AERIAL ALTERATION PROCESSES OF WOOD BY FUNGI: A BIOMARKER INVESTIGATION

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Following death and prior remineralisation, the lipidic constituents from living organisms undergo various transformation pathways, which depend on the nature of the environmental conditions and degrading microorganisms. In the frame of a study aimed at characterizing chemotaxonomic higher plant triterpenoid biomarkers allowing altered wood to be identified at the species level, notably in an archaeological context, novel aromatic triterpenoids functionalized at C-2 have been characterized in oak wood, revealing a novel (bio)degradation pathway (Schnell et al., 2012). However, to date, the formation of these compounds seems to be restricted to oxygen-poor, freshwater environments, and very little is known on the degradation intermediates of wood triterpenoids in oxic (aerial) environments, such as some archaeological soils, in which numerous wooden archaeological remains (tombs, wood beams, …) can be found.

In the present study, we have investigated the lipid composition of two wood species (*Quercus robur* and *Populus alba*) degraded by soft/white rot fungi and brown rot fungi, respectively, a particular attention being paid to the wood triterpenoid and steroid distributions.

In the case of *Q. robur*, the lipid distribution of unaltered wood was strongly dominated by three polyfunctionalysed triterpenoids, comprising bartogenic acid **4** and two related hydroxylated analogues **5** (Fig. 1a). These compounds, which represent chemotaxonomic compounds specifically biosynthesized by *Q. robur* (Schnell et al., 2014), are the precursor molecules of the diagenetic C-2 oxygenated aromatic triterpenoids predominantly formed upon wood alteration under anaerobic conditions (Schnell et al., 2012). Compounds **4** and **5** were absent from the lipid distribution of the wood sample altered under aerobic conditions (Fig. 1b), which was almost entirely made of phytosteroids. The latter comprised biosynthetic steroids also occurring in the unaltered sample (e.g., **2**,**3**), together with their oxidized counterparts (e.g., **8**,**11**) as well as a series of ergosteroids (**6**,**7**,**9**) likely originating from the soft/white rot fungi involved in wood degradation. An interesting feature was the (almost) complete absence of triterpenoids in the altered wood sample, whereas these compounds largely predominated the unaltered distribution, which suggests that plant triterpenoids - at least polyfunctionalized ones like **4** and **5**- are more prone to remineralisation than phytosteroids upon aerial degradation.

In contrast to *Q. robur*, phytosterols **2** and **3** dominated the lipid distribution of the unaltered wood from *P. alba* (Fig. 1c), together with tetracyclic C_{31} triterpenes of the cycloartenol series (**12**,**13**) and C_{30} α- and β-amyrin triterpenoids (**14**-**19**), all these compounds being widespread among the triterpenoids from the Plant kingdom. A close terpenoid signature was observed in the case of the altered wood degraded by brown rot fungi. However, these compounds did not predominate the lipid signature, which showed a series of late-eluting major compounds (**20**-**23**). The latter could be identified by mass spectrometry as lanosterol derivatives and related 24-methylene homologues bearing a keto (**20**,**22**) or hydroxy (**21**,**23**) group at C-3, an hydroxy group at C-16 and a carboxylic acid at C-21 (side-chain). The structure of additional compounds (empty circles, Fig. 1d), likely related lanosteroids and bearing extra functional

group(s), could not be determined. The major compound, polyporenic acid (**20**), and related compounds **21**-**23**, mainly occur in Polyporaceae involved in wood degradation, predominantlty from brown rot species (Yokoyama et al., 1975), whereas they are absent in white rot strains, and can be considered as potential indicators of brown rot degradation of wood.

In conclusion, aerial degradation of wood triterpenoids results either in their complete degradation, or in their transformation in keto derivatives, and does not lead to the formation of wood chemotaxonomic triterpenoid biomarkers such as those formed under anaerobic/disaerobic conditions (e.g., aromatized terpenoids). The molecular contribution of the fungi involved in wood degradation can be detected from the presence of ergosterol and lanosterol derivatives, the latter being associated to brown rot fungi and the former to white/soft rot species. The absence of newly-formed specific triterpenoid markers suggests that in an archaeological context, it might be difficult to determine precisely the nature of buried wood species degraded under aerobic/aerial conditions based on their triterpenoid signatures.

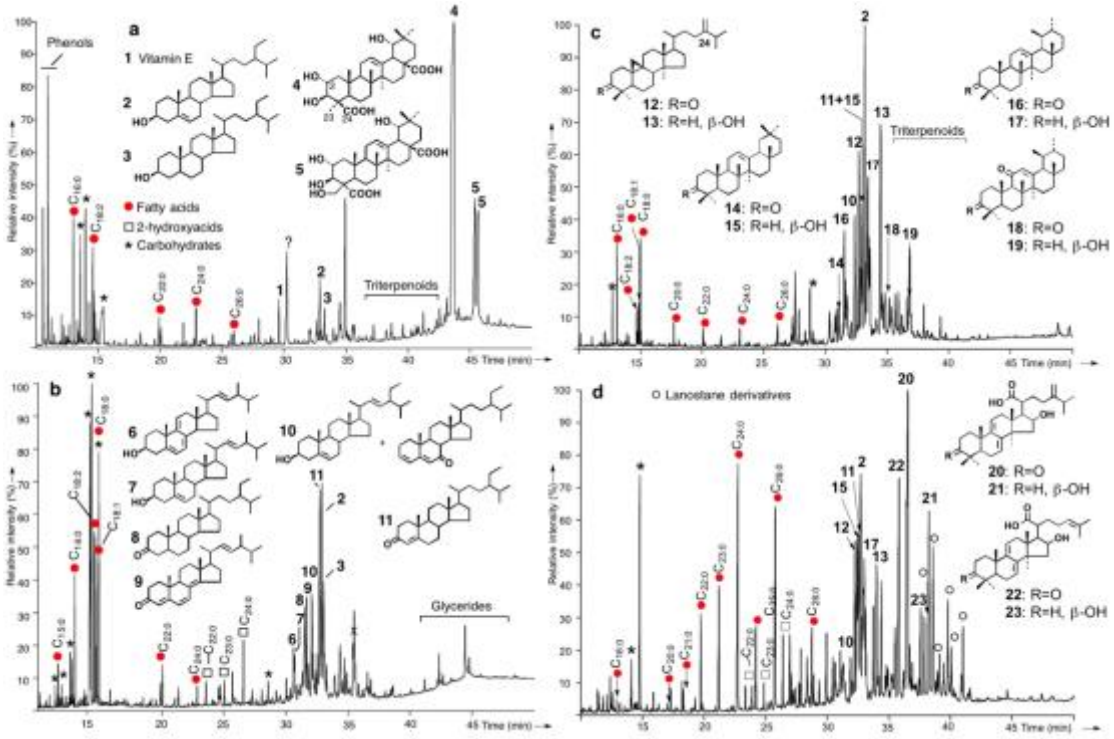

Figure 1: *Gas chromatograms showing the lipid distributions from (a) unaltered oak (Q. robur) wood; (b) oak wood altered by soft/white rot fungi; (c) unaltered poplar (P. alba) wood; (d) poplar wood altered by brown rot fungi.*

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