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Secondary metabolites of *Bagassa guianensis* Aubl. wood, a study of the chemotaxonomy of the Moraceae family.

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Abstract

In effort to explain wood durability of Moraceae plants family, a phytochemical study was undertaken on *Bagassa guianensis*. The phytochemical investigation of the ethyl acetate extract obtained from the heartwood led to the isolation of 18 secondary metabolites, including 6 moracins [the new 6-*O*-methyl-moracin M (**3**), 6- *O*-methyl-moracin N (**4**) and moracin Z (**5**); the known moracin M (**1**), moracin N (**2**) and moracin P (**6**)], 8 phenolic derivatives [the new (-)-epialboctalol (**12**), arachidin 4 (**10**) and the known alboctalol (**11**), *trans*-resveratrol (**7**), arachidin 2 (**9**), *trans*-oxyresveratrol (**8**) and artogomezianol (**13**)], the 3 known flavonoids steppogenin (**14**), katuranin (**15**), dihydromorin (**16**), the β -sitosterol (**17**) and the resorcinol (**18**). Comparison with literature data indicates that stilbenoids are presumably responsible for the natural durability of the wood. In addition, chemical composition points out that *B. guianensis* is closely related to *Morus* sp. in the phylogeny and should be placed within the Moreae s. s. tribe in the Moraceae family.

Keywords: *Bagassa guianensis*, Moraceae, secondary metabolites, stilbenes, moracins, flavonoids, natural durability

43

44 **1. Introduction**

45 Wood as a material is used extensively in construction and other applications where it can be
46 degraded by many different organisms, mainly fungi and insects. However, some trees have
47 specialized considerably long-lasting heartwoods. It has been demonstrated in the past that
48 wood natural durability can be ascribed to the presence of extractives (Smith et al., 1989;
49 Wang et al., 2005; Hsu et al., 2007), although structural components of the cell wall may also
50 contribute to its resistance to biodegradation (Silva et al., 2007). Heartwood natural durability
51 can also result from synergetic or additive effects of compounds with various modes of action
52 (toxic, hydrophobic, free radical scavengers and so on) (Suttie and Orsler, 1996; Okitani et al.,
53 1999; Schultz and Nicholas, 2000; Schultz et al. 2007; Binbuga et al., 2008). Future processes
54 to preserve wood constructions may involve returning to mankind's historical use of naturally
55 durable heartwood as well as discovering eco-friendly wood protection agents inspired from
56 long-lasting woods (Schultz et al., 2007).

57

58 *Bagassa guianensis* Aubl. (Moraceae) commercially known as tatajuba is a large rather
59 infrequent unbuttressed canopy tree naturally occurring in French Guiana. *Bagassa guianensis*
60 is a member of Moraceae family, which is divided in 5 unequal tribes when comparing the
61 number of species in these tribes (Mabberley, 2002). *Bagassa guianensis* (the only member of
62 its genus) was originally classified in the Artocarpeae tribe, but Weiblen genoma-based
63 classifications have suggested recently that this species would better be included in Moreae
64 tribe (Datweyler and Weiblen, 2004; Zerega et al, 2005).

65

66 Species in the Moraceae family have important economic and medicinal value. They are
67 widely acknowledged as a rich source of bioactive secondary metabolites such as flavonoids,

stilbenes, triterpenoids and xanthones (Lee et al., 2009; Ngadjui et al., 2005; Han et al., 2006; Jayasinghe et al., 2008). Also, some of them like *Maclura pomifera* and *B. guianensis* are capable of specializing very long-lasting woods (Scheffer and Morrell, 1998; Schultz et al., 1995), although in the latter case, the substances responsible for this high durability were unknown. We therefore embarked upon identifying secondary metabolites of tatajuba wood that may responsible for its natural durability. In addition, our secondary goal here was to confirm (or refute) botanical classification of the *Bagassa* genus by chemotaxonomy.

2. Results and Discussion

The dried heartwood of *Bagassa guianensis* was extracted with ethyl acetate. This extract was fractionated by silicagel column chromatography to give 9 fractions. Subsequent preparative HPLC purifications of these fractions allowed us to isolate compounds **1-18** (figure 1).

Figure 1 Compounds **1-18** isolated from *Bagassa guianensis* (Moraceae). (a) New compounds; (b) New names.

Compounds **1** to **6** shared several common spectral characteristics. The ^1H and ^{13}C NMR spectral data (Table 1) indicate the presence of two independent aromatic systems with a 3,5-dihydroxyphenyl and a substituted benzofuran. For example, **3** exhibited the 3,5-dihydroxyphenyl with characteristic ^1H spectrum composed of one doublet at δ 6.78 for H-2'/H-6' and a triplet at δ 6.25 for H-4'. These protons are coupled to each other with a 4J coupling of 2.1 Hz. In addition, ^{13}C spectrum indicates the presence of two equivalent aryl hydroxyl groups at δ 159.7. The 3,5-dihydroxyphenyl moiety was linked to C-2 by the observation of a long range ^1H - ^{13}C correlation between H-2'/H-6' and C-2 at δ 156.5. The second aromatic system appeared characteristic of a 6-monosubstituted benzofuran with

signals of protons H-4, H-5 and H-7 being a broad doublet at δ 7.43 ($J = 8.5$ Hz), a doublet of doublet at δ 6.85 ($J = 8.5$ and 2.0 Hz) and a doublet at δ 7.09 ($J = 2.0$ Hz), respectively. On the furan ring H-3 gives a doublet at δ 6.95 ($J = 0.6$ Hz) due to a long range 5J coupling with H-7 (confirmed by the presence of crosspeak between H-3 and H-7 on COSY NMR spectrum). When compared to moracin M (**1**), it became obvious from signal at δ 3.85 (3H, s) and the presence of crosspeak at δ 56.2 in the ^1H - ^{13}C HSQC spectra that compound **3** was a moracin M methyl ether. The ^1H - ^{13}C long-range HMBC spectra gave a crosspeak with C-6 at δ 159.6 unambiguously placing the methoxy group on C-6. HREIMS of **3** allowed us to ascertain molecular formula $\text{C}_{15}\text{H}_{12}\text{O}_4$ further confirming that we had isolated the new 6-*O*-methyl-moracin M (**3**).

Table 1 ^1H and ^{13}C NMR spectroscopic data for moracins **3-5** in CD_3OD

Compound **4** was isolated as yellowish amorphous powder. The HREIMS indicated a molecular formula $\text{C}_{20}\text{H}_{20}\text{O}_4$ deduced from the ion peak at m/z 325.1437 $[\text{M} + \text{H}]^+$ (calcd 325.1434). The ^1H and ^{13}C NMR spectral data of **4** were closely related to those of moracin N (**2**) (Lee et al., 2001) except for the replacement of hydroxyl group by a methoxy group as described for the above compound **3**. Indeed, the ^1H NMR data of **4** (Table 1) demonstrated the presence a methoxy group on C-6 in the benzofuran ring, with a signal at δ 3.88 (3H, s), a crosspeak at δ 56.2 in the ^1H - ^{13}C HSQC experiment and a crosspeak with C-6 at δ 157.4 in the ^1H - ^{13}C long-range HMBC spectra. This novel molecule was named 6-*O*-methyl-moracin N.

Compound **5** was isolated as an amorphous brown powder. The molecular formula $C_{20}H_{22}O_5$ was deduced from the HREIMS at m/z 343.1542 $[M + H]^+$ (calcd 343.1540). The 1H - and ^{13}C -NMR spectral data of **5** were closely related to those of 6-*O*-methyl-moracin N (**4**) (Table 1). The main difference was observed in the prenyl moiety at C-5. The double bond is absent in **5** and it was unambiguously established that side chain at C-5 is hydrated and is therefore a 3-hydroxy-3-methylbutyl group, with the upfield shifts of methylene group H-1'' from δ 3.34 to δ 2.73 and the apparition of a methylene H-2'' at δ 1.74 in place of the vinyl proton at δ 5.52; in addition, the two methyl groups H-4'' and H-5'' became equivalent at δ 1.27 (Table 1). The 1H - ^{13}C long-range HMBC spectra exhibited a crosspeak between the methylene group H-1'' and H-2'' with C-5 at δ 128.6 proving the linkage C-1''/C-5 between the 3-hydroxy-3-methylbutyl moiety and the benzofuran ring. This molecule is a hydrate of 6-*O*-methyl-moracin N and was named moracin Z.

Spectral data along with HREIMS of **1**, **2** and **6** allowed us to determine and ascertain by comparison with literature data that we had also isolated moracin M (**1**) (Basnet et al. 1993, Zhou et al., 1999), moracin N (**2**) (Lee et al. 2001) and moracin P (**6**) (Dat et al., 2009).

Stilbenoids *trans*-resveratrol (**7**) (Lee et al. 2001; Su et al., 2002), *trans*-oxyresveratrol (**8**) (Likhitwitayawuid and Sritularak, 2001; Lee et al., 2001; Su et al., 2002; Li et al., 2007), arachidin 2 (**9**) (Orsini et al., 2004) and artogomezianol (**13**) (Likhitwitayawuid and Sritularak, 2001) were identified by comparison of the respective spectral and chemical data with those described in the literature (Figure 1).

Compound **10** was a colorless syrup with molecular formula $C_{19}H_{22}O_4$ as deduced from the HREIMS at m/z 315.1592 $[M + H]^+$ (calcd 315.1591). The 1H spectral data of **10** were closely

related to those of arachidin 2 (**9**) (Table 2) and suggested a stilbenoid compound with a *para*-disubstituted aromatic ring A, a *trans* double bond between the aromatic rings, and a 1',3',4',5'-tetrasubstituted aromatic ring B. Ring A is symmetrical, with 2 doublets at δ 7.32 ($J = 8.7$ Hz, H-2/H-6) and δ 6.75 ($J = 8.7$ Hz, H-3/H-5). The *trans* configuration of the double bond can be ascertained by the very large coupling constant between the two protons at δ 6.90 ($J = 16.5$ Hz, H- α) and δ 6.74 ($J = 16.5$ Hz, H- β), and the B ring is symmetrical as well and was characterized by a singlet at δ 6.46 (H-2'/H-6'). In the same way as we identified a hydrated side chain in the moracins series, the main difference here between **9** and **10** is in the side chain in position 4', the double bond of which is also hydrated. This has been established by the observation of methylene group H-1'' at δ 2.66 instead of δ 3.28 and the apparition of a second methylene H-2'' at δ 1.68. In addition, the two methyl groups H-4'' and H-5'' became equivalent at δ 1.25. The chromatography collected quantities was too low to observe heteronuclear ^1H - ^{13}C HSQC / HMBC correlations and direct ^{13}C chemicals shifts by ^{13}C /DEPTQ sequence. However, the above-described data in comparison with those of arachidin 2 are sufficient to ascertain identification of compound **10** as *trans*-4'-(3-hydroxy-3-methylbutyl)-oxyresveratrol. We named this new compound arachidin 4.

Table 2 ^1H and ^{13}C NMR spectroscopic data for stilbenes **9** and **10** in CD_3OD

Compounds **11** and **12** both isolated as brownish syrups presented the ion peak at m/z 489.1540 $[\text{M} + \text{H}]^+$ in HREIMS indicating that they are isomers with molecular formulas $\text{C}_{28}\text{H}_{24}\text{O}_8$ (calcd 489.1544). The ^1H -NMR allowed us to identify a 3,5-dihydroxyphenyl group and two distinct 2,4-dihydroxyphenyl groups in both compounds. By comparison of the respective spectral and chemical data with those described in the literature, compound **11** was

identified as alboctalol (Bates et al., 1997). Compound **12** has an $[\alpha]_D^{20}$ value of -7.4° (c 0.004, CH₃OH). It was clear that **12** was a diastereoisomer of **11** with equivalent H-18/H-22 protons at δ 6.01 (Table 3). In **11**, H-18/H-22 pair gives a doublet at a strong upfield shift of δ 5.77 typical of the π -stacking effect of the neighboring 2,4-dihydroxyphenyl groups. In addition, on this aliphatic ring, the main differences with **11** are on methylene H-5 and methines H-6, H-7 and H-8. H-5_{ax} at δ 3.19 exhibited a broad triplet with large couplings ($J = 13.7$ Hz) with the gem H-5_{eq} and the vicinal H-6 suggesting that the 6-aryl group should be equatorial and proton H-6 axial. This observation was corroborated by the multiplicity of H-5_{eq} signal at δ 2.72. This signal is a doublet of doublet with a large coupling constant $J = 15.6$ Hz with H-5_{ax} and a small coupling constant $J = 3.0$ Hz with H-6_{ax}. Signal of H-6_{ax} at δ 3.51 is a broad triplet of doublet with two large coupling constants $J = 11.6$ Hz with H-5_{ax} and H-7 and a small coupling constant $J = 2.1$ Hz with H-5_{eq}. This pattern indicates that the 7-aryl group is equatorial and H-7 axial. H-7_{ax} at δ 3.41 exhibited one doublet of doublet with one large coupling constant ($J = 11.3$ Hz) with H-6_{ax} and a second rather large coupling constant ($J = 8.2$ Hz) with H-8 indicating that the 8-aryl group might be equatorial and proton H-8 axial. These assumptions were confirmed by NOESY experiment with cross peaks observed between H-5_{eq} and H-6_{ax}, H-6_{ax} and H-8_{ax}, H-6_{ax} and H-18, H-8_{ax} and H-22 and between H-5_{ax} and H-16, H-7_{ax} and H-16, H-7_{ax} and H-28 (Figure 2). All data permitted to confirm that we had isolated a new epimer of alboctalol (**11**) therefore named (–)-epialboctalol (**12**).

Table 3 ¹H and ¹³C NMR spectroscopic data for distilbenes **11** and **12** in CD₃OD

Figure 2 Pertinent NOE interactions observed for (–)-epialboctalol (**12**) from NOESY experiment

189

190 In addition to these moracins and stilbenoids, we isolated flavanones steppogenin (**14**) (Lee et
191 al., 2001), katuranin (**15**) (Lee et al., 2001) and dihydromorin (**16**) (Su et al., 2002), together
192 with β -sitosterol (**17**) (Basnet et al., 2003, Aldrich Library of ^{13}C and ^1H FT NMR spectra,
193 1992) and resorcinol (**18**) (Aldrich Library of ^{13}C and ^1H FT NMR spectra, 1992). These
194 known compounds were identified by comparison of the respective spectral and chemical data
195 with those described in the literature.

196

197 Essentially three classes of compounds were isolated in this study: moracins, stilbenes and
198 flavanones. Only resorcinol **18** and β -sitosterol **17** do not belong to these classes. These two
199 compounds are widely distributed in nature and cannot be viewed as chemotaxonomic
200 markers.

201

202 Moracin N, M and P have been isolated before from *Morus alba*. In general, it was found
203 from the literature that *Morus* genus is purveyor of moracins (Tagasuki et al., 1979; Hirakura
204 et al., 1986; Basnet et al., 1993; Nguyen et al., 2009). The only one exception is the isolation
205 of moracin M from *Artocarpus dadah* (Su et al., 2002).

206

207 Among stilbenes, *trans*-oxyresveratrol was isolated from various plants including *Morus* sp.
208 and *Artocarpus* sp. (Hirakura et al, 1986; Su et al, 2002; Shimizu et al., 1998; Song et al,
209 2009). *Trans*-resveratrol was isolated from many sources including the Moraceae *Cudrania*
210 *javanensis* classified today as *Maclura cochinchinensis* (Murti et al., 1972, Chapman & Hall,
211 2006). The distylbene artogomezianol **13** is a constituent of *Artocarpus gomezianus* roots and
212 albolactol **11** was isolated from heartwood of *Morus alba* (Likhitwitayawuid and Sritularak
213 2001, Ferlinahayati et al., 2008).

214
215 Regarding flavonoids, it has been described that many Moraceae can produce steppogenin
216 (El-Sohly et al, 1999; Su et al, 2002; Sheu et al., 2005). Katuranin was also isolated from
217 various biological sources in *Morus* and *Maclura* genera (El-sohly et al., 1999, Lee at al.,
218 2009) and dihydromorin was isolated from *Morus*, *Artocarpus*, and *Maclura* genera (Shimizy
219 et al., 1998, El-Sohly et al, 1999, Su et al., 2002).

220
221 It has been hypothesized before that stilbenes are the major types of compounds isolated from
222 Moraceae and may be useful chemotaxonomic markers (Rowe and Conner, 1979). Also,
223 Schultz has shown that stilbenoids play an important role in the high natural durability of
224 *Maclura pomifera* wood (Schultz et al., 1990). Stilbenes are known as fungicide, termicides
225 and bactericide (Hart and Shrimpton, 1979; Likhitwitayawui and Sritularak, 2001; Javasinghe
226 et al., 2004), and may also exhibit antioxidant properties (Dani et al., 2008; Iacopini et al.,
227 2008; Luo et al., 2005). If it is reasonable to believe that stilbenes are responsible for *Bagassa*
228 *guianensis* heartwood natural durability based on literature precedents, stilbenes can be
229 considered as a secondary chemotaxonomic marker here indicating that *Bagassa* is related to
230 *Morus*, *Artocarpus*, and *Maclura* genera. In Weiblen classification, *Artocarpus* belongs to the
231 Artocarpeae tribe and *Maclura* belongs to the Moreae sensu largo tribe, and both Moreae and
232 Artocarpeae tribes are rather closely related genetically.

233 The peculiarity of *B. guianensis* in comparison with other Moraceae is the very high
234 proportion of moracins. In this matter, it can be hypothesized that *Bagassa* genus is closely
235 related to *Morus* and that moracins are specific to these two genera. These findings are in
236 agreement with Weiblen genetic-based classification where both *Bagassa* and *Morus* belong
237 to the Moreae sensu stricto tribe. It should be mentioned that the *Sorocea* genus, which also
238 belongs to the Moreae s. s. tribe, has been investigated before in the literature and apparently

does not contain moracins (see for example Ferrari et al., 2003; Ross et al., 2008). This observation speaks in favor of a very close relationship between *Bagassa* and *Morus*.

3. Concluding remarks

Studies of defensive wood chemicals in *Bagassa guianensis* allowed us to identify large amount of diversely functionalized stilbenes presumably responsible for wood natural durability. In addition, it was found based on the presence of moracins that *Bagassa* is very closely related to *Morus* genus, therefore corroborating Weiblen phylogenetic classification where *B. guianensis* belongs to the Moreae s. s. tribe rather than to the Artocarpeae tribe.

4. Experimental

4.1 General experimental procedure

The ^1H and ^{13}C -NMR spectra were recorded on a Bruker Avance DRX500 spectrometer (^1H -500.13 MHz) equipped with a 5 mm triple resonance inverse Cryoprobe TXI (^1H - ^{13}C - ^{15}N), with z gradient. Spectra were recorded with 1.7 mm NMR capillary tube in 40 μL of 99.99% CD_3OD solvent (δ_{H} 3.31 ppm - δ_{C} 49.00 ppm) at 300 K. The ^1H (500 MHz) and ^{13}C NMR (125 MHz) data are reported in ppm downfield from tetramethylsilane. Coupling constants are in Hz and s stands for singlet, d for doublet, t for triplet, q for quartet, m for multiplet and br for broad. Hydrogen connectivity (C, CH, CH_2 , CH_3) information was obtained from edited HSQC and/or DEPTQ-135 experiments. Proton and carbon peak assignments were based on 2D NMR analyses (COSY, NOESY, HSQC and HMBC). HREI-MS were performed using a QStar Elite mass spectrometer (Applied Biosystems SCIEX, Concord, ON, Canada) equipped with an ESI source operated in the positive ion mode. The capillary voltage was set at 5,500 V, the cone voltage at 20 V and air was used as the nebulizing gas (20 psi). In this hybrid instrument, ions were measured using an orthogonal acceleration time-of-flight (oa-TOF)

mass analyzer. Analyst software version 2.1 was used for instrument control, data acquisition and data processing. The accurate mass measurements were performed in triplicate with two internal calibrations. Direct sample introduction was performed at a 5 $\mu\text{L}/\text{min}$ flow rate using a syringe pump. The UV spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Optical rotations were measured with a Perkin-Elmer 241 polarimeter equipped with a sodium lamp (589 nm) and a 1 dm cell. The HPLC separations were performed on a Supelco Discovery[®] HS PEG column (250 $\times$ 21.1 mm, 5 μm) using a Waters system equipped with a W600 pump and a W2996 photodiode array absorbance detector. The samples were injected manually through a Rheodyne injector and the flow rate was 15 $\text{mL}\cdot\text{min}^{-1}$. Silica gel 60 (35-70 μm) and analytical TLC plates (Si gel 60 F 254) were purchased from SDS (France). All other chemicals and solvents were analytical grade and purchased from SDS (France).

4.2 Plant Material

Bagassa guianensis was collected in Régina, French Guiana. A voucher specimen is kept at the herbarium of Cayenne (CAY-RA13), French Guiana.

4.3 Extraction and isolation

The dried powdered heartwood of *Bagassa guianensis* (140 g) was extracted with ethyl acetate (3 $\times$ 500 mL) at room temperature to give a crude extract which was fractionated first on a silica gel column chromatography with polarity gradient of hexane/ethyl acetate mixtures: 80/20; 50/50; 20/80; 0/100. 9 fractions numbered F1 to F9 were obtained. Fractions F1 to F5 were purified on HPLC with a linear gradient of hexane/isopropanol, by the following method: 70:30 changing over 2 min to 60:40, then to 40:60 at 10 min and pure isopropanol at 15 min and remaining as is for 5 min. The fractions F6 and F9 were analyzed and purified with an isocratic method: 30:70 hexane/isopropanol. These methods allowed us to isolate moracin M **1** (6.2 mg; w/w 0.019%), moracin N **2** (6.7 mg; w/w 0.020%), 6-*O*-

289 methyl-moracin M **3** (3.3 mg; w/w 0.010%), 6-*O*-methyl-moracin-N **4** (9.1 mg; w/w 0.027%),
290 moracin Z **5** (5.2 mg; w/w 0.016%), moracin P **6** (1.2 mg; w/w 0.003), *trans*-resveratrol **7**
291 (12.6 mg; w/w 0.038%), *trans*-oxyresveratrol **8** (112.3 mg; w/w 0.343%), arachidin 2 **9** (5.1
292 mg; w/w 0.015%), arachidin 4 **10** (0.4 mg; w/w 0.001%), alboatolol **11** (0.5 mg; w/w
293 0.001%), (–)-epialboatolol **12** (5.4 mg; w/w 0.016%), artogomezianol **13** (12.7 mg; w/w
294 0.038%), steppogenin **14** (11.5 mg; w/w 0.035%), katuranin **15** (1.5 mg; w/w 0.004%),
295 dihydromorin **16** (20.4 mg; w/w 0.062%), the β -sitosterol **17** (8.4 mg; w/w 0.025%) and the
296 resorcinol **18** (1.8 mg; w/w 0.005%). Compounds 1-6, 9-10 and 17-18 were obtained from
297 the purification of the fractions F1-F5 while compounds 7-8 and 11-16 were isolated from the
298 fractions F6-F9.

299 4.3.1 6-*O*-Methyl-moracin M (**3**)

300 Yellowish amorphous powder; HR-EIMS $[M + H]^+$ m/z 257.0805 $[M + H]^+$ (calcd 257.0808);
301 1H and ^{13}C NMR (500 MHz; CD₃OD) see table 1.

302 4.3.2 6-*O*-Methyl-moracin N (**4**)

303 Yellowish amorphous powder; HR-EIMS $[M + H]^+$ m/z 325.1437 $[M + H]^+$ (calcd 325.1434);
304 1H and ^{13}C NMR (500 MHz; CD₃OD) see table 1.

305 4.3.3 Moracin Z (**5**)

306 Yellowish amorphous powder; HR-EIMS $[M + H]^+$ m/z 343.1542 $[M + H]^+$ (calcd 343.1540);
307 1H and ^{13}C NMR (500 MHz; CD₃OD) see table 1.

308 4.3.4 Arachidin 4 (**10**)

309 Colorless syrup; HR-EIMS $[M + H]^+$ m/z 315.1592 $[M + H]^+$ (calcd 315.1591); 1H and ^{13}C
310 NMR (500 MHz; CD₃OD) see table 2.

311 4.3.5 (–)-Epialboatolol (**12**)

312 Brownish syrup; $[\alpha]_D^{20}$ -7.4° (c 0.004, CH₃OH); HR-EIMS $[M + H]^+$ m/z 489.1540 $[M + H]^+$
313 (calcd 489.1544); 1H and ^{13}C NMR (500 MHz; CD₃OD) see table 3.

The 3 known moracins M (**1**), N (**2**) and P (**6**) and the other known compounds **7-9**, **11**, and **13-18** were identified by comparison of their physical and spectral data with those reported in the literature.

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References

- Aldrich Library of ¹³C and ¹H FT NMR Spectra, 1992, 2, 207A; 243A (nmr).
- Basnet P., Kadota S., Terashima S., Shimizu M., Namba T., 1993. Two new 2-arylbenzofuran derivatives from hypoglycemic activity-bearing fractions of *Morus insignis*. Chemical and Pharmaceutical Bulletin 41, 1238–1243.
- Bates R.B., Caldera S., Deshpande V.H., Malik B.L., Paknikar S.K., 1997. Revised structure of alboatolol. Journal of Natural Products 60, 1041–1042.
- Binbuga N., Ruhs C., Hasty J.K., Henry W.P., Schultz T.P., 2008. Developing environmentally benign and effective organic wood preservatives by understanding the biocidal and non-biocidal properties of extractives in naturally durable heartwood. Holzforschung 62, 264–269.
- Chapman E., Hall W., 2006. Dictionary of Natural Products , CRC, Version 14:2.
- Dani C., Bonnato D., Salvador M., Pereira M.D., Henriques J.A.P., Eleutherio E., 2008. Antioxidant protection of resveratrol and catechin in *Saccharomyces cerevisiae*. Journal of Agricultural and Food Chemistry 56, 4268–4272.

338 Dat N.T., Jin X., Lee K., Hong Y.-S., Kim Y.H., Lee J.J., 2009. Hypoxia-Inducible Factor-1
 339 Inhibitory Benzofurans and Chalcone-Derived Diels-Alder Adducts from *Morus*
 340 Species. *Journal of Natural Products* 72, 39–43.

341 Datwyler S.L., Weiblen G.D., 2004. On the origin of the fig: phylogenetic relationships of
 342 Moraceae from *ndhF* sequence. *American Journal of Botany* 91, 767–777.

343 El-Sohly H.N., Joshi A., Li X-C., Ross S.A., 1999. Flavonoids from *Maclura tinctoria*.
 344 *Phytochemistry* 52, 141–145.

345 Ferlinahayati S.Y.M., Juliawaty L.D., Achmad S.A., Hakim E.H., Takayama H., Said I.M.,
 346 Latip J., 2008. Phenolic constituents from the wood of *Morus australis* with cytotoxic
 347 activity. *Zeitschrift fur Naturforschung – Section C. Journal of Biosciences* 63, 35–39.

348 Ferrari F., Cechinel Filho V., Cabras T., Messana I., 2003. Sorocein L and sorocein M: two
 349 Diels-Alder type adducts from *Sorocea ilicifolia*. *Journal of Natural Products* 66, 581–
 350 582.

351 Han A-R., Kang Y-J., Windono T., Lee S.K., Seo E-K., 2006. Prenylated flavonoids from
 352 heartwood of *Artocarpus communis* with inhibitory activity on lipopolysaccharide-
 353 induced nitric oxide production. *Journal of Natural Products* 69, 719–721.

354 Hart J.H., Shrimpton D.M., 1979. Role of stilbenes in resistance of wood to decay.
 355 *Phytopathology* 69, 1138–1143.

356 Hirakura K., Fujimoto Y., Fukai T., Nomura T., 1986. Two phenolic glycosides from the root
 357 bark of the cultivated mulberry tree (*Morus lhou*). *Journal of Natural Products* 49,
 358 218-224

359 Hsu, F.-L., Chang H.-T., Chang S.T., 2007. Evaluation of antifungal properties of octyl
 360 gallate and its synergy with cinnamaldehyde. *Bioresource Technology* 98, 734–738.

361 Iacopini P., Baldi M., Storchi P., Sebastiani L., 2008. Catechin, epicatechin, quercetin, rutin
 362 and resveratrol in red grape: content, *in vitro* antioxidant activity and interactions.
 363 Journal of Food Composition and Analysis 21, 589–598.

364 Jahasinghe U.L.B., Samarakoon T.B., Kumarihamy B.M.M., Hara N., Fujimoto Y., 2008.
 365 Four new prenylated flavonoids and xanthenes from the root bark of *Artocarpus*
 366 *nobilis*. Fitoterapia 79, 37–41.

367 Jayasinghe U.L.B., Puvanendran S., Hara N., Fujimoto Y., 2004. Stilbene derivatives with
 368 antifungal and radical scavenging properties from the stem bark of *Artocarpus nobilis*.
 369 Natural Products Research 18, 571–574.

370 Lee D., Bhat K.P.L., Fong H.H.S., Farnsworth N.R., Pezzuto J.M., Kinghorn A.D., 2001.
 371 Aromatase Inhibitors from *Broussonetia papyrifera*. Journal of Natural Products 64,
 372 1286–1293.

373 Lee Y.J., Kim S., Lee S.J., Ham I., Whang W.K., 2009. Antioxydant activities of new
 374 flavonoids from *Cudrania tricuspidata* root bark. Archives of Pharmacal Research 32,
 375 195–200.

376 Li H., Cheng K.W., Cho C.H., He Z., Wang M., 2007. Oxyresveratrol as an antibrowning
 377 agent for cloudy apple juices and fresh-cut apples. Journal of Agricultural and Food
 378 Chemistry 55, 2604–2610.

379 Likhitwitayawuid K., Sritularak B., 2001. A new dimeric stilbene with tyrosinase inhibitory
 380 activity from *Artocarpus gomezianus*. Journal of Natural Products 64, 1457–1459.

381 Luo M., Liang X.Q., Dang P., Holbrook C.C., Bausher M.G., Lee R.D., Guo B.Z., 2005.
 382 Microarray-based screening of differentially expressed genes in peanut in response to
 383 *Aspergillus parasiticus* infection and drought stress. Plant Science 169, 695–703.

384 Mabberley D.J. (2002) The Plant Book, second Ed, Cambridge University Press, 858 p.

385 Murti V.V.S., Seshadri T.R., Sivakumaran S., 1972. Cudriniaxanthon and butyrospermol
386 acetate from the roots of *Cudrania javanensis*. *Phytochemistry* 11, 2089–2092.

387 Ngadjui B.T., Watchueng J., Keumedjio F., Nagmeni B., Simo I.K., Abegaz B.M., 2005.
388 Prenylated chalcones, flavones and other constituents of the twigs of *Dorsteronia*
389 *angusticornis* and *Dorsteronia barteri* var. *subtriangularis*. *Phytochemistry* 66, 687–
390 692.

391 Nguyen T.D., Jin X., Lee K., Hog Y-S., Young H.K., Jung J.L., 2009. Hypoxia-inducible
392 factor-1 inhibitory benzofurans and chalcone-derived Diels-Alder adducts from *Morus*
393 species. *Journal of Natural Products* 72, 39–43.

394 Okitani T., Takabe K., Takahashi M., 1999. The role of extractives involved in the natural
395 durability of domestic softwood. *Wood Research* 86, 51–52.

396 Orsini F., Verotta L., Lecchi M., Restano R., Curia G., Redaelli E., Wanke E., 2004.
397 Resveratrol derivatives and their role as potassium channels modulators. *Journal of*
398 *Natural Products* 67, 412–426.

399 Ross S.A., Rodríguez-Guzmán R., Radwan M.M., Jacob M., Ding Y., Li X.-C., Ferreira D.,
400 Manly S.P., 2008. Sorocenols G and H, anti-MRSA oxygen heterocyclic Diels-Alder-
401 type adducts from *Sorocea muriculata* roots. *Journal of Natural Products* 71, 1764–
402 1767.

403 Rowe J.W., Conner A.H., 1979. Extractives in Eastern Hardwood. A review. USDA Forest
404 Service General Technical Report FPL 18. Forest Products Laboratory, Madison, WI,
405 66 pp.

406 Scheffer T.C., Morell J.J., 1998. Natural durability of wood: A worldwide checklist of
407 species. Forest Research Laboratory, Oregon State university; College of Forestry,
408 Research Contribution 22, 45 pp.

409 Schultz P., Hubbard J.T.F., Jin L., Fisher T.H., Nicholas D.D., 1990. Role of stilbenes in the
 410 natural durability of wood: Fungicidal structure-activity relationships.
 411 Phytochemistry 29, 1501–1507.

412 Schultz T.P., Harms W.B., Fischer T.H., McMurtrey K.D., Minn J., Nicholas D.D., 1995.
 413 Durability of angiosperm heartwood: the importance of extractives. *Holzforschung* 49,
 414 29–34.

415 Schultz P., Nicholas D., 2000. Naturally durable heartwood: evidence for a proposed dual
 416 defensive function of the extractives. *Phytochemistry* 5, 47–52.

417 Schultz P., Nicholas D., Preston A.F., 2007. A brief review of the past, present and future of
 418 wood preservation. *Pest Management Science* 63, 784–788.

419 Sheu Y-W., Chiang L-C., Chen I-C., Tsai I-L., 2005. Cytotoxic flavonoids and new
 420 chromenes from *Ficus formosana* f. *formosana*. *Planta Medica* 71, 1165–1167.

421 Shimizu K., Kondo R., Sakai K., Lee S-H., Sato H., 1998. The inhibitory component from
 422 *Artocarpus incisus* on melanin biosynthesis. *Planta Medica* 64, 408–412.

423 Silva C.A., Monteiro B.B., Brazolin S., Lopez A.C.G., Richter A., Braga M.R., 2007.
 424 Biodeterioration of brazilwood *Caesalpinia echinata* Lam. (Leguminosae-
 425 Caesalpinioideae) by rot fungi and termites. *International Biodeterioration and*
 426 *Biodegradation* 60, 285–292.

427 Smith A.L., Campbell C.L., Diwakar M.P., Hanover J.W., Miller R.O., 1989. Extracts from
 428 black locust as wood preservatives: A comparison of the methanol extract with
 429 pentachlorophenol and chromated copper arsenate. *Holzforschung* 43, 293–296.

430 Song W., Wang H-H., Bucheli P., Zhang P-F., Wei D-Z., Lu Y-H., 2009. Phytochemical
 431 profiles of different mulberry (*Morus* sp.) species from China. *Journal of Agricultural*
 432 *and Food Chemistry* 57, 9133–9140.

433 Su B.N., Cuendet M., Hawthorne M.E., Kardono L.B.S., Riswan S.F., Harry H.S., Mehta
 434 R.G., Pezzuto J.M., Kinghorn A.D., 2002. Constituents of the bark and twigs of
 435 *Artocarpus dadah* with cyclooxygenase inhibitory activity. Journal of Natural
 436 Products 65, 163–169.

437 Suttie E.D., Orsler R.J., 1996. The influence of the natural extractives of Opepe (*Nauclea*
 438 *diderrichii*) and African Padauk (*Pterocarpus soyauxii*) timbers on their durability.
 439 IRG/WP N° 96-30098, 1–15.

440 Takasugi M., Nagao S., Masamune T., 1979. Structure of moracins E, F, G and H, new
 441 phytoalexins from diseased mulberry. Tetrahedron Letters 48, 4675–4678.

442 Wang S.Y., Chen P.F., Chang S.T., 2005. Antifungal activities of essential oils and their
 443 constituents from indigenous cinnamon (*Cinnamomum osmophloeum*) leaves against
 444 wood decay fungi. Bioresource Technology 96, 813–818.

445 Zerega N.J.C., Clement W.L., Datwyler S.L., Weiblen G.D., 2005. Biogeography and
 446 divergence times in the mulberry family (Moraceae). Molecular Phylogenetics and
 447 Evolution 37, 402–416.

448 Zhou C.X., Tanaka J., Cheng C.H.K., Higa T., Tan R.X., 1999. Steroidal alkaloids and
 449 stilbenoids from *Veratrum taliense*. Planta Medica 65, 480–482.

450

451

452 **Figures and legends****Moracins**

	R ¹	R ²
1	H	H
2	H	Prenyl
3^a	Me	H
4^a	Me	Prenyl
5^a	Me	3-Hydroxy-3-methylbutyl

Moracin M
Moracin N
6-O-Methyl-moracin M
6-O-Methyl-moracin N
Moracin Z^b

6 Moracin P**Stilbenoids**

	R ¹	R ²	
7	H	H	<i>trans</i> -Resveratrol
8	OH	H	<i>trans</i> -Oxyresveratrol
9	H	Prenyl	Arachidin 2
10^a	H	3-Hydroxy-3-methylbutyl	Arachidin 4 ^b

11 C₁₇ Alboctanol
12^a C₁₇ (-)-Epialboctanol^b

13 Artogomezianol**Flavanones**

	R ¹	R ²	
14	H	OH	Steppogenin
15	OH	H	Katuranin
16	OH	OH	Dihydromorin

Others **17** β-Sitosterol **18** Resorcinol

453

454 **Figure 1** Compounds **1-18** isolated from *Bagassa guianensis* (Moraceae). (a) New
455 compounds; (b) New names.

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458

459 **Figure 2** Pertinent NOE interactions observed for (-)-epialboctanol (**12**) from NOESY
460 experiment

461

462

463 **Tables**464 **Table 1** ^1H and ^{13}C NMR spectroscopic data for moracins **3-5** in CD_3OD

Atom	3		4		5	
	δ_{C}	δ_{H} (<i>J</i> in Hz)	δ_{C}	δ_{H} (<i>J</i> in Hz)	δ_{C}	δ_{H} (<i>J</i> in Hz)
2	156.5	-	156.2	-	156.2	-
3	96.5	6.95, d (0.6)	102.1	6.90, s	102.0	6.91, d (0.6)
4	121.9	7.43, d (8.5)	121.3	7.25, s	121.6	7.30, s
5	112.9	6.85, dd (8.5, 2.1)	127.5	-	128.6	-
6	159.6	-	157.4	-	157.5	-
7	102.0	7.09, brd (2.0)	94.7	7.09, s	94.7	7.09, s
8	157.0	-	155.7	-	155.8	-
9	123.7	-	123.0	-	123.1	-
1'	133.6	-	133.9	-	133.6	-
2'/6'	104.0	6.78, d (2.1)	103.9	6.77, d (2.1)	103.5	6.77, d (2.1)
3'/5'	159.7	-	159.9	-	160.0	-
4'	103.5	6.25, t (2.1)	103.5	6.24, t (2.1)	103.4	6.25, t (2.1)
1''	-	-	29.7	3.34, brd (7.3)	26.7	2.73, m
2''	-	-	124.3	5.32, tm (7.3)	45.5	1.74, m
3''	-	-	132.7	-	71.5	-
4''	-	-	17.8	1.73 brs	28.9	1.27, s
5''	-	-	26.0	1.74 brs	28.9	1.27, s
MeO	56.0	3.85, s	56.2	3.88 s	56.0	3.89, s

465

466

467 **Table 2** ^1H and ^{13}C NMR spectroscopic data for stilbenes **9** and **10** in CD_3OD

Atom	9		10
	δ_{C}	δ_{H} (J in Hz)	δ_{H} (J in Hz)
1	130.6	-	-
2	128.6	7.31, d (8.6)	7.32, d (8.7)
3	116.5	6.75, d (8.6)	6.75, d (8.7)
4	158.1	-	-
5	116.5	6.75, d (8.6)	6.75, d (8.7)
6	128.6	7.31, d (8.6)	7.32, d (8.7)
α	128.3	6.88, d (16.3)	6.90, d (16.5)
β	127.2	6.74, d (16.3)	6.74, d (16.5)
1'	137.6	-	-
2'	105.7	6.46, s	6.46, s
3'	157.2	-	-
4'	116.0	-	-
5'	157.2	-	-
6'	105.7	6.46, s	6.46, s
1''	23.3	3.28, d (7.1)	2.66, m
2''	124.6	5.23, tm (7.1)	1.68, m
3''	131.4	-	-
4''	26.0	1.62, brs	1.25, s
5''	18.0	1.75, brs	1.25, s

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470

471 **Table 3** ^1H and ^{13}C NMR spectroscopic data for distilbenes **11** and **12** in CD_3OD

Atom	12		11
	δ_{C}	δ_{H} (<i>J</i> in Hz)	δ_{H} (<i>J</i> in Hz)
1	156.7	-	-
2	101.8	6.10, d (2.2)	6.32, d (2.2)
3	156.2	-	-
4	107.3	6.19, d (2.2)	6.32, d (2.2)
5 _{ax}	40.1	3.19, brt (13.7)	2.98, dd (16, 14)
5 _{eq}		2.72, dd (15.6, 3.0)	2.53, dd (16.3, 4.3)
6 _{ax}	40.3	3.51, brtd (11.6, 2.1)	3.75, dt (14, 3.7)
7 _{ax}	56.2	3.41, dd (11.3, 8.2)	-
7 _{eq}	-	-	3.28, d (3.3)
8 _{ax}	44.1	4.42, d (8.2)	4.67, brs
9	119.6	-	-
10	142.2	-	-
11	123.7	-	-
12	156.4	-	-
13	103.3	6.16, d (2.2)	?
14	156.4	6.12, dd (8.4, 2.3)	6.13, dd (8.4, 2.3)
15	107.3	-	-
16	129.7	6.82, d (8.2)	6.44, d (8.2)
17	149.2	-	-
18	108.4	6.01, d (1.9)	5.77, d (1.9)
19	157.9	-	-
20	100.8	5.93, t (2.2)	6.02, t (2.2)
21	157.9	-	-
22	108.4	6.01, d (1.9)	5.77, d (1.9)
23	125.2	-	-
24	156.1	6.76, d (8.2)	6.25, d (8.2)
25	103.2	6.23, dd (8.2, 2.5)	6.04, dd (8.2, 2.5)
26	156.7	-	-
27	108.1	6.19, d (2.2)	6.25, d (2.2)
28	131.2	-	-

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