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Pyrolysis-GC/MS of charred purified condensed tannin: towards identification of tannin-derived black carbon in environmental samples

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Tannins account for a significant proportion of plant biomass and are therefore a possible source of Black C in the charred remains from wildfires. Nonetheless, in contrast with other major biocomponents such as lignin and cellulose, the thermal degradation of tannins has not been investigated in laboratory charring experiments. We used pyrolysis-GC/MS to investigate the effects of furnace charring (30 min at fixed temperatures up to 600 ºC under limited oxygen supply) on the degradation of pure condensed tannin (CT) isolated from Corsican pine (Pinus nigra) needles. The experiments showed a rapid loss (at 300 ºC and higher) of the pyrogallol moieties of the B-ring of prodelphinidin-type CT, due to dehydroxylation. The relative abundance of catechols (from procyanidin-type CT) decreased at 350 ºC and higher temperatures. This led to the formation of phenols that were strongly enriched between 300 and 400 ºC. At higher temperatures, further dehydroxylation caused a decline in contributions of phenols producing a series of monocyclic aromatics ((alkyl)benzenes) and condensation of aromatics produced polycyclic aromatic hydrocarbons (PAHs), i.e. the typical pyrolysis fingerprint of strongly charred biomass. We conclude that (i) the thermal degradation of CT can be successfully monitored by pyrolysis-GC/MS, (ii) thermal degradation of CT is characterized by dehydroxylation of phenolic groups and condensation of aromatics that increase with temperature and (iii) CT-derived Black C may be recognized by catechol enrichments at low temperatures and possibly (relative) abundance of phenol and biphenyl at higher levels of thermal breakdown. Applying the same method to natural charcoal from gorse bushfires indicated that pyrolysis-GC/MS fingerprinting may allow for tannin identification in environmental Black C samples.