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TERPENES FROM BOGWOOD OF CRIPTOMERIA JAPONICA D. DON

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The essential oils from a bogwood stump of sugi (*Cryptomeria japonica* D. Don) from Fukui, Japan, (F-bogwood) preserved for c. 3,000-3,500 years in sediment of a muddy field were analyzed using gas chromatography-mass spectrometry (GC/MS).

Twenty-six sesquiterpenes and 6 diterpenes were identified. The main components were *cis*-calamenene (23.1%), cadalene (18.1%), δ-cadinene (7.9%) and simonellite (4.5%). These results were compared with previous results for oils from a stump of sugi fresh wood and two bogwood samples from Yamaguchi (Y-bogwood, muddy field, c. 3,000 years) (Narita *et al.*, 2006a) and Shimane (S-bogwood, volcanic ash, c. 3,500-3,800 years) (Narita and Yatagai, 2006b).

The yields of the oils from 100 g oven-dried wood powder were 1.6 ml for F-bogwood, 2.3 ml for Y-bogwood, 0.19 g for S-bogwood and 1.6 ml for fresh wood; the sesquiterpene contents were 86.8%, 97.0%, 42.4% and 98.5%, respectively. Thus the essential oil in F-bogwood is preserved in a fairly high level. Sesquiterpene alcohols, abundant in fresh wood, seems to have been dehydrated to hydrocarbons in the early stage of diagenesis; therefore the alcohol/ketone fraction was lost in the bogwoods in the order of S- > F- > Y-. This order agrees with that of maturity (Narita and Yatagai, 2006b).

Sesquiterpene hydrocarbons can be classified by *m/z* value (Fig. 1). Fresh wood is rich in *m/z* 204 compounds. The *m/z* 202 and 198 compounds, *i.e.* the dehydrogenation products from *m/z* 204, are abundant in F-bogwood, whereas *m/z* 208 compounds, hydrogenation products from *m/z* 204, are scarce. Thus, dehydrogenation seems to have been dominant in F-bogwood; however, it also contains small amount of *m/z* 206 (partially hydrogenated). On the other hand, the *m/z* 202 component of F-bogwood contains small amount of tetrahydrocadalene, which is found in no other samples. It is known that the early degradation stage of cadinane-type sesquiterpenes is dehydrogenation to form calamenenes *m/z* 202, which are different from tetrahydrocadalene in dehydrogenation position. Based on these results we propose a new possible diagenetic process of cadinane-type hydrocarbons in F-bogwood as follows: Firstly, both hydrogenation and dehydrogenation take place simultaneously; secondly, the *m/z* 208 species are dehydrogenated to cadalene (*m/z* 198) via compounds *m/z* 202. In the case of F-bogwood, this dehydrogenation may proceed via multiple pathways at the *m/z* 202 stage containing tetrahydrocadalene, which has not been found in other bogwoods and fresh wood.

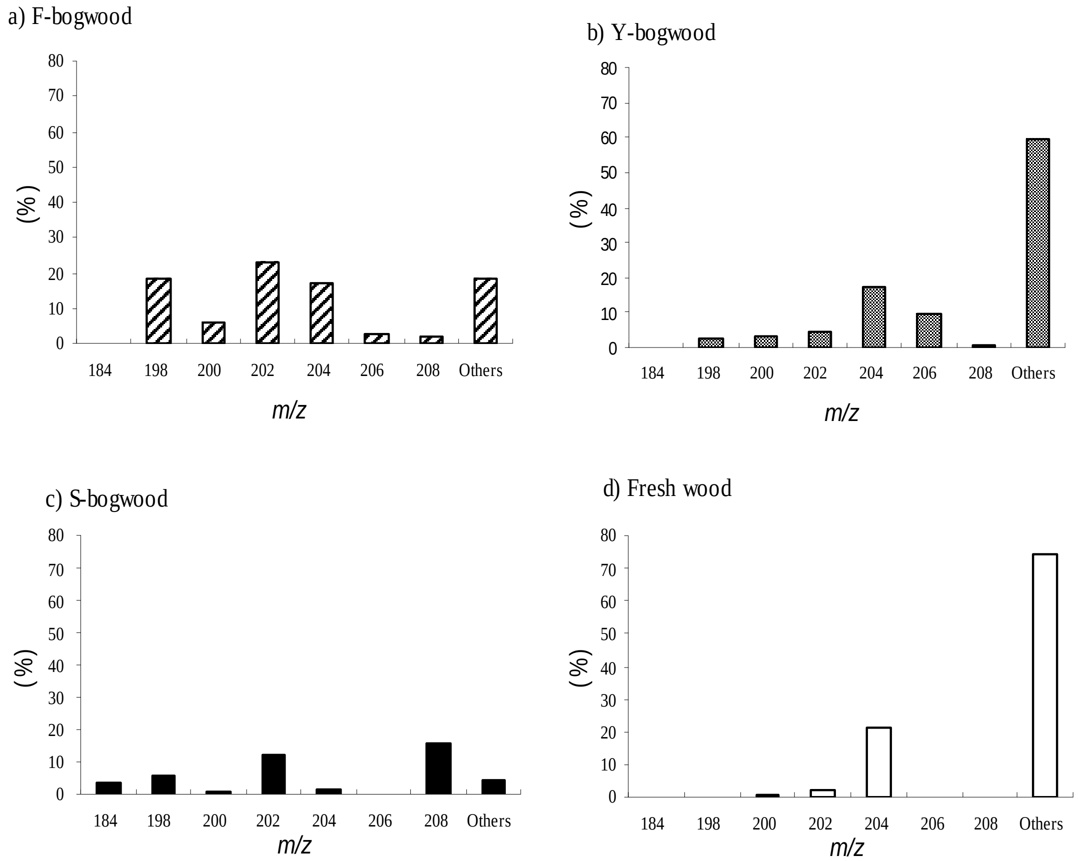

Figure 1. Compositions of sesquiterpenes in essential oils from *Cryptomeria japonica* D. Don: a) F-bogwood, b) Y-bogwood, c) S-bogwood and d) Fresh wood. “Others” represents alcohols and ketones.

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