

Influence of extractives on the color of woods from Caatinga

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ABSTRACT: Wood extractives, direct or indirect, influence several wood properties, among them the organoleptics, for example the color, a visual characteristics that affect the product perception by the consumer. Thus, the aim of this work was characterize and correlate the chemical properties of five species from Caatinga with their wood color. Were evaluated wood of Angico (*Anadenanthera colubrina* var. *cebil* (Griseb.) Altschul), Cajueiro (*Anacardium occidentale* L.), Jurema-de-Embira (*Mimosa ophthalmocentra* Mart. ex Benth.), Pereiro (*Aspidosperma pyriforme* Mart.) and Sabiá (*Mimosa caesalpinifolia* Benth). The results of the correlation showed that while yellow pigments are mainly affected by lipophilic substances, the red pigment of the wood is influenced by the components that can be extracted by hot water and acetone.

Influência dos extrativos na cor de madeiras da Caatinga

RESUMO: Os extrativos, direta ou indiretamente, exercem influência em diversas propriedades da madeira, entre elas as organolépticas, como por exemplo a cor, uma característica visual que afeta a percepção do produto pelo seu consumidor. Diante disso, o objetivo desse trabalho foi caracterizar e correlacionar as propriedades químicas de cinco espécies do bioma Caatinga com a cor de suas madeiras. Foram avaliadas as madeiras de Angico (*Anadenanthera colubrina* var. *cebil* (Griseb.) Altschul), Cajueiro (*Anacardium occidentale* L.), Jurema-de-Embira (*Mimosa ophthalmocentra* Mart. ex Benth.), Pereiro (*Aspidosperma pyriforme* Mart.) e Sabiá (*Mimosa caesalpinifolia* Benth). Os resultados da correlação mostraram que a coloração amarelada é afetada apenas por substâncias lipofílicas e o pigmento vermelho da madeira é influenciado por compostos extraídos em água quente e acetona.

Introduction

Wood is a renewable and extremely versatile material, which can be used as raw material for construction, furniture industries, lute making, wood based panels industries, among countless applications. This material versatility is due its anatomic structure, physic-mechanical properties and chemical composition. As an organic material, wood is basically made of three macromolecular components that form the cell wall: cellulose, hemicelluloses and lignin. However, among its composition, it is also possible to observe low molecular weight components, non-structural, know as extractives and ash.

The complex chemical composition is responsible for, but not only, the wood color that is present to the consumer of the final product. And the color can be considered one of the most important consumer trigger, once it is related to sensory, perceptual, cognitive and affective effects (Cheng et al., 2019). In wood materials, color is formed by a combination of chemical factors, e.g. atomic group with isolated electron pairs such as hydroxyl (-OH) placed on the main components, intensifies the coloration and enable the absorption of light; yellow hue is related to the presence of lignin, and red hue is associated with extractive content of wood (Sandoval-Torres et al., 2010). So, became essential to understand the presence of extractives in wood and their influence on the color, once this characteristic may direct affect the final product marketing.

Extractive composition and amount can change considerable among species and genus. Some of those substances have metabolic function, while others have the capacity of wood preservation due to their antifungal properties (Valette et al., 2017) and termite control potential (Hassan et al., 2017). Extractives can be defined as chemical components that are extracted from wood with several solvents. Thus, the extraction method should always be described as it affect the yield and composition (Jansson & Nilverbrant, 2009). Water soluble extractives are usually carbohydrates (Ribeiro, 2016), salts, simple sugars (Sarto & Sansigolo, 2010) and some phenol substances (Silvério, 2008). Among the substances soluble in organic solvents, it can be found esters and fatty acids, long chain alcohols, steroids (Ribeiro, 2016) and unsaponifiables substances (Sarto & Sansigolo, 2010).

Another problems usually found when color is studied is the unclear definition of this property, as it can be subjective and depends of the viewer perception (Byrne & Hilbert, 2003). To be able to compare, color must be converted to mathematical models and the CIELab (International Commission on Illumination) model is one of the most used to measure wood color. This method defines the color sense based on three elements: luminosity or

lightness (L^*), a a^* hue (color variation from red to green) and b^* hue (color variation from yellow to blue) (Ibraheem et al., 2012).

The aim of this study was evaluate the influence of extractives on the wood color formation from Caatinga typical species. Forest exploitation on this biome happens mainly for firewood production, and a major part of this process is extractive activity (Moreira, 2011). Thus, it is important to know and understand this region species to suggest new products with higher added value and promote a sustainable production. This study evaluated five species with different color perception.

Material and Methods

Wood samples from five species from the Caatinga biome were collected: Angico (*Anadenanthera colubrina* var. *cebil* (Griseb.) Altschul), Cashew tree (*Anacardium occidentale* L.), Jurema-de-Embira (*Mimosa ophthalmocentra* Mart. ex Benth), Pereiro (*Aspidosperma pyrifolium* Mart.) and Sabiá (*Mimosa caesalpinifolia* Benth). Cashew tree wood was provenient of individuos collected on Embrapa Agroindústria Tropical plantations located in Ceará. Angico, Jurema-de-Embira, Pereiro and Sabiá wood were cut from fallen trees in a managed area in Assu, RN, municipality.

The logs were hand peeled and, with a circular saw, tangential cut to produce specimens of 10 x 5 x 2 cm length, width and thickness, respectively. The residual wood were reduced to shavings for the chemical analysis.

Five specimens for each species were produced, and their colorimetric parameters were measured by Konica Minolta CR-410 equipment using CIE- $L^*a^*b^*$ system. For each specimens, three reads of the colorimetric parameters were made in different spots: L (values range from 0, absolute black, to 100, absolute white), a^* (positive values indicates red hue) and b^* (positive values indicates yellow hue). Based on the measured parameters, C (chroma or saturation) and h^* (hue angle) were calculated according to equation (1) and (2).

$$C = (a^{*2} + b^{*2})/2 \quad (1)$$

$$h^* = \tan^{-1}(b^*/a^*) \quad (2)$$

Where: a^* is the red-green axis coordinates, b^* is the blue-yellow axis coordinates, C is the relative saturation and h^* is the hue angle.

Shavings designated to chemical characterization were reduced in a hammer mill. Particles that pass through a 40 mesh sieve and were retained in a 100 mesh sieve were used. Three repetitions for each species were made for determine hot water soluble polar extractives content, according to TAPPI T 207 standard (TAPPI, 1999), acetone and dichloromethane soluble apolar

extractives content according to TAPPI T 204 standard (TAPPI, 1997). Total extractive content were obtained by the sum of hot water and dichloromethane soluble extractive contents.

Analysis of variance (ANOVA) was applied to evaluate the chemical characteristics and the wood colorimetric parameters. For significant results, Tukey test were applied to evidence average difference ($p < 0.05$) using the statistical tool Sisvar 5.6. The correlation among the variables was determined by Pearson linear correlation. P-value lower than 0.05 indicated statistical significance at a 95% level. For this test the software Statgraphics Centurion XV was used.

Results and discussion

Among tropical hardwoods, total extractives content values can be as high as 7.6% (4.6% for ethanol-benzene soluble extractives) (Brémaud et al., 2011). Based on this average value, it could be observed that two wood species, Angico and Sabiá, presented a high amount of total extractives (table 1). However, the composition of those extractives were different for those two species, as the polar extractive content of Angico wood was statistically different from the one of Sabiá wood, and so, acetone soluble extractive content was statistically lower. Among the others studied species, the Cashew tree and Pereiro wood showed statically similar values for total extractive content, but Jurema-de-Embira wood, even though showed a statistically similar value for hot water soluble extractive, when used acetone as solvent, showed a higher value.

Table 1. Extractive content of five species from Caatinga biome

Species	Extractive content			Total Extractive (%)
	Hot H ₂ O (%)	Acetone (%)	Dichloromethane (%)	
Angico	6.18 a (11.91)	7.63 b (1.61)	1.22 ab (21.11)	7.40
Cashew tree	0.81 c (39.19)	1.03 d (12.04)	0.84 b (36.88)	1.65
Jurema-de-Embira	1.49 c (10.84)	4.84 c (9.17)	0.89 ab (6.81)	2.38
Pereiro	0.73 c (13.95)	2.06 d (11.86)	1.55 a (17.83)	2.28
Sabiá	4.82 b (4.79)	9.06 a (16.51)	1.08 ab (4.38)	5.90

The values followed by same letter, in the same column, do not statistically differ from each other; The values in parentheses correspond to the variant coefficients in percentage.

Caatinga woods originated in Rio Grande do Norte state that were evaluated in this study showed polar extractive content lower than same species samples from others regions, For example, Angico wood collected in Patos, PB, presented average values of 8.53 and 9.50% for sapwood and heartwood, respectively (Paes et al., 2013b). Sabiá wood from Seropédica, RJ, was reported to present a average value of 9.14% (Gonçalves et al., 2010). Pereiro wood, also from the municipality of Patos, PB, showed a variation from 3.21 to 4.93% for hot water extractive content depending on the pith-bark direction spot analyzed (Paes et al., 2009).

The average apolar extractive content was higher when acetone solvent was used instead of dichloromethane. However, these higher values not necessarily indicate a higher lipophilic extractive content, as acetone is also capable of extract hydrophilic components due its higher polarity than dichloromethane (Barbosa et al. 2005).

When acetone solvent was used, Sabiá wood showed a apolar extractive content statistically higher than other woods, a numeric value close to 9%, amount reported in literature for the same species when cyclohexane solvent was used (Gonçalves et al. 2010). Angico wood also showed a

content higher than Cashew tree, Jurema-de-Embira and Pereiro wood. The average value found for Angico wood was lower, but close, than literature when a sequence of cyclohexane, ethyl acetate and methanol solvent (8.87%) (Gonçalves et al. 2013) or when alcohol:toluene was used (8.86%) (Paes et al. 2013b).

Jurema-de-Embira wood (4.84%) showed a lower average value than the one reported on literature for species of the same genus. For example, alcohol:toluene solubles content of Jurema Preta (*Mimosa tenuiflora* (Willd.) Poir) was between 8.77% (Brito et al. 2014) and 9.96% (Paes et al. 2013a), and Jurema Vermelha wood (*Mimosa arenosa* (Willd.) Poir.) showed an average value of 5.80% (Paes et al. 2013a).

Pereiro and Cashew tree wood didn't show statistically difference for acetone soluble extractive content values, however those average values were lower than the other studied woods. On the other hand, on those two species, it was observed the lower difference between acetone and dichloromethane soluble content, and that fact confirms the low polar extractive content indicated by the hot water soluble extractives. When dichloromethane solvent was used, Pereiro wood extractive content (1.55%) was

statistically different than Cashew tree wood (0.84%) and statistically similar to other species.

In the colorimetric analysis, lightness of Pereiro (68.05), Angico (59.99), Sabiá (58.23) and Cashew tree (56,81) wood were considered high according to Camargos and Gonçalves (2001), which

classified woods with average "L" value higher than 56 as light color (Table 2). On the other hand, Jurema-de-Embira (51.53%) presented a lightness value ($L < 56$) statistically lower than others, indicating that it was the only dark wood among the studied species.

Table 2. Colorimetric parameters from five Caatinga wood species.

Species	CIELAB 1976				
	L	a*	b*	C	h*
Angico	59.99 b (6.65)	11.85 b (9.63)	22.54 b (9.61)	25.52 b (6.69)	62.09 c (6.37)
Cashew tree	56.81 c (2.01)	4.56 e (2.58)	10.96 d (6.43)	11.87 d (5.77)	67.34 b (1.45)
Jurema-de-Embira	51.53 d (4.42)	9.59 c (6.98)	16.94 c (7.44)	19.49 c (9.67)	60.69 cd (4.08)
Pereiro	68.05 a (1.27)	8.10 d (5.22)	31.83 a (3.75)	32.85 a (3.76)	75.71 a (0.62)
Sabiá	58.23 bc (5.43)	13.75 a (5.38)	22.44 b (7.09)	26.33 b (5.98)	58.44 d (2.92)

The values followed by same letter, in the same column, do not statistically differ from each other; The values in parentheses correspond to the variant coefficients in percentage. Where: L is lightness, a* is red hue, b* is yellow hue, C is chroma and h* is hue angle.

Comparing a* and b* parameters for each species, it was possible to see that Pereiro wood showed a biggest gap between red hue (8.10) and yellow hue (31.83) average values, those numbers were close to the one found by another researchers: a* (10.44) and b* (20.54) (Camargos e Gonçalves, 2001). The strong yellow tone of Pereiro wood was also confirmed by the statistically superior average value of hue angle. Hue angle values near 90° indicate a color close to the positive b axis (yellow), meanwhile near 0° indicates a proximity to the positive a axis (red).

Angico (11.85) and Sabiá (13,75) wood presented values higher than the average for a* and

b* parameters, 22.54 and 22.44, respectively. For those samples, there was a mix of heartwood and sapwood parts, thus for those two species reddish or yellowish woods depend on the spot measured, as the heartwood (reddish) and sapwood (yellowish) colors are discernible to the naked eye

Jurema-de-Embira wood presented average values of 9.59 for red hue and 16.94 for yellow hue, what results to a tendency to be a brown color wood. Those average values showed characteristics of darker color, with a reddish hue, less saturated and low tones (Mori et al., 2005)

Table 3. Pearson's correlation between color parameters and extractive contents

Solvent	L	a*	b*	C	h*
Hot water	-0.3424 (0.2115)	0.7352 (0.0018)*	-0.1096 (0.6973)	0.039 (0.8904)	-0.7081 (0.0031)*
Acetone	-0.501 (0.0571)	0.8762 (0)*	-0.0323 (0.909)	0.1392 (0.6207)	-0.7965 (0.0004)*
Dichloromethane	0.5717 (0.026)*	0.1679 (0.5497)	0.765 (0.0009)*	0.749 (0.0013)*	0.3918 (0.1486)

The values in parentheses correspond to the P-value. * ($p < 0.05$) Where: L is lightness, a* is red hue, b* is yellow hue, C is chroma and h* is hue angle.

Saturation, evaluated by the C parameter, was statistically higher for Pereiro wood when compared to the other species, thus the tendency to present a more intense yellow color. Sabiá (26.33) and Angico (25.52) wood did not statistically differ from each other, and also presented chroma average values considered high, superior than 23.39 (Camargos e Gonçalves 2001). However, Cashew tree wood was the sample that showed the statistically lower value of C, and together with the other parameters, explains the gray hue of its wood.

Polar extractives, observed on the hot water and acetone extracts, positive influenced the red hue (a*) (Table 3). As consequence, h* parameter was negative influenced by those extractives, as wood color tends to become closer to a* axis. Moya et al. (2012) also observed a positive statistical relation between a* parameter and hot water extractive content for heartwood or sapwood of *Acacia mangium*.

Dichloromethane soluble extractives positively affected the other color parameters: lightness (L), chroma (C) and yellow hue (b*). This behavior was also reported by Nzokou and Kamdem (2006) for *Prunus serotina*, *Quercus rubra* and *Pinus resinosa*. The authors observed that extraction only made with ethanol or ethanol:toluene did not affect lightness values. However, lightness became significantly lower when extraction with organic solvents was followed by water extraction. For *Vochysia guatemalensis* and *Acacia mangium*, species studied by Moya et al. (2012), there was a correlation between lightness and ethanol:toluene soluble extractive content, but a different from the Caatinga species analyzed in this work, as the correlation was negative.

Conclusions

Understanding how the chemical composition of the wood affects an important product marketing characteristic as the color is essential to allowed the commercialization of wood not traditionally fully exploited, as Caatinga species. After evaluation of five representative species, it was possible to conclude that yellow hue of the wood is direct influenced by the presence of lipophilic substances, while red hue is defined by the effect of hydrophilic extractives. Those information can be important for future studies of silviculture techniques or genetic improvement of those species, as inducing a specific extractive production during the tree growth would affect the appearance of its wood.

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