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# A hard, high-carbon, lignomor with conchoidal fracture: Cunnite, from mature myrtle beech (*Nothofagus cunninghamii* (Hook. f.) Oerst.)

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## ABSTRACT

Introduced here is a newly discovered, hard, high-carbon, macroscopically homogenous, solid lignomor that is part of the natural decomposition product of mature, rainforest hardwood trees of the species myrtle beech (*Nothofagus cunninghamii* (Hook. f.) Øerst.). The substance, named cunnite, exhibits conchoidal fracture (indicating isotropic bonding), whereas all other tree decomposition products noted were readily friable, with no evidence of strong bonding. It is a dehydrated form of lignomor and its pre-dehydrated form also has conchoidal fracture. Cunnite was examined by carbon assay, radiocarbon dating, scanning electron microscopy (SEM) and Fourier transform infra-red spectroscopy (FT-IR). All wood cell walls had decomposed but the FT-IR results suggested that cunnite is high in lignin, and therefore it is most likely formed by a brown-rot fungi. Cunnite appears to be unique in that it is a product of natural decomposition but has relatively strong bonding. This bonding may be either from re-polymerisation or hydrogen bonding. If original polymer segments remain then they are most likely often cross-linked. Although cunnite appears to be stable beyond the decomposition of the entire tree, the age determined from radiocarbon dating for our samples does not imply that it is particularly long-lived thereafter. Cunnite is part of the forest carbon cycle but forms only a small fraction of the soil organic carbon pool. If the composition of cunnite is determined accurately in future work, and a synthetic version made, then it may be useful on a commercial scale as an adsorbent of hydrogen (i.e. storage for renewable energy) or of toxic substances; or it may provide other products useful in materials science or chemical engineering.

## 1. Introduction

Conchoidal fracture in biogenic substances is rare, and is found in diverse sources: some animal spines and shells (Berman et al., 1993), grain husks, air-dried plant resins (Simmonds, 1895), some high-lignin nut shells (Van der Pyl, 1948). It is also found in some minerals derived from plant matter: anthracite (Stopes, 1919) and the high-lignin form of fossilised timber, vitrinite (Kaelin et al., 2006). Conchoidal fracture can also occur in materials synthesised from vegetative matter, such as lignin-based activated-carbon synthesised from black liquor, pyrolised agricultural waste, pyrolised Kraft lignin, and waste products from wood pulping (e.g. Sharma et al., 2004; Maldhure and Ekhe, 2011; Huang et al., 2012).

The uses of lignin are diversifying and its chemical and physical properties remain a vibrant topic of research (Norgren and Edlund, 2014). The commonest source of lignin— waste from wood pulping— has most often been burnt as fuel (Ragauskas et al., 2014). That burning increases greenhouse gas concentrations relative to using low-emission renewables and it is exacerbated if sourced from primary forests (Dean et al., 2017). Generally, understanding a form of lignin with new textural properties may help to elucidate its chemical structure and process of formation. In turn, that may lead to a more environmentally friendly use for lignin that could be made synthetically to meet industrial demand. Determination of the chemical reasons for the differences between types of lignin-based products should also bolster understanding of the forest carbon cycle.

The term 'lignomor', is from the humus soil classification tuple of Englisch et al. (2005), Green et al. (1993) and Klinka et al. (1997). It describes a macroscopic, low pH, humic soil category in the soil organic matter (SOC) carbon pool. Lignomor, which can be below or aboveground, is derived from wood (trunk, branches and coarse roots) by decomposition but it does not have the original plant structures still discernible macroscopically. Reported here are preliminary investigations into a recently discovered type of lignomor found inside the trunks of mature, rainforest hardwood trees of the species myrtle/myrtle beech (*Nothofagus cunninghamii* (Hook. f.) Øerst.). That species has recently

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been renamed *Lophozonia cunninghamii* (Hook. f.) (Heenan and Smissen, 2013) but arguments have been made suggesting that the renaming need not be recognised (Hill et al., 2015).

The aim of the present work was to provide the fundamental steps in determining, through a range of standard analytical techniques, the origin and nature of the substance, and how it relates to known biological processes and the carbon cycle. Additionally, the understanding of the chemistry involved may help towards determining if the substance or a synthetic version of it could be used in chemical processing or energy storage.

## 2. Experimental methods

### 2.1. Definition of terms

The 'forest floor' includes the litter, fermentation and humus layers above the mineral soil (the solum) which is above the C-horizon.

The hard, dehydrated form of the lignomor, that we named 'cunnite', had a coal-like appearance and rock-like properties. The name cunnite is derived from the original species name of myrtle beech from which it is formed (*Nothofagus cunninghamii*) and suffixed with 'ite' to indicate its rock-like appearance and texture, and that although biogenic and found near the forest floor, it can be considered to be a mineral rock. The fresh, softer, hydrated form of the new lignomor had a cheese-like texture and was consequently named 'cunncaseus'— the prefix from the species name plus latin for cheese, 'caseus'; and to distinguish it from the other types of lignomor.

### 2.2. Study area and specimen collection

The specimens were obtained from several sites in mixed-forest in the Styx Valley, Tasmania, Australia, and a location map is given in Dean et al. (2018).

The first specimen of cunnite was found in a myrtle tree that had been pushed over during logging: diameter at breast height (DBH, measured at 1.3 m above the soil surface) 1.76 m, tree height 32(4) m (Fig. 1.b). Further details of the tree are given in Dean et al. (2018). In the trunk hollow several kilograms of dried decomposition product were found. In the centre of this product was the rock form, with visual similarities to coal (specimen CD089).

The second specimen was cunncaseus, the pre-dehydrated form, the wet lignomor, possibly still undergoing decomposition, although no timber structures were visible (specimen CD079). Both substance types had conchoidal fracture. Cunncaseus was also found in a myrtle that had been pushed over during logging. The fact that both the cunncaseus and cunnite were only found in myrtle trees, and that both had conchoidal fracture, led to the assumption that the cunnite was formed from cunncaseus by dehydration, which was verified by comparison of their spectra.

No material with structure similar to cunnite or cunncaseus was found in any other tree species. It was not uncommon however for mature eucalypts in mixed-forest to form lignomor in their hollow centres; none however had lignomor with conchoidal fracture.

Not all decomposing myrtle trees had the cunncaseus or cunnite as decomposition products. Two myrtle trees were found with a non-conchoidal lignomor which was aerated and friable and appeared to have no bonding between its particles (specimens CD064 and CD065).

For the cunncaseus (specimen CD079) (Fig. 1.e—g) a hand-held bulk-density head from a Eijkelkamp kit Eijkelkamp© soil corer (Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands) was used to acquire a known volume of sample.

### 2.3. Specimen processing and analysis

Subsamples of specimens were air dried at 20 °C. For elemental analysis subsamples were ground in a mortar and pestle followed by grinding to a fine powder using a ball mill (MM200 Mixer Mill, Retsch GmbH, Haan, Germany). For elemental analysis for total nitrogen, carbon and hydrogen a Thermo Finnigan EA 1112 Series Flash Elemental Analyser was used, operated by Thomas Rodemann at the Central Science Laboratory, University of Tasmania. In addition to the lignomor, samples of wood and charcoal from the same forest were also subject to elemental analysis.

The pH was determined after drying and grinding, by two-point calibration of a Hannah pH Meter on a gently stirred mixture of 1:5 soil:distilled water.

To help confirm their origins the two specimens, CD089 and CD103, were carbon dated at the Chrono Centre, Queens University, Belfast, Northern Ireland by James McDonald and Paula Reimer. The cunnite specimen CD089 responded to routine acid, alkali, acid ('AAA') processing: 4% HCl at 80 °C 1–2 h, then 0.5% NaOH at 20 °C 1 h, then 4% HCl at 80 °C 1 h, rinse with deionised water until neutral pH then dry (Kigoshi et al., 1980; Hoper et al., 1997; Brock et al., 2010). Cunnite specimen, CD103, did not respond to routine sample extraction and its pre-treatment was tailored: 'humics' extracted, 4%HCl at 80 °C 2 h, $H_2O$ wash, 0.5%NaOH at 50 °C 2 h, acidified with 4%HCl, centrifuged, liquid decanted and discarded, 'humics' freeze dried.

One subsample of cunnite specimen CD089 was also analysed by scanning electron microscopy (SEM) at the Central Science Laboratory, University of Tasmania, led by Karsten Goemann. The SEM sample was carbon coated.

### 2.4. FT-IR spectral analysis

Insights into the chemical composition of wood species and into the change in chemistry during decomposition of wood have been provided by Fourier Transform Infrared spectroscopy (FT-IR) (e.g. Faix, 1991; Facklera et al., 2010; Yilgor et al., 2013). Sub-samples were extracted from the samples prepared for elemental analysis, that had been ground to a fine powder in the ball mill (Section 2.3). FT-IR is deployed here to help elucidate the genesis and structure of the new lignomor. Samples of myrtle at different stages of decomposition and along different routes of decomposition were analysed using FT-IR spectroscopy. The spectral runs were performed on a Bruker Vertex 70 infrared spectrometer, at the Central Science Laboratory, University of Tasmania by Thomas Rodemann. Automated matching of cunnite spectra against a spectral library was performed, also by Thomas Rodemann. The spectral range was 4500 to 600 $cm^{-1}$ with a spectral resolution of 4 $cm^{-1}$.

The full FT-IR spectra for the specimens are shown in Fig. 3.a. To allow comparison between the spectra for the different specimens, we produced separate spectral graphs with the overlaying spectra normalized at:

1) the low wavenumber edge of the water peaks: 2400 $cm^{-1}$ (Fig. 3.b),
2) two absorption minima: 1176 and 1485 $cm^{-1}$, (Fig. 3.c, d), and
3) the three absorption peaks: 1109, 1034, and 1597 $cm^{-1}$, before the water peak range at 1670 $cm^{-1}$.

The FT-IR results are tabulated in Table 3 with the undecomposed myrtle wood, CD091, details given in the left columns 1–3, while the other sample details are given in columns 4–8. Spectral features recorded include peaks and absorption differences between specimens (e.g. column 7 expresses qualitatively the increase, decrease or peak shift). The spectra of the decomposition specimens were compared (in Table 3) with the myrtle wood in regards to change in relative peak heights and the formation of new peaks, and were assigned qualitative characteristics (e.g. absent, decrease, increase, shift) with respect to the undecomposed wood specimen. Furthermore, as is normal convention, the respective peak sizes and features are given in columns 2 and 6 (e.g. m, s, sh, w, etc.).