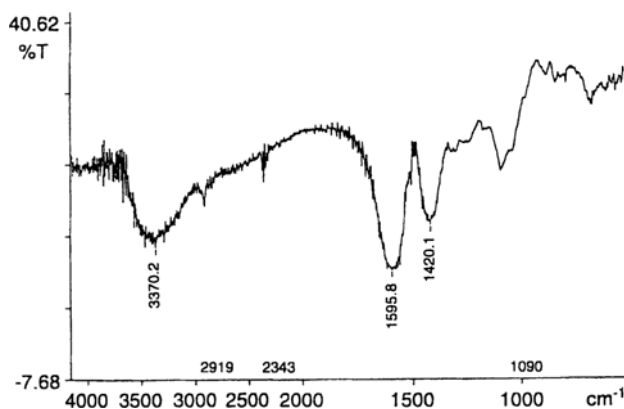


Fig. 4. FTIR spectrum of the water soluble extractives
Bild 4. FTIR-Spektrum der Heißwasser-Extrakte

main vibrational bands that were observed in this spectrum included an intermolecular bonded hydroxyl stretching at 3370 cm^{-1} , a methyl stretch at 2919 cm^{-1} , ring skeletal bands at 1595 and 1420 cm^{-1} and finally an aryl alkyl ether symmetrical stretching at 1090 cm^{-1} . Thus it may be recognized that the water soluble components of this wood comprise, similar to those of ethanol extractable compounds, of cyclized substances of an aromatic nature as shown by the predominance of ring vibrations in the spectrum (Fig. 4). Likewise the components were soluble in the acetone/water solvent mixture noted earlier. The identification of the bulk of the species' extractives as tannins helps explain the observed durability and termites resistance of the wood (Brown 1978). These findings are in agreement with other reports (Anon. 1988; Back 1991; Laks 1991).

4

Conclusions

Fourier transform infrared characterization of different extractive fractions removed from Pai wood using organic solvents and hot water have been conducted in order to shed light on the chemical nature of the various extractive compounds. Based on peak identification and assignment of the major functional groups in these components following conclusions have been drawn:

- (1) The extractive components recovered from the cell lumina and/or lumina surfaces of Pai wood are constituted of non-polar aliphatic substances such as fatty acids and their monohydric esters, gums and/or waxes with minor contributions from the aromatic compounds.
- (2) Ethanol and water-soluble fractions, derived mainly from within the wall structure, consisted of cyclized aromatic components of increased polarity as the solvent was changed from ethanol to water. Dissolution of such extracts, after evaporating ethanol in an acetone-water solvent mixture (50:50% v/v) confirmed the components to be tannins.
- (3) Ethanol-toluene mixture recovered aromatic compounds of intermediate polarity and some small amounts of non-polar low molecular weight aliphatics, all within the cell wall capillary structure.

References

Ajuong EA (1994) The influence of extractives on short-term creep in compression parallel to grain of pai (*Afzelia africana*

- Smith) Wood. Ph.D. thesis, School of Agricultural and Forest Sciences, Univ. of Wales Bangor, Gwynedd LL57 2UW, UK
- Ajuong EA, Breese MC (1997) The role of extractives on short term creep in compression parallel to the grain of pai wood (*Afzelia africana* Smith). *Wood and Fiber Sci.* 29 (2): 161-170
- Anonymous 1979: American Society for Testing and Materials. Preparation of extractive-free wood. ASTM D1105-56, Philadelphia, Pa.
- Anonymous 1988: Technical Association for Pulp and Paper Industry. Tappi Standard T 204 om-88. Solvent extractives of wood and pulp
- Back EL (1991) Oxidative activation of wood surfaces for glue bonding. *For. Prod. J.* 41(2): 30-36
- Bate-Smith EC (1962) Simple phenolic constituents of plants. In: Hillis, W. E. (ed.): *Wood extractives and their significance to the pulp and paper industry*, Academic Press, New York
- Brown WH (1978) *Timbers of the World. 1: Africa*. Timber Research and Development Association, Hughenden Valley, High Wycombe, Buckinghamshire HP14 4ND, UK
- Chow S (1972) Infrared spectral study of wood tissues from four conifers. *Wood Sci.* 5(1): 27-33
- Gardner R, Gibson EJ, Laidlaw RA (1967) Effect of organic vapours on the swelling of wood and its deformation under load. *Forest Prod. J.* 17(4):50-51
- Hillis WE (ed.) (1962) *Wood extractives and their significance to the pulp and paper industry*. Academic Press, New York
- Hillis WE, Carle A (1959) The influence of extractives on Eucalypt pulping and paper making. *Appita* 13: 74
- Laks PE (1991) The chemistry of the bark. In: Hon, D. N.-S.; Shiraishi, N. (eds.): *Wood and Cellulosic Chemistry*, pp. 257-330. Marcel Dekker, New York/Basel
- Manville JF, Tracey AS (1989) Chemical differences between alpine firs of British Columbia. *Phytochemistry* 28(10): 2681-2686
- Morgan JWW, Orsler RJ (1969) The interaction of wood with organic solvents. II. Its significance for extractives location. *Holzforchung* 23: 48-51
- Nault JR, Manville JF (1992) Differentiation of some Canadian coniferous woods by combined diffuse and specular reflectance Fourier transform infrared spectrometry. *Wood and Fiber Sci.* 24(4): 424-431
- Obst JR (1982) Guaiacyl and syringyl lignin composition in hardwood cell components. *Holzforchung* 36: 143-152
- Owen NL, Thomas DW (1989) Infrared studies of "hard" and "soft" woods. *Appl. Spectroscopy* 43(3): 451-455
- Sarkanen KV, Chang H, Allan GG (1967) Species variation in lignins. II. Conifer lignins. *Tappi* 50(12): 583-587
- Silverstein RM, Bassler GC, Morrill TC (eds.) (1991) *Spectrometric Identification of Organic Compounds*, 5. ed. John Wiley & Sons, New York, Chichester, Singapore
- Sinclair GD, Evans RS, Sallan HR (1960) New methods for sizing fibrous products. *Pulp and Paper Mag. Canada* 62(1): T23 - T27
- Swanson JW, Cordingly S (1959) Surface chemical studies on pitch. II. The mechanism of the loss of absorbency and development of self-sizing in papers made from wood pulps. *Tappi* 42(10): 812-819