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► **To cite this version:**

Aida Se Golpayegani, Iris Brémaud, Joseph Gril, Marie-France Thévenon, Olivier Arnould, et al..  
Effect of extractions on dynamic mechanical properties of white mulberry (*Morus alba*). *Journal of  
Wood Science*, 2012, 58, pp.153-162. 10.1007/s10086-011-1225-7 . hal-00689021

**HAL Id: hal-00689021**

**<https://hal.science/hal-00689021>**

Submitted on 19 Apr 2012

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1 **Effect of extractions on dynamic mechanical properties of**  
2 **white mulberry (*Morus alba* L.)**

3 **Original article**

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14 Keywords: anisotropy, damping coefficient, DMA, extractives, vibrational properties, white  
15 mulberry wood (*Morus alba* L.).

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20 **Abstract:**

21 Vibrational properties of wood are affected by several parameters, of which extractives can be  
22 one of the most important ones. Wood for European musical instruments has been often  
23 studied, but traditional Middle Eastern ones had been left unnoticed. In this study white  
24 mulberry (*Morus alba* L.), the main material for long-necked lutes in Iran, was extracted by  
25 five solvents of various polarities (water included). Free-free bar forced vibrations were used  
26 to measure longitudinal (L) loss tangent ( $\tan\delta$ ), storage (elastic) modulus ( $E'$ ) and specific  
27 modulus ( $E'/\gamma$ ) in the acoustic range. Their anisotropy between the 3 axes of orthotropy was  
28 determined by DMA (dynamic mechanical analysis). Native wood had a quite low  $E_L'/\gamma$  but  
29 its  $\tan\delta$  was smaller than expected, and the anisotropy of  $\tan\delta$  and  $E'/\gamma$  was very low. Removal  
30 of extractives caused  $\tan\delta$  to increase and moduli to decrease. Acetone, the most effective  
31 solvent on damping despite a moderate extraction yield, increased  $\tan\delta_L$  by at least 20% but  
32 did not modify  $E'/\gamma$  as much. When used successively, its effects masked those of solvents  
33 used afterwards. Anisotropy of  $E'/\gamma$  was nearly unchanged after extraction in methanol or hot  
34 water, while  $\tan\delta$  was much more increased in R than in T direction. Results suggest that in  
35 white mulberry, damping is governed more by nature and localization of extractives rather  
36 than by their crud abundance.

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## 42 **Introduction:**

43 Wood has always been considered as a multifunctional material. Each of its versatile  
44 properties makes it appropriate for a particular final use. Wood historical use in musical  
45 instruments is in relation with its dynamic mechanical, or vibrational, properties, including  
46 mechanical damping (loss tangent)  $\tan\delta$ , storage (elastic) modulus  $E'$  and specific modulus  
47  $E'/\gamma$ . As a quasi-orthotropic material at the macroscopic scale, wood has different properties in  
48 longitudinal (L), radial (R) and tangential (T) directions (Backman and Lindberg<sup>1</sup>; Nairn<sup>2</sup>;  
49 Brémaud et al<sup>3</sup>). In the case of wood used for Western classical string instruments, it is  
50 generally accepted that a low  $\tan\delta$  and high  $E'/\gamma$  in axial direction, and a high anisotropy, are  
51 convenient for obtaining a soundboard of good quality. However, few studies have addressed  
52 the vibrational properties of wood used in Middle-East instruments. String instruments in Iran  
53 can be traced back to 970 B.C. Long-necked lutes *Tar*, *Setar* and *Kamancheh* are specifically  
54 made from white mulberry (*Morus alba* L.), which is also used for the Japanese short-necked  
55 lute *Biwa* (Yoshikawa<sup>4</sup>).

56 Sources of variations in dynamic mechanical properties of wood include cell arrangement and  
57 grain angle, microfibril angle within the cell wall, proportions of constitutive polymers, as  
58 well as the presence of additional compounds (Ono and Norimoto<sup>5,6</sup>; Obataya et al<sup>7</sup>; Noda et  
59 al<sup>8</sup>; Bucur<sup>9</sup>). Although in lower quantities than cell wall constitutive polymers, extractives can  
60 have a considerable effect on mechanical and damping properties of wood. Exceptionally low  
61 damping of some musically important woods was somehow correlated with their extractives.  
62 Extractives impact can be studied either through correlations between their amounts and  
63 vibrational properties variation resulting by their removal, or by the re-injection of extracts  
64 into a “neutral” wood. Methanol extraction increased the  $\tan\delta$  of heartwood by 15 to 37% in  
65 red cedar (*Thuja plicata*) and up to 60% in African Padauk (*Pterocarpus soyauxii*), while  $E'/\gamma$

66 slightly decreased (Yano<sup>10</sup>; Brémaud et al.<sup>11</sup>). Impregnation of water-soluble extractives of  
67 pernambuco (*Caesalpinia echinata*) into spruce decreased  $\tan\delta$  by a half (Matsunaga et al.<sup>12</sup>).  
68 The formation of hydrogen bonds between extractives and cell wall matrix was proposed as a  
69 possible cause of  $\tan\delta$  reduction (Matsunaga et al.<sup>13</sup>). Impregnation of Sitka spruce with  
70 isolated key chemical compounds from muirapiranga (*Brosimum rubescens*), a Moraceae as is  
71 mulberry, decreased  $\tan\delta$  by up to 25%, both in axial and radial directions. This was explained  
72 by motion restriction of matrix macromolecules due to extractives entering (Minato et al.<sup>14</sup>).  
73 Contrary to these studies, water-soluble extractives of Reed (*Arundo dunax* L.) increased both  
74  $\tan\delta$  and  $E'$  (Obataya and Norimoto<sup>15</sup>; Obataya et al.<sup>16</sup>). Extractives can also change wood  
75 equilibrium moisture content (EMC) (Hernandez<sup>17</sup>). Higher EMC induces higher  $\tan\delta$  and  
76 lower  $E'/\gamma$  (Akitsu et al.<sup>18</sup>; Obataya et al.<sup>19</sup>). The potential effect of extractives on vibrational  
77 properties could come from their chemical structure, cellular location and relation with basic  
78 polymers (Matsunaga et al.<sup>13</sup>; Brémaud et al.<sup>11</sup>). Removing extractives using solvents of  
79 different polarities could give a first idea about their polarity and possible cellular location.

80 Our work aims at evaluating the dynamic mechanical properties of white mulberry and  
81 understanding the possible contribution of extractives. Basic properties of samples from  
82 different regions of Iran were compared in a previous study (Se Golpayegani<sup>20</sup>; Pourtahmasi  
83 and Se Golpayegani<sup>21</sup>). In the present article, mulberry wood was extracted in five solvents of  
84 different polarities. In order to separate the overlapping effect of various solvents, they were  
85 used both as independent extracting agents, and in a successive order on the same specimens,  
86 to determine changes in acoustical properties along the grain. Furthermore, the effects on the  
87 anisotropy of  $\tan\delta$ ,  $E'$  and  $E'/\gamma$  were also studied after extraction by the two solvents with  
88 highest yields.

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## 90 **Material and Methods**

### 91 *Material*

92 Mulberry trees were cut in Iran and kept for one month in outdoor conditions. Wood was  
93 selected there by a professional instrument maker. Several 500×50×50 mm (L×R×T) rods  
94 were cut from the middle of the heartwood and sent to France, in three batches within one  
95 year. The 1<sup>st</sup> batch (used for powder samples and independent extractions on vibrational  
96 specimens) and 2<sup>nd</sup> batch (successive extractions on vibrational specimens) came from the  
97 same tree; the 3<sup>rd</sup> (specimens for DMA) came from another tree.

98 A portion of each rod was ground, the fraction passing through 40 mesh and retained on 60  
99 mesh sieves was kept for powder extractions (TAPPI standard method T207\_cm<sup>22</sup>). For  
100 vibrational tests, the rods were cut into approx. 200 axial specimens of dimensions  
101 150×15×2 mm<sup>3</sup> (L×R×T), from which 77 specimens were kept for extractions and controls  
102 (Table 1). For DMA (Dynamic Mechanical Analysis), specimens were cut to a cross section  
103 of 4×3 mm<sup>2</sup> and a length of 42-48 mm (Fig. 1). 14 specimens were prepared in each direction  
104 of orthotropy leading to a total number of 42.

### 105 *Conditioning and physical measurements*

106 The specimens were oven dried at 60°C for 48 h. This procedure ensured that the equilibrium  
107 was reached in adsorption. Residual moisture content, as compared with oven drying at  
108 103°C, was around 1.36±0.49%. Specimens were then kept for three weeks in controlled  
109 conditions of 20±2°C and 65±5% RH. This procedure was repeated before any mechanical  
110 measurement. Specific gravity  $\gamma$  (both oven dried and air dried) and EMC were recorded.  
111 EMC of native wood was of 7.9±0.8%.

112 Although mechanical measurements could not be run in a climatic chamber, mass change was  
113 small:  $-0.3 \pm 0.4\%$  for native state specimens, both during vibrational and DMA tests. For  
114 treated specimens, mass change was negligible ( $-0.1 \pm 0.1\%$ ) during vibrational tests, and less  
115 than during DMA tests ( $-0.6 \pm 0.7\%$ ).

### 116 ***Measurement of dynamic mechanical properties***

117 Axial dynamic mechanical properties were measured both by vibrational tests and by DMA,  
118 while anisotropy was studied only by DMA.

### 119 **Non-contact forced bending vibrations of free-free bars**

120 A frequency scan was imposed through an electric magnet facing a tiny steel plate (15-20 mg,  
121 a negligible additional weight) glued at one end of each specimen. A laser triangulation  
122 sensor measured the displacement. A program developed with LabView® software  
123 (Brémaud<sup>23</sup>) monitored vibration emission and detection. Specific elastic (storage) modulus  
124 ( $E_L'/\gamma$ ) was calculated from the first resonance frequency by the Euler-Bernoulli formula and  
125 elastic modulus ( $E_L'$ ) was obtained by multiplying  $E_L'/\gamma$  by specific gravity ( $\gamma$ ). Damping  
126 coefficient was measured using both bandwidth at half power in the frequency domain (or  
127 quality factor) and logarithmic decrement of amplitude in the time domain after stopping the  
128 vibration. Both measurements shall be equivalent to loss tangent  $\tan\delta$ , if  $\tan\delta \ll 0.1$ , which is  
129 the case for air-dry wood in this temperature/frequency range. Three repetitions were made  
130 for each specimen. Resonance frequencies were in the range of 200-400 Hz.

### 131 **DMA (Dynamic mechanical analyzer)**

132 The viscoelastic behavior of specimens was measured using a BOSE® ELF3230 DMA  
133 equipped with tension/compression fatigue grips, a 22 N ( $\pm 0.17\%$  maximum error) load cell

134 and a high-resolution displacement sensor (1 mm range with  $\pm 0.26\%$  maximum error). The  
135 specimens were fixed between two clamps with a working distance of 35 mm and tested in  
136 tension along their longest direction. The tests were done in purely alternative  
137 tension/compression loading controlled in displacement with an amplitude of  $\pm 0.0175$  mm  
138 corresponding to a maximum tension/compression strain of  $\pm 0.02\%$  (i.e., within the linear  
139 viscoelastic region, see Sun et al.<sup>24</sup>). Using BOSE WinTest® analysis software,  $E^*$  (norm of  
140 the complex modulus),  $E'$  (storage modulus),  $E''$  (loss modulus) and  $\tan\delta$  (loss tangent) were  
141 calculated. Both moduli and  $\tan\delta$  were corrected for the stiffness of the whole apparatus  
142 (around 1785 N/mm with a negligible viscous contribution), measured using a stiff steel  
143 specimen. Frequency sweeps from 0.1 to 10 Hz were run in triplicate for each specimen,  
144 native and then treated.

#### 145 *Extraction procedures*

146 Extractions used solvents of increasing polarity: hexane (HX), dichloromethane (DM),  
147 acetone (AC), methanol (ME) and hot water (HW). Most used Soxhlet extractors. Groups of  
148 specimens, with similar ranges in properties, were defined after vibrational tests in native  
149 state and subjected to different treatments (Table 1).

150 For extractions on powder and on solid specimens for vibrational tests, extractions were run  
151 both in an independent (or parallel) and in a successive (or serial) way. Independent extraction  
152 means that a sample is submitted to one extraction in a given solvent, and its properties are  
153 measured before and after this single treatment. In this case, hot water extraction from  
154 vibrational specimens was run (for 8h) at 70°C (not using Soxhlet). Successive extractions  
155 means that a given group of specimens is submitted to extraction, first by the less polar  
156 solvent (HX), then oven-dried (brief process: weighted, air-dry stabilized, weighted,



157 mechanically tested, and dried again for solid wood specimens), then extracted by the next  
158 solvent (DM), and so on. In this case, a “standard” Soxhlet extraction (<95°C) was run for  
159 water (complete description of conditions can be found in table 1).

160 Specimens were dried before being extracted, so that less polar solvents could not enter cell  
161 walls. Control specimens underwent only physical steps (drying and stabilization) and were  
162 measured in the same time and condition as extracted ones. For determination of extractive  
163 content, 3 g of powder were put in a cellulose cartridge, extracted for 8 h, and their oven-dry  
164 (48 h at 60°C) weight loss was measured. For solid wood, as color hardly changed during  
165 extraction, duration of 12 h was chosen. Based on the yields of extractions in vibrational  
166 specimens, ME and HW were applied as independent solvents on DMA specimens. For each  
167 anisotropic direction, 4 specimens served as controls, 5 were extracted in ME and 5 in HW  
168 (70°C, without Soxhlet). Although hemicelluloses may be partially depolymerized at  
169 moderately high temperatures for water-saturated wood (Placet et al<sup>25</sup>; Assor et al<sup>26</sup>),  
170 treatment temperatures and duration were sufficiently low to neglect such effect.

## 171 **Results and Discussion**

### 172 *Properties of native mulberry wood*

173 The specific gravity  $\gamma$  of the mulberry wood under study ranged from 0.45 to 0.61 (Fig. 2).  
174 This was significantly lighter than wood from different regions in a previous study (Se  
175 Golpayegani<sup>20</sup>). The 1<sup>st</sup> batch (used for independent extractions) was significantly denser than  
176 the 2<sup>nd</sup> one (used for successive extractions), although they came from the same tree. The 3<sup>rd</sup>  
177 batch (used for DMA), which came from a different tree, covered a broad range, but its

178 average  $\gamma$  was not significantly different from the 2<sup>nd</sup> batch. Differences in density were not  
179 clearly related to those in vibrational properties (Fig. 3).

180 The specific dynamic modulus in L direction of all studied batches of wood was rather low  
181 (Fig. 3) and variable (11-18 GPa). Although dispersion was quite large,  $\tan\delta_L$  was negatively  
182 related to  $E'_L/\gamma$ . However, all batches generally had a lower  $\tan\delta_L$  than the “standard trend”  
183 from Ono and Norimoto<sup>5, 6</sup>, a statistical relationship obtained on 20 softwoods and 30  
184 hardwoods that can be considered as a reference. In the 1<sup>st</sup> and 3<sup>rd</sup> batches  $\tan\delta_L$  was in  
185 average 6% and 11% lower than “standard”, but with a higher dispersion than in 2<sup>nd</sup> batch and  
186 in wood from a previous study (Se Golpayegani<sup>20</sup>), for which  $\tan\delta$  was always within the  
187 lower range (21% and 23% lower than the standard).

188  $\tan\delta_L$  measured with DMA method was higher than that measured with free-free vibration.  
189 However, it exhibited a decreasing trend against frequency, so that the difference could be  
190 attributed to the higher frequency of the free-free vibration. This decrease of  $\tan\delta$  with  
191 frequency was also observed in other directions, as well as a slight increase of elastic moduli.  
192 However, the anisotropic ratios remained constant in the observed frequency range. In the  
193 following analysis, only the values measured at 10 Hz will be used. Ordering of the different  
194  $\tan\delta$  in the 3 principal directions was the same as previously reported, i.e.,  $\tan\delta_T > \tan\delta_R >$   
195  $\tan\delta_L$  (Ono and Norimoto<sup>27</sup>). However, damping anisotropies between the three main  
196 directions were small:  $R/L \approx 1.03$ ,  $T/L \approx 1.34$ , and  $T/R \approx 1.30$ . These values were lower than  
197 those collected from several studies by Brémaud et al.<sup>3</sup> in which the average ratios were of 2.7  
198 (R/L), 2.9 (T/L) and 1.14 (T/R) for hardwoods. Similarly, the anisotropy of  $E'$  agrees with  
199 well-known relationships, i.e.,  $E'_L \gg E'_R \geq E'_T$ , but actual values of ratios ( $L/R \approx 4$ ,  $L/T \approx 8$   
200 and  $R/T \approx 1.9$ ) were in the lower range of anisotropy compared with literature reviews (e.g.,  
201 Guitard and El Amri<sup>28</sup>, Nairn<sup>2</sup>). It can be noted that mulberry has a low longitudinal  $E'/\gamma$  and a

202 very reduced anisotropy when compared with resonance spruce that is used for top plates of  
203 Western string instruments, and is closer to maple (used for back and sides) in this respect.

#### 204 *Yield of extraction*

205 In wood powder (Fig. 4a), approximately the same cumulated amount of extractives was  
206 removed when applying solvents independently or successively. In solid wood (Fig. 4b), on  
207 the contrary, cumulated weight losses differed between these two extraction procedures,  
208 suggesting some structural effect on the accessibility to various solvents. This was supported  
209 by different extraction yields from axial, radial and tangential DMA specimens: 9, 14 and  
210 18% respectively for ME.

211 Less polar solvent HX and DM, which should reach only the lumen, removed small and  
212 comparable amounts (1.6% and 1.7%) when used independently on powder. Their yields were  
213 much smaller in solid wood. When DM was used after HX, its yield was very low, suggesting  
214 that HX had already removed most of extractives accessible to apolar solvents. Similarly, AC  
215 had a smaller yield when used after HX and DM, suggesting that when used independently, it  
216 also removed compounds from lumens. Although AC and ME are thought to be able to  
217 solubilize similar types of compounds, ME caused the most exhaustive extraction from solid  
218 wood: 6.2% when used independently. Its efficiency was even increased when used after AC  
219 (7.14% from solid wood). On the contrary, in powder, HW had the highest yield (8.31%)  
220 when used independently, while it had a much smaller yield on solid. This suggests that in  
221 solid wood, polar extractives are more easily removed by ME than by HW, as the final  
222 cumulated yields were however similar between powder and solid.

#### 223 *Extraction effects on $E_L'/\gamma$*

224 As extractions change the mass and specific gravity (Table 2, Table 3) of wood specimens,  
225  $E_L'/\gamma$  values should be corrected for the contribution of extractives to  $\gamma$ :

$$226 \quad \left( \frac{E_L'}{\gamma} \right)_c = \left( \frac{E_L'}{\gamma} \right)_{ap} \times \frac{\gamma_{ap}}{\gamma_{ef}}, \quad (1)$$

227 where  $(E_L'/\gamma)_{ap}$  and  $\gamma_{ap}$  are the apparent measured values, and  $(E_L'/\gamma)_c$  is the corrected value  
228 taking into account the specific gravity  $\gamma_{ef}$  after the most effective extraction (ME).  $(E_L'/\gamma)_c$   
229 should be more representative of an “extractives-free cell wall” modulus, and appeared 0.01  
230 to 1.2 GPa higher than the apparent one (Table 2, Table 3).

231 Corrected  $E_L'/\gamma$  gradually decreased due to extractions. HX, DM, AC, ME and HW modified  
232  $E_L'/\gamma$  by 0.2%, -0.6%, -5%, -11% and -1.8% respectively after independent extractions (Fig.  
233 5a). Cumulated changes (i.e. relative to native state) after successive extractions followed a  
234 similar trend but with a bigger amplitude (Fig. 5b).  $E_L'$  shows a similar gradual decrease.  
235 Decrease in  $E_L'/\gamma$  appears nearly proportional to weight loss for different solvents (Fig. 5b),  
236 which suggests that extractives removed by AC, ME and HW bulked the cell wall matrix, and  
237 affected elasticity independently of compounds removed by these various solvents.

### 238 *Changes in $\tan\delta_L$ related to weight loss*

239 Figure 6 shows relative changes in  $\tan\delta_L$  caused by each solvent either used individually or  
240 after others (successively). Apolar solvents (HX and DM) removed small amounts (approx.  
241 1%) of extractives, probably from the lumens, resulting in small changes in  $\tan\delta_L$ . In  
242 successive extraction, however, DM increased  $\tan\delta_L$  by 14%, which might be linked to  
243 previous exposition to HX. On the other hand, in another species (Padauk), DM was able to

244 slightly attain cell wall and increase  $\tan\delta_L$  of approx. 20% for approx. 3% extracts removed  
245 (Brémaud et al.<sup>11</sup>).

246 More polar solvents (AC, ME and HW) are expected to remove higher proportions of cell  
247 wall extractives, more susceptible to alter  $\tan\delta_L$ . However, the highest change in  $\tan\delta_L$   
248 resulted from AC extraction ( $\approx+20\%$  independently or used after DM,  $\approx+38\%$  for cumulated  
249 successive effect), although its weight loss was moderate. ME and HW, despite their higher  
250 yields, had smaller effects on  $\tan\delta_L$  both in independent and in successive-cumulated order.  
251 When used after AC, ME even reduced  $\tan\delta_L$  lower than the value for the previous state (AC-  
252 extracted, Fig. 6b). On the contrary, in other species, methanol extractives often have a high  
253 “anti-damping” effect in wood (Yano<sup>10</sup>; Minato et al.<sup>14</sup>; Brémaud et al.<sup>11</sup>). Acetone has also  
254 been used recently in this kind of study, on two tropical species (Brémaud<sup>23</sup>; Brémaud et  
255 al.<sup>11</sup>). It was more efficient than ME in one species, and less in the other. The contrasted  
256 effects observed in mulberry could be explained by different hypotheses: (i) AC reached all  
257 extractives able to alter damping, leaving only “inactive” compounds for subsequent ME or  
258 HW extractions. As drying cycles could reduce  $\tan\delta_L$  by  $\leq 8\%$ , changes in  $\tan\delta_L$  after ME and  
259 HW in successive order could partly reflect drying history of specimens. However, a smaller  
260 effect on  $\tan\delta_L$  of ME and HW than that of AC was also observed for independent extractions,  
261 without cumulated drying cycles. This brings us to the second hypothesis ; (ii) Two kinds of  
262 extractives compounds would co-exist in cell walls, some decreasing, and some increasing,  
263  $\tan\delta_L$  in native wood. AC would have removed the first ones, so that extraction of remaining,  
264 “ $\tan\delta_L$  raising”, compounds by ME and HW would decrease again the  $\tan\delta_L$  of solid wood.

265 In various woods, methanol is reported to take out non-structural carbohydrates and phenolics  
266 (e.g. Rowe and Conner<sup>29</sup>). White mulberry has quite important content of phenolic extractives  
267 (De Rosso et al.<sup>30</sup>). In some woods, polyphenols can form part of the fiber cell wall matrix

268 (Kleist and Bauch<sup>31</sup>), while in some other woods, they may be either preferentially in vessels,  
269 parenchyma walls (Dünisch et al.<sup>32</sup>), or too much condensed to enter the cell wall substance  
270 (Koch and Kleist<sup>33</sup>). In the later hypothesis, ME might have removed some lumen deposits,  
271 resulting in a lower ratio between changes in  $\tan\delta_L$  and extraction yield. However, decreases  
272 in  $E'_{L/\gamma}$  after ME or HW suggested cell wall location. Thus, ME could have removed  
273 compounds such as sugars or simple phenols, which presence will increase  $\tan\delta_L$  (Obayata et  
274 al.<sup>15</sup>; Sakai et al.<sup>34</sup>). A decrease in  $\tan\delta_L$  is also observed after ME extraction of *Thuja plicata*  
275 sapwood – which should contain non-structural carbohydrates – whereas a completely  
276 opposite effect is observed in the heartwood of the same species (Yano<sup>10</sup>). In mulberry,  
277 extraction in HW, following ME, did not bring additional changes in  $\tan\delta_L$ , although it further  
278 removed  $\approx 4\%$  extractives. In *Caesalpinia echinata*, water soluble extractives decrease  $\tan\delta_L$   
279 in wood, which was first ascribed to their ability to form hydrogen bonds with cell walls  
280 components (Matsunaga et al.<sup>12</sup>). But other extractives, without hydroxyl groups and/or  
281 insoluble in water, also reduce  $\tan\delta_L$  (Minato et al.<sup>14</sup>; Brémaud et al.<sup>11</sup>). Finally, differences in  
282  $\tan\delta_L$  might be related to changes in wood moisture content (Dunlop<sup>35</sup>; Obayata et al.<sup>19</sup>;  
283 Inokuchi et al.<sup>36</sup>). However, changes in EMC due to independent extractions were small  
284 (Table 2). In successive extractions (Table 3), with higher cumulated yields, EMC was more  
285 significantly increased after ME and HW. This, however, should lead to an increase in  $\tan\delta_L$ ,  
286 instead of the observed decrease for successive use of ME and HW.

287 Therefore, the present results suggest the co-existence of some “ $\tan\delta$  – lowering” and of some  
288 “ $\tan\delta$  – raising” compounds in the heartwood of white mulberry. The first ones are extractable  
289 by ME but also with AC and HW, consequently independent extraction with those solvents  
290 had always resulted in an increase in  $\tan\delta_L$ . The latter compounds, being probably  
291 hydrophilic, are not extractable by HX, DM or AC. Thus a successive extraction using ME

292 and HW had reduced  $\tan\delta_L$ , as the “ $\tan\delta$  – lowering” had been already removed by previous  
293 solvents and there were only the “ $\tan\delta$  – raising” components left. The methodology using  
294 both independent and successive series of extraction might reveal similar trends in other  
295 species.

### 296 *Changes in anisotropic properties due to extractions*

297 Figure 7 shows the variations in  $E'/\gamma$  and  $\tan\delta$  in the three principal directions of orthotropy  
298 after extractions with HW and ME or 2 drying cycles (controls). Variations in  $E'/\gamma$  after ME  
299 extraction were similar in all three directions: -18% to -20%, although weight losses were  
300 different (9%, 14% and 18% for L, R and T specimens respectively). Hot water caused both  
301 lower weight losses (6-8% in L, R and T), and smaller decrease in  $E'/\gamma$  along L and R  
302 directions, while it was similar to ME in T direction.

303 Concerning  $\tan\delta$ , uncertainty was high in L direction, as clamping of specimens may crush  
304 wood in the softer transverse direction. Even controls showed important variations, which  
305 cannot be ascribed to physico-chemical changes. However, after ME extraction, change in  
306 radial  $\tan\delta$  was at least twice more important than in L (DMA estimations and changes in  
307 vibrational tests) and T direction (Fig. 7).

308 The quasi-isotropic effect of extractions on  $E'/\gamma$  is quite surprising. In previous works,  
309 extractives stiffened the transverse moduli (Yano et al.<sup>37</sup>; Minato et al.<sup>14</sup>), but not the axial  
310 one, in which the influence of the microfibrillar reinforcement predominates (Ono and  
311 Norimoto<sup>5, 6</sup>; Obataya et al.<sup>7</sup>). However, mulberry wood has a low longitudinal  $E'/\gamma$ ,  
312 suggesting high microfibril angle, and is characterized by a very low anisotropy in native  
313 state. Effects of extractions on  $\tan\delta$  were clearly different in radial and tangential directions.  
314 This is interesting, as there are relatively few works on the  $\tan\delta_R/\tan\delta_T$  anisotropy and sources

315 of variations. Backman and Lindberg<sup>1</sup> stated that, for softwood, in tensile test latewood  
316 contributes mostly to the response in tangential direction while most of the strain occurs in  
317 early wood in radial direction. In mulberry, a ring-porous hardwood, the response in radial  
318 tension tests would more involve vessels and rays, whose cell walls are thinner, but are also  
319 susceptible to contain higher proportions of extractives (Koch<sup>38</sup>; Kleist and Bauch<sup>31</sup>; Dünisch  
320 et al.<sup>32</sup>). Thus, the very high change in  $\tan\delta_R$  after ME extraction ( $\approx 50\%$ ) could express a  
321 bigger modification of rays and vessels, than of fibers.

## 322 **Conclusion**

323 Dynamic mechanical properties  $E'/\gamma$ ,  $\tan\delta$ , and their anisotropic ratios in the 3 principal axes  
324 were measured on white mulberry wood (*Morus alba* L.), a representative raw material for  
325 musical instruments in Iran. They were compared before and after extractions by different  
326 solvents in order to investigate extractives effects. Results could be synthesized as follows:

- 327 - Mulberry wood has a quite low  $E'_L/\gamma$  but its damping factor ( $\tan\delta_L$ ) is lower than  
328 expected. The anisotropy of these two properties is also much lower than average.
- 329 - Combining two methods of extractions -using each solvent as an individual agent and  
330 using solvents in a successive order on a single sampling- could suggest the  
331 importance of extractives nature compared to their amount.
- 332 - The highest changes in  $\tan\delta_L$  were not due to the most polar solvents, with highest  
333 extraction yields, but to acetone. Nevertheless, acetone did not alter  $E'_L/\gamma$  with the  
334 same intensity, suggesting that the extracted amounts or compounds were not essential  
335 for wood stiffness.



336 - The different effects of methanol extraction on  $\tan\delta_L$ , between individual extraction  
337 and when used successively after acetone, suggest the existence of two types of  $\tan\delta$   
338 altering compounds in white mulberry. Some would be able to increase, some other  
339 would be able to reduce the damping, and both types would be accessible by acetone  
340 and methanol independently.

341 - Changes in  $E'/\gamma$  were nearly isotropic between the 3 principal axes of orthotropy, may  
342 be due to the very low anisotropy of mulberry in native state. On the contrary,  $\tan\delta$   
343 was much more modified in radial than in tangential direction, suggesting different  
344 responses to extractions of rays and vessels walls as compared to fibers ones.

345 It should be noted that even though extractives are found to definitely affect vibrational  
346 properties of *Morus alba* L., it would be enlightening to identify the most important  
347 compounds present in those extractives and how they cause changes in vibrational properties.

348

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455 **Acknowledgments** Authors are grateful to SCAC (Service de Coopération et d'Action Culturelle) of French  
456 embassy in Tehran and ISMO (Iranian Center for international research and collaboration) for supporting this  
457 project.

458 **Tables**

459 Table 1: Specimens number and treatments for both independent and successive methods of extraction

Number of specimens	Solvent	Drying and stabilization condition	Number of cycles of drying and stabilization
12	Hexane (HX)	60°C for 48 h followed by 20±2°C & 65±5% RH for 3weeks	2
12	Dichloromethane (DM)		2
12	Acetone (AC)		2
12	Methanol (ME)		2
5	Hot Water (HW, 70°C)		2
12	HX/DM/AC/ME/HW (100°C)		6
12	Controls		6
15 DMA(5L, 5R, 5T)	ME		2
15 DMA(5L, 5R, 5T)	HW (70°C)		2
12 DMA(4L, 4R, 4T)	Controls		2

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474 Table 2: Basic statistics for differences in properties between groups submitted to independent extractions and to  
 475 one cycle of drying/re-stabilization (=control).

Treatment	EMC (%) <sup>d</sup>		Specific gravity $\gamma$		$E'_L/\gamma$ Corrected (GPa)		$\tan\delta_L$ ( $10^{-3}$ )	
	Corrected				$E'_L/\gamma$ Apparent (GPa)			
	Native	Treated	Native	Treated	Native	Treated	Native	Treated <sup>f</sup>
Control <sup>e</sup>	9.2±0.5	9.2±0.2 <i>ns</i>	0.556±0.027	0.553±0.030 <i>ns</i>	15.0±2.2	15.2±2.4 <i>ns</i>	8.6±0.3	7.9±0.5 **
	8.2±0.4 (a)	8.2±0.2 (ab)	(a)	(ab)	14.0±1.6 (b)	14.2±1.6 (a)	(a)	(a)
Extracted								
HX	9.1±0.2	8.9±0.4 <i>ns</i>	0.570±0.031	0.566±0.030 **	13.5±2.0	13.7±2.0 **	10.2±0.6	9.6±0.6 **
	8.1±0.2 (a)	7.9±0.4 (a)	(a)	(b)	12.3±1.4 (a)	12.5±1.4 (a)	(b)	(bc)
DM	9.0±0.3	9.6±0.4 **	0.560±0.031	0.557±0.031 **	14.3±2.2	14.3±2.2 <i>ns</i>	9.6±1.0	9.3±0.8 *
	8.0±0.3 (a)	8.6±0.3 (c)	(a)	(b)	13.2±1.6 (ab)	13.3±1.6 (a)	(b)	(bc)
AC	9.1±0.4	9.4±0.4 *	0.567±0.026	0.550±0.025 **	14.6±1.6	13.9±1.6 **	8.7±0.4	9.8±0.6 **
	8.1±0.3 (a)	8.6±0.3 (c)	(a)	(ab)	13.3±1.1 (ab)	13.2±1.1 (a)	(a)	(c)
ME	9.2±0.4	8.7±0.2 **	0.554±0.026	0.520±0.025 **	14.4±2.2	12.9±2.0**	8.9±0.5	9.5±0.5 **
	8.2±0.4 (a)	8.3±0.3 (bc)	(a)	(a)	13.5±1.4 (ab)	12.9±1.4 (a)	(a)	(bc)
HW	9.2±0.3	9.0±0.2 <i>ns</i>	0.550±0.015	0.530±0.017 **	14.1±1.7	14.0±1.9 <i>ns</i>	8.5±0.5	8.6±0.6 <i>ns</i>
	8.2±0.3 (a)	8.3±0.1 (bc)	(a)	(ab)	13.3±1.3 (ab)	13.7±1.7 (a)	(a)	(ab)

476 “Apparent” stands for measured values; “Corrected” take into account the contribution of extractives to weight  
 477 (for EMC) and specific gravity (for  $E'_L/\gamma$ ).

478 (a, b, c): homogenous subsets in one-way ANOVA at a level  $\alpha:0.05$  (=comparison between groups in a given  
 479 column, based on measured values).

480 (*ns*, \*, \*\*): differences between untreated and treated properties of a given group (based on corrected values  
 481 whenever applicable) in *t*-test for paired samples; \*\*: significant at  $\alpha: 0.01$ , \*:  $\alpha: 0.05$ , *ns*: not significant.

482 d) EMC relative to 103°C oven-drying. “Apparent” are measured values; “Corrected” is calculated by taking into  
 483 account the total extractive content (cumulated % on powder) from 1<sup>st</sup> batch of wood (see Hernandez 2007).

484 e) “Treated” state for controls stands for values measured after one cycle of oven-drying followed by air-dry re-  
 485 stabilization.

486 f)  $\tan\delta_L$  are raw values, whereas  $\tan\delta_L$  variations in Fig. 6 are corrected for controls.

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490 Table 3: Basic statistics for the successive ranges in properties for the group of specimens submitted to  
 491 successive extractions.

Treatment	EMC (%) <sup>a</sup> Corrected Apparent	Specific gravity $\gamma$	$E'_{\perp}/\gamma$ Corrected (GPa) $E'_{\perp}/\gamma$ Apparent (GPa)	$\tan\delta_{\perp}$ ( $10^{-3}$ )
Untreated	7.0± 0.3 6.1± 0.3	0.515± 0.011	13.72± 1.47 12.99± 1.25	8.2± 0.5
HX	7.1± 0.3 <i>ns</i> 6.2± 0.2	0.512± 0.016 <i>ns</i>	13.46± 1.68 <i>ns</i> 12.82± 1.35	7.9± 0.4 **
DM	9.2± 0.2 ** 8.0± 0.2	0.515± 0.012 <i>ns</i>	13.51± 1.26 <i>ns</i> 12.78± 1.07	9.3± 0.6 **
AC	9.0± 0.4 <i>ns</i> 8.0± 0.3	0.515± 0.016 <i>ns</i>	13.53± 1.64 <i>ns</i> 12.79± 1.30	11.3± 0.8 **
ME	8.6± 0.1 ** 8.2± 0.1	0.505± 0.014 **	12.69± 1.38 ** 12.24± 1.13	10.6± 0.6 **
HW	8.8± 0.1 ** 8.8± 0.1	0.488± 0.011 **	11.85± 1.23 ** 11.84± 1.05	10.2± 0.5 *

492 “Apparent” stand for measured values; “Corrected” take into account the contribution of extractives to weight  
 493 (for EMC) and specific gravity (for  $E'_{\perp}/\gamma$ ).

494 a) EMC relative to 103°C oven-drying. “Apparent” are measured values; “Corrected” is calculated by taking into  
 495 account the total extractive content (cumulated % on solid specimens) from 2<sup>nd</sup> batch of wood (see Hernandez  
 496 2007).

497 (*ns*, \*, \*\*): differences between each successive extracted state in relation to the previous phase of treatment  
 498 (based on corrected values whenever applicable) in *t*-test for paired samples; \*\*: significant at  $\alpha$ : 0.01, \*:  $\alpha$ : 0.05,  
 499 *ns*: not significant.

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## 509 **Figure legends**

510 Fig. 1. Cutting plan for vibrational and DMA specimens. Variations in length of DMA specimens were due to  
511 limitations in raw material.

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513 Fig. 2. Box plot of specimens **specific gravity ( $\gamma$ )** for the three batches of wood under study, and for previous  
514 data on wood from different origins (Se Golpayegani<sup>20</sup>). (a, b, c) significantly different groups (one-way  
515 ANOVA).

516

517 Fig. 3. Relationship between  $E'_L/\gamma$  and  $\tan\delta_L$  for 4 batches of native mulberry wood ( $N$  specimens: see Fig. 2).

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519 Fig. 4: Comparison of weight loss due to independent and successive extraction in (a) powder, and (b) solid  
520 (vibrational) specimens. “Successive” weight losses are relative to the previous step; “independent” and  
521 “successive-cumulated” are relative to native oven-dry weight.

522

523 Fig. 5. Relationship between weight loss (%) and relative change of  $E'_L/\gamma$  (%) after (a): **independent extractions**  
524 and (b): **successive extractions where changes are relative to initial state of native specimens** (i.e. cumulated  
525 changes).  $E'_L/\gamma$  was corrected for contribution of extractives to  $\gamma$ .

526

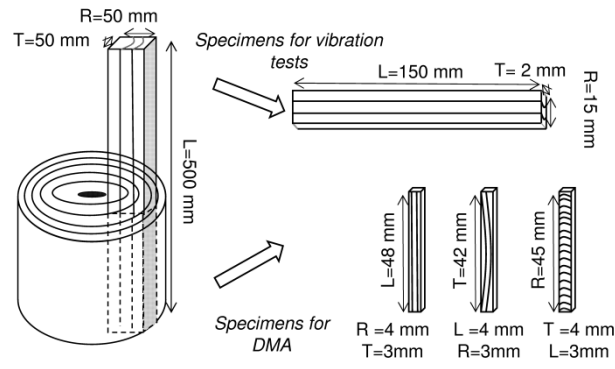
527 Fig. 6. Relative changes (%) in  $\tan\delta_L$  plotted against weight loss (%) for (a) independent and (b) successive  
528 extractions. Changes are relative to initial state of native specimens (independent and successive-cumulated).  
529 Arrows: order of successive extractions. Values of  $\tan\delta_L$  in independent extractions are corrected for controls.

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531 Fig. 7. Variations in mechanical properties after extractions measured by DMA at 10 Hz. Values for controls  
532 were not deduced from treated ones.

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534 **Figures**

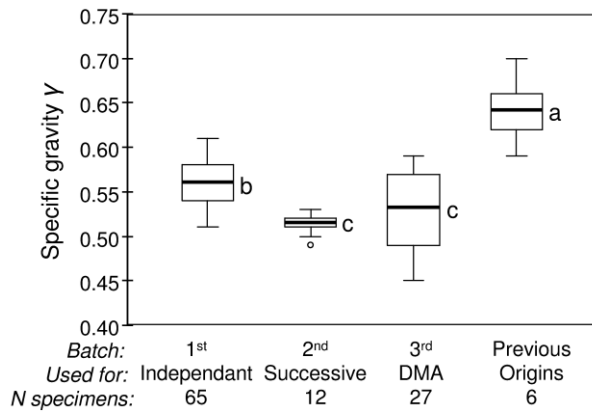


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Fig. 1.



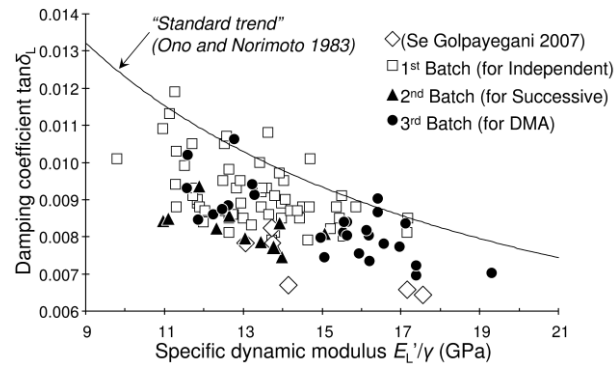
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Fig. 2.

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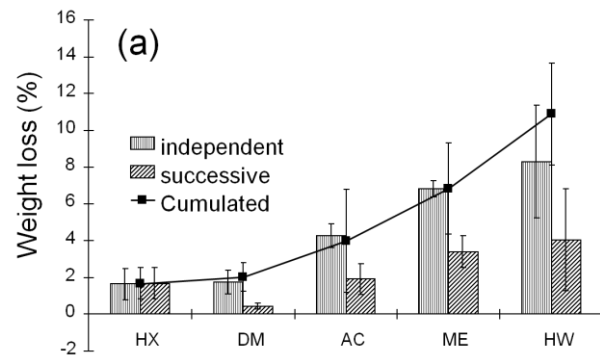
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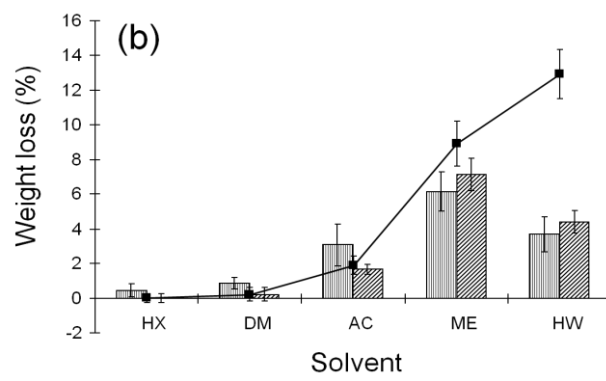
Fig. 3.

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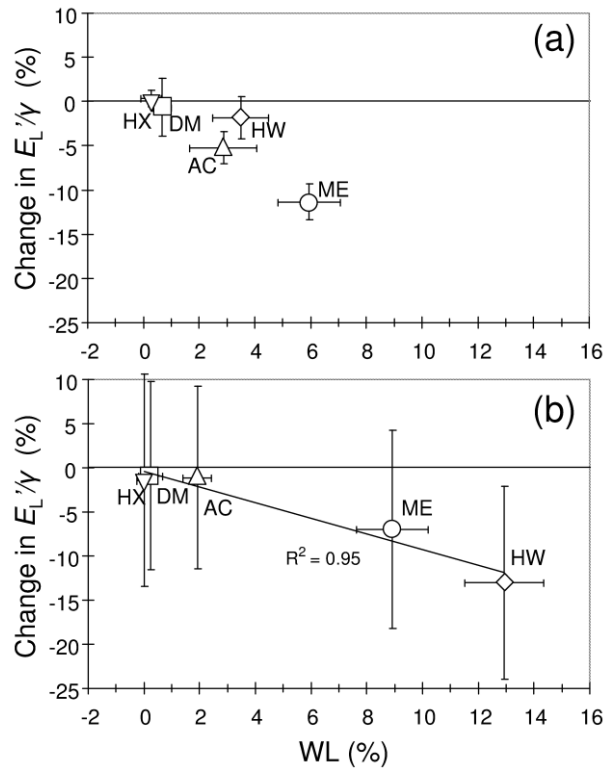
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Fig. 4.



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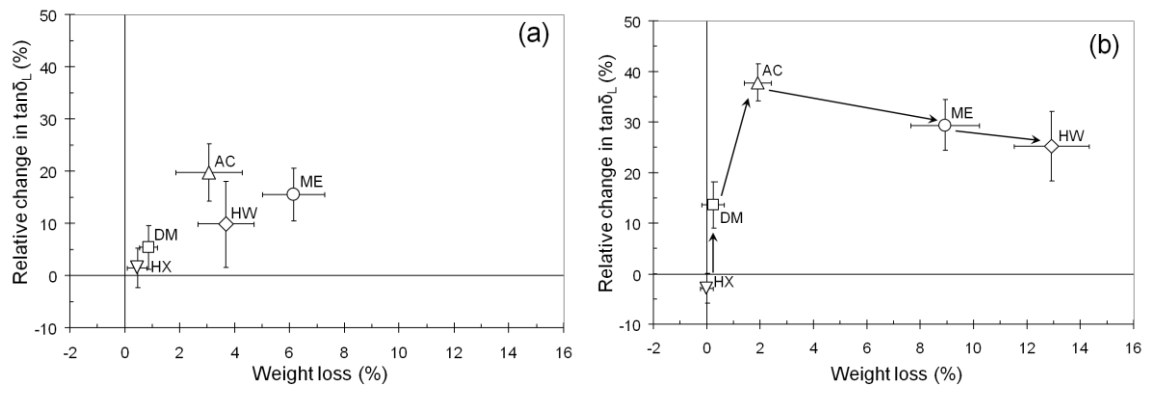


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Fig. 5.



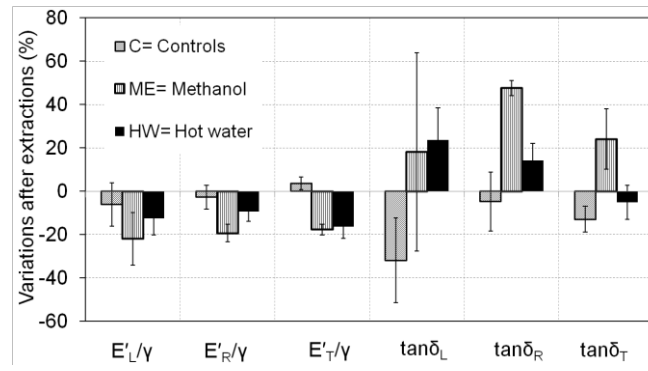
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Fig. 6.

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Fig. 7.