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Characteristic Raman bands for *Artocarpus heterophyllus* heartwood

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Abstract The Raman spectrum of *Artocarpus heterophyllus* heartwood, which proved to be a rich source of flavonoids, exhibited two characteristic bands, at $1247\,cm^{-1}$ and $745\,cm^{-1}$. The bands also appeared in the Raman spectrum of the yellow-brown needles extracted from the heartwood with methanol. Based on the Raman measurements of flavones and related compounds, it was predicted that the Raman band at $1247\,cm^{-1}$ may be attributed to flavonoid-type compounds. No vibrational band corresponding to the characteristic Raman bands was observed by diffuse reflectance infrared spectroscopy. Thus, it was suggested that observation of the characteristic bands is an advantage of Fourier transform-Raman spectroscopy for nondestructive analysis of wood.

Key words Raman spectroscopy · *Artocarpus heterophyllus* · Flavonoid · Infrared spectroscopy · Nangka

Introduction

Raman spectroscopy provides a powerful tool for analyzing solid organic substances. Druing the past 10 years a number of Fourier transform (FT)-Raman spectroscopic studies[1–7] of wood have been reported, and a near-infrared laser was employed as an excitation source. However, for chemical analysis of wood, the utilization of Raman spectroscopy is much less satisfactory than infrared (IR) spectroscopy.

Artocarpus heterophyllus is an evergreen distributed over tropical regions in Asia. This hardwood species is frequently used for construction and furniture; and it has been investigated from both biological and medical viewpoints because of its abundance of flavonoid-type compounds such as flavones and flavanones (Fig. 1).[8] To improve the weathering resistance of wood, we have investigated the weathering deterioration mechanism of several tropical wood species using various analytical methods and, in particular, explored the chemical changes in the surface layers of weathered wood by vibrational spectroscopy.[9,10] In these studies we found that *Artocarpus heterophyllus* heartwood exhibits characteristic Raman bands.

In this preliminary study we studied the FT-Raman spectra of *A. heterophyllus* heartwood and extracts with methanol. The results are reported here, and the characteristic Raman bands are discussed.

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Materials and methods

Wood and chemicals

Table 1 lists the common, scientific, and family names of tropical and Japanese hardwood species whose Raman spectra are discussed in this paper. The flavones and flavanones (purchased from Tokyo Kasei Kogyo Co.) were used for Raman measurements without further purification.

Extraction

Air-dried heartwood powder (100 g) of *Artocarpus heterophyllus* was suspended in 1000 ml *n*-hexane, left for 24 h at room temperature, and then filtered. This procedure was repeated two times. The residual powder was extracted with ethyl acetate and methanol successively in the same way. Extracts with methanol were obtained as yellow-brown needles by evaporating the solvent under reduced pressure.

FT-Raman and FT-IR spectroscopy

Fourier transform-Raman spectra were recorded using a JEOL JIR7000W spectrometer connected to an RS-RSU-

Table 1. Common, scientific, and family names of wood samples

Common name	Scientific name	Family name
Nangka[a]	*Artocarpus heterophyllus* Lamk	Moraceae
Albizia[a]	*Paraserianthes falcata* Becker	Leguminoceae
Mahoni[a]	*Switenia macrophylla* King	Meliaceae
Puspa[a]	*Schima wallichii* Korth	Theaceae
Yamaguwa[b]	*Morus bommbycis* Koidzumi	Moraceae
Itayakaede[b]	*Acer mono* Maximowicz	Aceraceae
Buna[b]	*Fagus crenata* Blume	Fagaceae

[a] Tropical hardwood
[b] Japanese hardwood

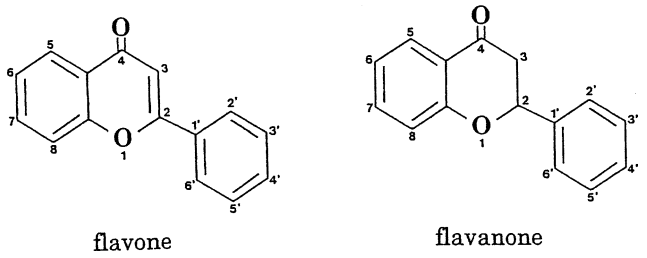

Fig. 1. Structures of flavone and flavanone

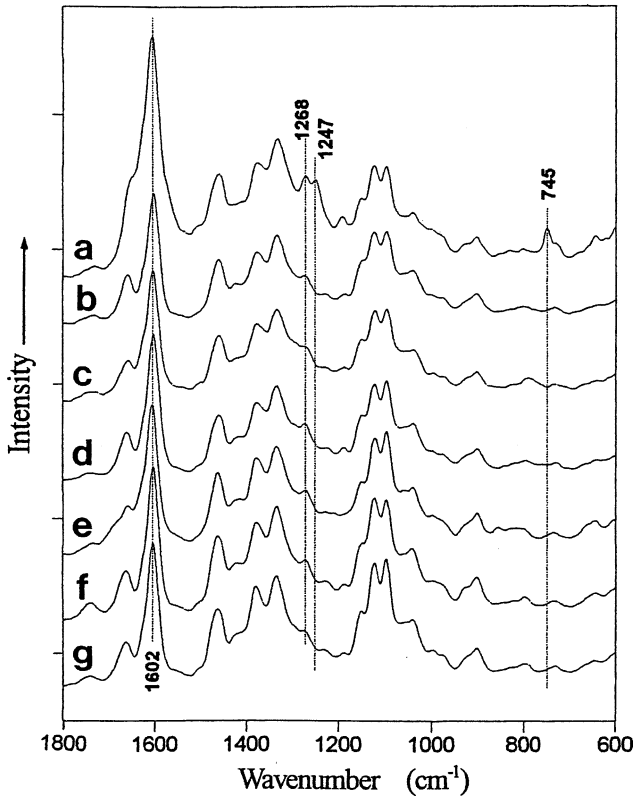

Fig. 2. Fourier transform (FT)-Raman spectra of tropical and Japanese hardwood species. *a, Artocarpus heterophyllus; b, Paraserianthes falcata; c, Switenia macrophylla; d, Schima wallichii; e, Morus bombycis; f, Acer mono; g, Faus crenata*

Table 2. Raman band positions in the 1260–1220 cm^{-1} region of flavones and flavanones

Compounds	Raman band position (cm^{-1})
Flavone	1235m
3-Hydroxyflavone	1247m, 1224m
6-Hydroxyflavone	1256s, 1235s
7-Hydroxyflavone	1256s
5,7-Dihydroxyflavone	1247s
7,8-Dihydroxyflavone	1247s
4′,5,7-Trihydroxyflavone	1245s
3,4',5,7-Tetrahydroxyflavone	1249w, 1224w
Flavanone	1225s
6-Hydroxyflavanone	1243s
7-Hydroxyflavanone	1258s

s, strong; m, middle; w, weak

200 Raman module with 4 cm^{-1} spectral resolution. The excitation source was an Nd^{3+}:YAG laser (1064.1 nm) in the 180° back-scattering configuration. FT-IR spectra of the wood samples diluted in KBr by grinding were obtained using the same spectrometer by means of the diffuse reflectance technique with 4 cm^{-1} spectral resolution. All the Raman and IR measurements were performed on the heartwood of wood samples.

Results and discussion

Figure 2 depicts the Raman spectra of four tropical and three Japanese hardwood species in the region 1800–600 cm^{-1}. The Raman line shapes of the wood species other than *Artocarpus heterophyllus* are similar to one another. However, the spectrum of *A. heterophyllus* has several features different from those of the others, the most significant of which are the Raman bands occurring at 1247 and 745 cm^{-1}. These Raman bands cannot be detected in *Morus bombycis* (Fig. 2e), despite being in the same family as *A. heterophyllus*, and have not been reported in the previous Raman studies of woody materials by other groups.[1–7,11–14] Moreover, except *A. heterophyllus*, we have not observed such bands in the Raman measurements of more than 60 hardwood species used frequently as construction materials.

Artocarpus heterophyllus heartwood has proven to be a rich source of flavonoids, as mentioned above. Table 2 summarizes the Raman bands observed in the 1260–1220 cm^{-1}

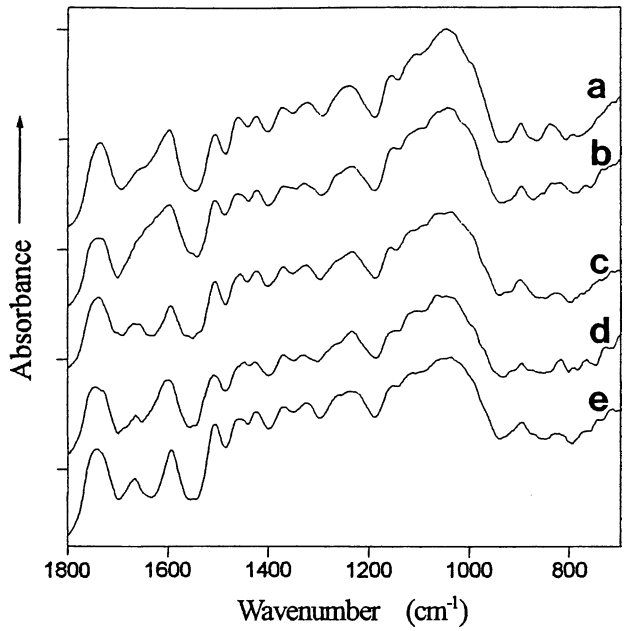

Fig. 3. FT-infrared (IR) spectra of tropical hardwood species. *a, Morus bommbycis; b, Artocarpus heterophyllus; c, Paraserianthes falcata; d, Switenia macrophylla; e, Schima wallichii*

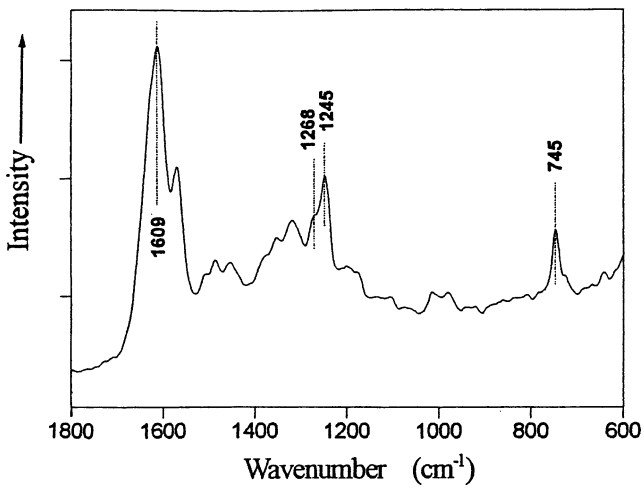

Fig. 4. FT-Raman spectrum of the extract mixture from *Artocarpus heterophyllus* heartwood with methanol

region of various flavones and flavanones. As can be seen, almost all the compounds showed strong or middle Raman bands in this region. Therefore, the band at 1247 cm^{-1} for *A. heterophyllus* may be due to some flavonoids or their derivatives.

Figure 3 illustrates the IR spectra of *A. heterophyllus* and other tropical wood species. Inspection of the IR data in Fig. 3 reveals that all the spectral contours resemble one another in the 1500–900 cm^{-1} region. We were therefore unable to specify any vibrational bands corresponding to the Raman band at 1247 cm^{-1} in the IR spectrum of *A. heterophyllus*. This is a remarkable result that suggests the advantage of Raman spectroscopy over IR spectroscopy for chemical analysis of wood. It is expected that the presence of certain compounds in lignocellulosics can be readily determined by detecting the Raman band at 1247 cm^{-1}. The more valuable the detectable compounds, the greater is the importance of Raman spectroscopy as a rapid nondestructive analytical technique.

The Raman spectrum of the extract mixture from *A. heterophyllus* heartwood with methanol is shown in Fig. 4. As for heartwood, both the characteristic Raman bands are clearly observed. Accordingly, it is apparent that the extracts contain the compounds causing the Raman bands, whereas it is not clear whether both bands are attributed to the same compounds. To identify the compounds, we are currently investigating the extracts by nuclear magnetic resonance (NMR) techniques.

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