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Extractives of muirapiranga (*Brosimum* sp.) and its effects on the vibrational properties of wood

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Abstract The potential of muirapiranga (*Brosimum* sp.) as a substitute material for violin bows was estimated in terms of vibrational properties, and the influence of extractives on the vibrational properties was examined. The loss tangent of muirapiranga was somewhat higher and the specific dynamic Young's modulus was rather lower than the respective values for pernambuco, which is regarded as the best material for violin bows. Therefore, muirapiranga is a poorer bow material in terms of vibrational properties. Impregnation of crude extractives from muirapiranga decreased the loss tangent of other wood specimens. The main compounds of the extractives were identified as xanthyletin and luvangetin. Impregnations of isolated xanthyletin and commercially available methoxsalen, which was tested as an analogue of luvangetin, markedly decreased the loss tangent of other wood specimens. Methoxsalen and xanthyletin differ from conventional loss tangent-decreasing substances, namely protosappanin B and hematoxylin, in terms of water insolubility and the absence of hydroxyl groups. From the similarity in molecular characteristics of loss tangent-decreasing substances found so far, restriction of molecular motion due to an impregnated substance in the wood matrix is suggested as one loss tangent-decreasing mechanism.

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Introduction

Muirapiranga (*Brosimum* sp.) is a wood species of Moraceae, mainly distributed in South America, and is commonly used in furniture manufacture, wood work, interiors, percussion instruments, and so on. We studied whether this wood species could be a substitute for pernambuco (*Guilandina echinata*) for making violin bows. Although pernambuco is the best material for bows, it is a limited resource and a replacement for it is urgently needed. In previous studies,^{1,2} we found that the loss tangent of pernambuco is peculiarly low due to extractives. A low loss tangent is one of the most important requirements for the soundboard of wooden musical instruments.³ Pernambuco itself is not appropriate for musical instruments because of its high density, but we have found that the impregnation of extractives obtained from pernambuco decreases the loss tangent of other wood specimens.^{4,5} The extractives were identified as protosappanin B and braziline.⁶ On the other hand, the reason that the extractives of pernambuco decrease the loss tangent has not been clarified.

In previous studies,^{4,7} we investigated the dependence of the vibrational properties on the chemical structure of numerous impregnated aromatic compounds. To date, we have found that only protosappanin B and hematoxylin decrease the loss tangent. Hematoxylin is the main extractive of logwood (*Haematoxylon campechianum*) and has the same structure as braziline except for the number of attached hydroxyl groups. Because pernambuco and logwood belong to the Leguminosae family, their extractives are analogous in origin. On the other hand, muirapiranga belongs to the Moraceae family; therefore, we may find additional compounds that decrease the loss tangent.

At first, we evaluated the vibrational properties of muirapiranga as a substitute material for violin bows. Second, we examined the vibrational property changes after applying

the crude extractives of muirapiranga to other wood specimens. Isolation and identification of the extractives of muirapiranga were followed by verifying the effect of applying isolated compounds to other woods on the vibrational properties. In the course of this study, we primarily intended to find novel compounds that decrease the loss tangent. The chemical and physical characteristics of the novel compounds will offer the key to understanding the decreasing mechanism of loss tangent.

Materials and methods

Materials

A single block of muirapiranga was used by cutting it to 2 mm (T) × 12 mm (R) × 150 mm (L) for mechanical property measurements and by breaking it into wood meal (150–355 μm) for extraction. Longitudinal [2 mm (T) × 12 mm (R) × 150 mm (L)] and radial specimens [12 mm (T) × 150 mm (R) × 2 mm (L)] of Sitka spruce (*Picea sitchensis*) were used for the impregnation of crude extractives, although only longitudinal specimens were used for impregnation of isolated compounds.

Measurement of vibrational properties

Specific dynamic Young's modulus (E/ρ , where E is dynamic Young's modulus, ρ is specific gravity) and loss tangent ($\tan \delta$) of muirapiranga were measured by the free-free flexural vibration method,³ after equilibration at 20°C and 65% relative humidity (RH). Twelve specimens were used for the test. The same procedures were also applied to Sitka spruce specimens subjected to the impregnation tests described below.

Extraction and impregnation of crude extractives

Muirapiranga meal was successively extracted with *n*-hexane, diethyl ether, chloroform, and methanol for 6 h each; much larger amounts of extractives were obtained by the extractions with diethyl ether and methanol. For impregnation of crude extractives into Sitka spruce specimens, diethyl ether-soluble and methanol-soluble fractions were successively extracted by means of a large scale Soxhlet extractor (flask volume: 2 l). Each fraction was dried once, and the solid component was dissolved with methanol to give four different prescribed concentrations. Methanol was chosen because of its high swelling ability for wood and solubility for crude extractives. The impregnation of the solution into Sitka spruce specimens, for which the vibrational properties were measured, was conducted under successive reduced pressures by tap aspiration, compression at 0.3 MPa for 3 h, and 0.8 MPa for 20 h at room temperature. After impregnation, the specimens were dried in an oven, weighed, and then conditioned at 20°C and 65% RH until equilibrated to the ambient atmosphere. The vibrational

properties were measured again. Three specimens were assigned to each solution concentration and each measurement direction.

The percent changes of specific Young's modulus [$\Delta(E/\rho)$] and loss tangent [$\Delta \tan \delta$], due to the impregnation were defined as:

$$\Delta(E/\rho) = \left\{ \frac{(E/\rho)_1}{(E/\rho)_0} - 1 \right\} \times 100 \quad (1)$$

$$\Delta \tan \delta = \left\{ \frac{(\tan \delta)_1}{(\tan \delta)_0} - 1 \right\} \times 100 \quad (2)$$

where subscripts 0 and 1 mean before and after impregnation, respectively. Moisture-excluding efficiency (MEE) was evaluated from the equilibrium moisture content at 20°C and 65% RH before (M_0) and after (M_1) impregnation:

$$\text{MEE} = \left\{ 1 - \frac{M_1}{M_0} \right\} \times 100 \quad (3)$$

Identification of extractives

The heartwood meal was extracted successively with diethyl ether and methanol using a Soxhlet apparatus for 6 h. The resultant extracts were individually evaporated. Two large spots were observed under ultraviolet (UV) light on thin-layer chromatography (TLC) plates (Kieselgel 60 F₂₅₄, Merck) when developed with methanol/CH₂Cl₂ (1:49, v/v) (Fig. 1). Compounds at $R_f = 0.52$ and 0.31 were designated as compounds A and B, respectively. Purification of the compounds used crude crystals derived from the diethyl ether extract. The crude crystals were dissolved in CH₂Cl₂, developed on a TLC plate (Kieselgel 60 F₂₅₄, Merck) with CH₂Cl₂, and the bands corresponding to compounds A and B were recovered. The recovered silica gels were eluted with methanol/CH₂Cl₂ (1:4, v/v) and the solvents evaporated, which gave rise to needle crystals (compound A) and powder (compound B).

The chemical structures of the compounds were analyzed by nuclear magnetic resonance (NMR) spectroscopy and electron ionization high-resolution mass spectrometry (EI-HRMS). NMR analysis was conducted on a NM-LA400MK FT-NMR system (400 MHz, JEOL). Samples were dissolved in CDCl₃. Chemical shifts (δ) were standardized using those of CDCl₃ (7.26 in ¹H NMR; 77.1 in ¹³C

Fig. 1. Thin-layer chromatography profile under ultraviolet light (253.7 nm). Developing solvent methanol : CH₂Cl₂ = 1 : 49. *Left*, methanol-extracted fraction; *right*, diethyl ether-extracted fraction; A, compound A; B, compound B

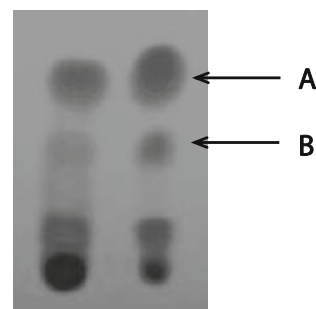


Table 1. Mean values of physical and vibrational properties

Wood species	Sample no.	Oven-dry specific gravity	E/ρ (GPa)	$(\tan \delta) \times 10^3$
Muirapiranga	12	0.96 (0.01)	17.9 (1.2)	4.92 (0.35)
Pernambuco ^a	100	0.92 (0.07)	19.8 (3.7)	4.12 (1.04)

Standard deviations are given in parentheses

^aFrom Matsunaga et al.²

NMR). Mass spectrometry was carried out on a JMS-DX303HF instrument (JEOL) equipped with a JMA-DA5000 data system.

Compound A (xanthyletin). ¹H NMR (400 MHz, CDCl₃): δ 1.46 (6H, s, CH₃ \times 2), 5.69 (1 H, d, $J_{7,6}$ = 10.00 Hz, 7-H), 6.22 (1 H, d, $J_{3,4}$ = 9.52 Hz, 3-H), 6.34 (1 H, d, $J_{6,7}$ = 9.76 Hz, 6-H), 6.72 (1 H, s, 10-H), 7.05 (1 H, s, 5-H), 7.58 (1 H, d, $J_{4,3}$ = 9.52 Hz, 4-H); ¹³C NMR (100 MHz, CDCl₃): δ 28.43, 77.81, 104.51, 112.81, 113.14, 118.59, 120.86, 124.83, 131.31, 143.39, 155.54, 156.93, 161.27; m/z (EI): 228.0787 (M⁺, 19%; C₁₄H₁₂O₃ requires 228.0786), 213 (100), 185 (17), 128 (5), 92 (6).

Compound B (luvangetin). ¹H NMR (400 MHz, CDCl₃): δ 1.51 (6H, s, CH₃ \times 3), 3.98 (3 H, s, OCH₃), 5.71 (1 H, d, $J_{7,6}$ = 10.40 Hz, 7-H), 6.24 (1 H, d, $J_{3,4}$ = 9.52 Hz, 3-H), 6.33 (1 H, d, $J_{6,7}$ = 9.80 Hz, 6-H), 6.83 (1 H, s, 5-H), 7.57 (1 H, d, $J_{4,3}$ = 9.52 Hz, 4-H); ¹³C NMR (100 MHz, CDCl₃): δ 28.30, 29.79, 61.51, 77.88, 113.08, 113.35, 119.17, 121.16, 131.33, 135.74, 143.67, 148.39, 149.39, 160.72; m/z (EI): 258.0902 (M⁺, 27%; C₁₅H₁₄O₄ requires 258.0892), 243 (100), 228 (11), 213 (5), 200 (8), 149 (9), 129 (5), 115 (6).

Impregnation of isolated compounds

Among the isolated compounds, sufficient compound A (xanthyletin) could be obtained for the wood specimen impregnation, but for compound B (luvangetin) it was impossible to collect an adequate amount. Therefore, a commercially available methoxsalen (Wako) was used instead of luvangetin. Methoxsalen (Fig. 2) is a chemical analogue of luvangetin and has the same chemical structural moiety. Because xanthyletin and methoxsalen are insoluble in methanol, dimethyl sulfoxide (DMSO), which has a wood swelling ability comparable with water, was used as a common solvent. The impregnation procedures were the same as described above. Four longitudinal specimen pieces were assigned for each compound and each concentration level. After impregnation, the residual DMSO was extracted with water by rinsing. After successive oven drying and conditioning at 20°C, 65% RH, E/ρ and $\tan \delta$ were measured again. The changes in vibrational properties due to the impregnation were evaluated according to Eqs. 1 and 2, although the values were corrected by subtracting the mean value of four blank specimens that were immersed in DMSO and then rinsed with water.

Fig. 2. Chemical structure of methoxsalen used for the impregnation in place of luvangetin

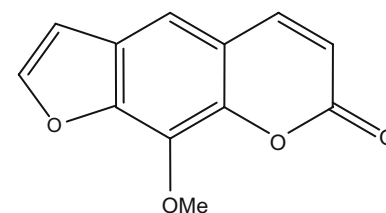


Table 2. Yields by successive extractions with a series of solvents

Solvent	Yield (%)
<i>n</i> -Hexane	1.08
Diethyl ether	6.74
Chloroform	0.72
Methanol	15.38

Percentages based on oven-dried wood meal

Results and discussion

Physical and mechanical properties and aptitude of muirapiranga for violin bows

Table 1 shows the oven-dry specific gravity and vibrational properties at 20°C and 65% RH. Because these values were obtained for a single block, they may not be representative values for muirapiranga; nevertheless, the specific gravity was comparable with pernambuco. The value of $\tan \delta$ was a little higher than for pernambuco, but much lower than that for common Japanese hardwood ($7 - 13 \times 10^{-3}$) reported by Sugiyama et al.,¹ so it is likely that the extractives lower the value of $\tan \delta$ for muirapiranga. The E/ρ of muirapiranga was much lower than that for pernambuco. A high Young's modulus is an important condition for violin bow materials, because a slender bow is preferred, so muirapiranga may be unfavorable in this respect.

Amount of extractives

Table 2 shows the amounts of extractives obtained by successive extraction with some solvents. Among the four solvents, the amounts of extractives found in diethyl ether and methanol were much larger. No significant amount of water-soluble fraction was found.

Changes in vibrational properties and hygroscopicity due to impregnation of crude extractives

Figure 3 shows the weight gain due to impregnation of crude extractives. The weight gain increased proportionally with the concentration of the impregnation solution.

The change in $\tan \delta$ is shown in Fig. 4. The $\tan \delta$ decreased significantly with increasing weight gain in both longitudinal and radial directions, irrespective of the extracting solvents. However, the decreases were smaller than the impregnation of protosappanin B or hematoxylin, for which $\tan \delta$ decreased about 25% and 20% for weight gains of 5% and 10%, respectively.⁵ The increase in $\tan \delta$ found at high weight gain may merely be an experimental error, because a plausible explanation such as damage to the cell wall microstructure due to excessive impregnation is unlikely.

The E/ρ in the longitudinal direction decreased a few percent, but it increased considerably in the radial direction (Fig. 5). The dashed line in Fig. 5 represents the case when the change of E/ρ is attributable only to the increase in specific gravity. Higher E/ρ values than the dashed line in the longitudinal direction, increased E/ρ in the radial direction, and decreased $\tan \delta$ in both directions suggest that the

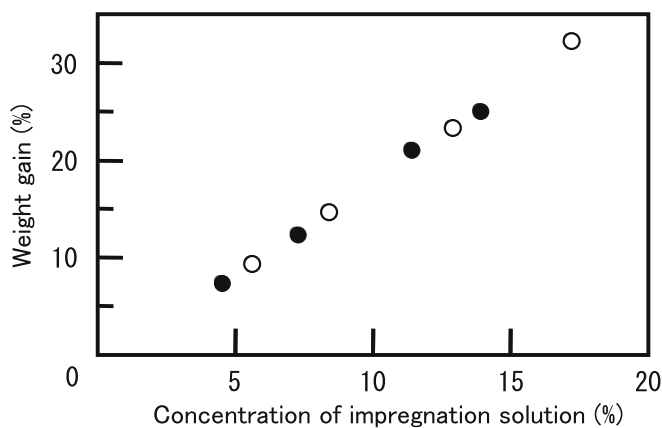
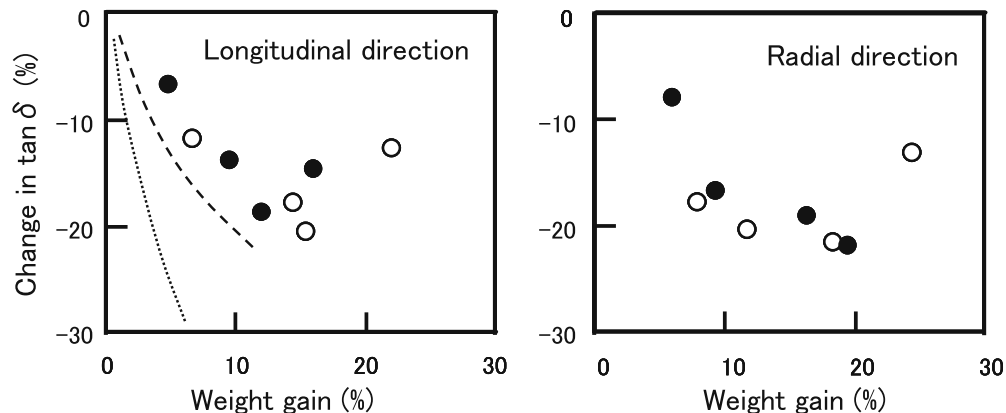


Fig. 3. Dependence of weight gain on the concentration of the extractive solution. *Open circles*, crude diethyl ether extractives; *filled circles*, crude methanol extractives

Fig. 4. Change in $\tan \delta$ due to the impregnation of crude extractives. *Open circles*, crude diethyl ether extractives; *filled circles*, crude methanol extractives; *dotted and dashed lines*, cited from Matsunaga et al.,⁶ for crude extractives of pernambuco and hematoxylin, respectively



impregnated compound enhanced the cohesive force between microfibrils and/or between constituent molecules in the wood matrix.

Figure 6 shows the MEE at 20°C and 65% RH against weight gain. After impregnation of crude extractives, the MEE increased. However, the increase was small because when the weight gain due to the impregnation of the hydrophobic substance was deducted, MEE did not increase substantially.

Identification of compounds

The ^1H NMR spectra indicate that compounds A and B were identical to xanthyletin (8,8-dimethyl-2H,8H-benzo[1,2-b:5,4-b']dipyran-2-one) and its methoxylated analogue, luvangetin (10-methoxy-8,8-dimethyl-2H,8H-benzo[1,2-b:5,4-b']dipyran-2-one), which were previously reported.⁸ The measured masses of the two compounds (by EI-HRMS) were also identical to those of xanthyletin and luvangetin. In addition to the results of ^{13}C NMR analysis, data from two-dimensional NMR experiments (HMQC and HMBC analyses; data not shown) also strongly support the above chemical structures. The chemical structures of these compounds are shown in Fig. 7. These two compounds have already been isolated from *Brosimum* sp.⁹

Changes in vibrational properties due to impregnation of isolated and related compounds

Figure 8 shows that $\tan \delta$ decreased significantly after impregnation with xanthyletin and methoxsalen to an extent comparable with that observed using crude extractives. This suggests that xanthyletin contributes to the decrease in $\tan \delta$ following impregnation of crude muirapiranga extractives. Because the impregnation of methoxsalen, which is an analogous compound of luvangetin, decreased $\tan \delta$, it is probable that it also contributes to the decrease in $\tan \delta$.

The authors have reported that the $\tan \delta$ of wood was increased by the impregnations of simple phenolic compounds, but significantly decreased by protosappanin B or hematoxylin.^{4,7} Because the latter two compounds have

Fig. 5. Change in E/ρ due to the impregnation of crude extractives. *Open circles*, crude diethyl ether extractives; *filled circles*, crude methanol extractives; *dashed lines*, calculated assuming that E does not change

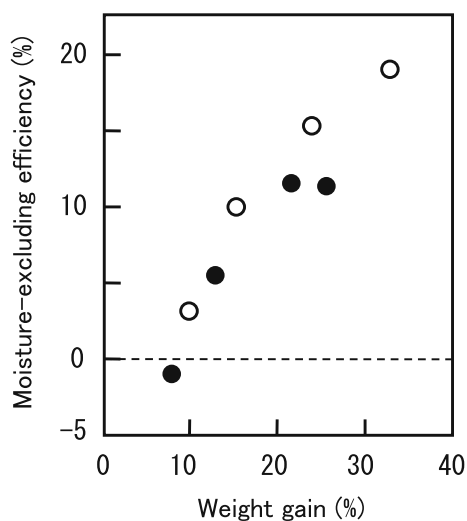
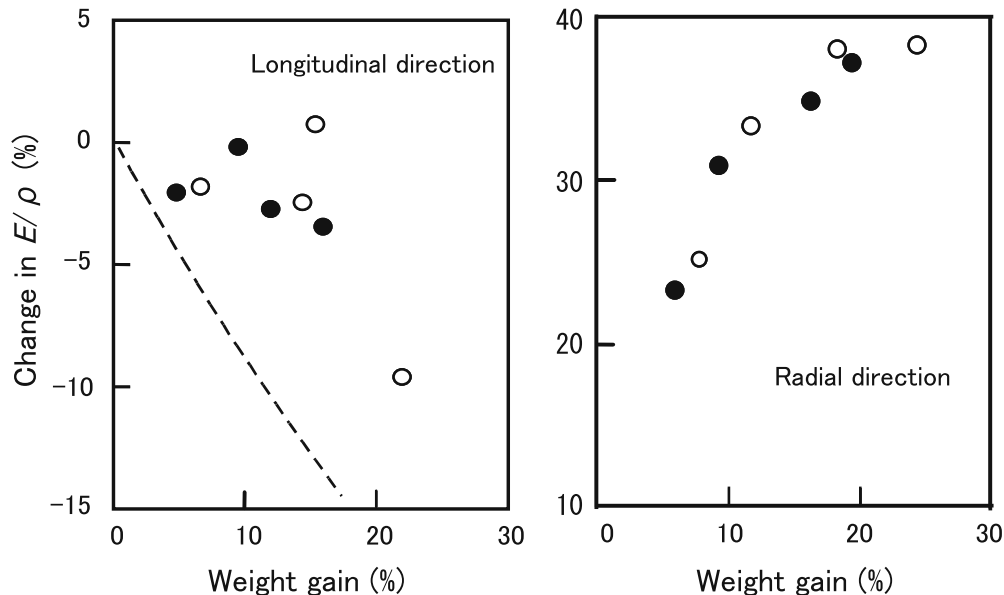
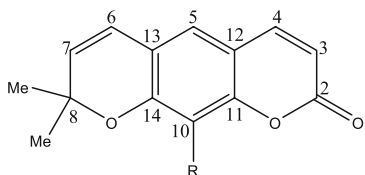


Fig. 6. Moisture-excluding efficiency at 20°C and 65% relative humidity due to the impregnation of crude extractives. *Open circles*, crude diethyl ether extractives; *filled circles*, crude methanol extractives

Fig. 7. Chemical structures of the main components found in muirapiranga



Compound A (R = H) : Xanthyletin
Compound B (R = OMe) : Luvangetin

many hydroxyl groups and are water soluble, we assumed that the enhanced cohesive force due to hydrogen bonding in the wood matrix caused the decrease in $\tan \delta$. However, xanthyletin and methoxsalen do not have hydroxyl groups and are not water soluble. Protosappanin B, hematoxylin,

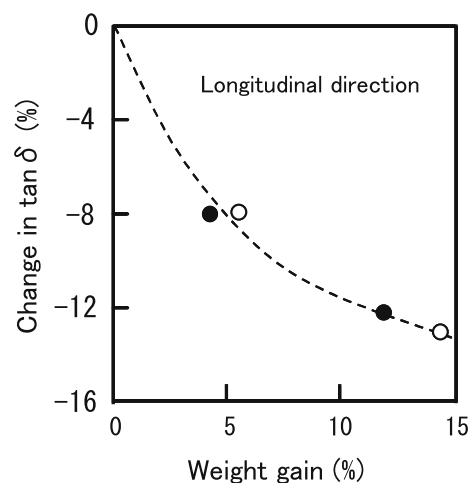


Fig. 8. Change in $\tan \delta$ after impregnation of xanthyletin and methoxsalen. *Open circles*, xanthyletin; *filled circles*, methoxsalen

xanthyletin, and methoxsalen are common natural polycyclic compounds with molecular weights of 200 to 300. Therefore, the participation of steric factors, which restrict molecular movement in the wood matrix, was a more likely explanation for the $\tan \delta$ -decreasing mechanism.

Conclusions

Muirapiranga has a fairly low $\tan \delta$, but is not ideal as a material for violin bows. As a cause of low $\tan \delta$, participation of extractives was predicted, and xanthyletin and luvangetin were found to be the major extractive compounds. The impregnations of isolated xanthyletin and commercially available methoxsalen, which is an analogue of luvangetin, markedly decreased the $\tan \delta$ of other wood specimens. From the similarity in polycyclic structure and molecular size of $\tan \delta$ -decreasing substances found so far, we propose

restriction of the molecular motion in the cell wall matrix by the impregnated substance as the reason why particular compounds decrease $\tan \delta$.

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