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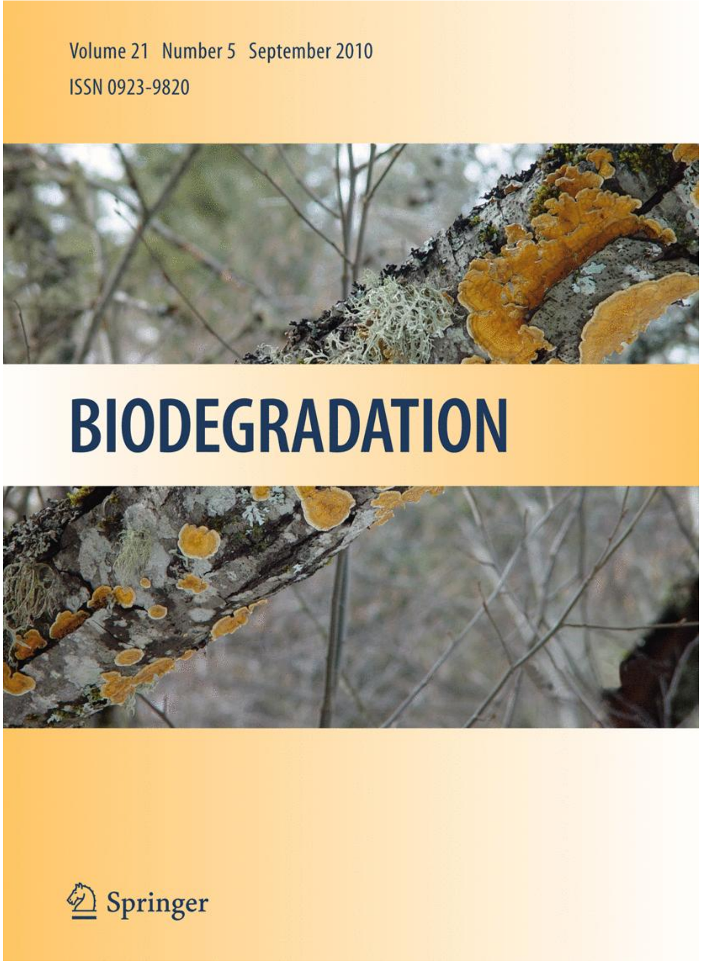

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ORIGINAL PAPER

Durability of five native Argentine wood species of the genera *Prosopis* and *Acacia* decayed by rot fungi and its relationship with extractive content

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Abstract The natural durability of four Argentinean species of *Prosopis* and one of *Acacia* was evaluated in laboratory tests, according to European standards, using three brown rot and one white rot fungi. These tests were complemented by assessing the wood chemical composition. All the species were from moderately slightly durable to very durable (classes 4–1), and in all cases the heartwood was the most resistant to fungal attack. Chemical extractives content (organic, aqueous, tannic and phenolic) was higher in the heartwood. However, species durability was not related to extractive contents nor with wood density. Instead, it is possible that extractives could contribute to natural durability in different ways, including the effects related to the antioxidant properties of some of them.

Keywords *Prosopis* · *Acacia* · Natural durability · Extractive content

Introduction

The genus *Prosopis* contains about 44 woody species distributed in arid and semi-arid regions of America, Africa and Asia. Most of the species are native to the Americas, where three centres can be recognized: (1) northern Mexico/USA, (2) southern Argentina, including all neighbouring countries, and (3) intermediate tropical region. The distribution of *Prosopis* species in the Americas ranges from approximately 37°N in the USA to 48°S in Argentina. Numerous native species occur in central and western Argentina, and this area is considered the centre of polymorphism for the genus. The genus *Acacia*, has a pantropical distribution and comprises approximately 1,450 species (Luckow 2005) of which 21 are native to Argentina (Cialdella 1984, 1997). Most of the species of both genera are considered multipurpose trees and shrubs by FAO because almost all their biomass can be used. Many of these species are used in reforestation programs because they fulfil an important role against desertification of eroded soils.

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Some also are used to produce forage, human food, coal, furniture, medicinal substances, alcohol, dyes, and other products (Karlin et al. 1997). *Prosopis* was a valuable resource for the early European settlers who consumed the high sugar content pods during droughts and used the wood for charcoal and building materials (D'Antoni and Solbrig 1977). Contemporary furniture makers in Argentina have discovered that the hard *Prosopis* lumber can be sanded very finely to provide beautifully finished furniture. In addition, the lumber of this species has exceptional dimensional stability. This characteristic results in furniture and flooring with much less tendency to warp and twist than that which can be obtained from other fine woods.

Decay produced by fungi is one of the most important factors that affect the durability of wood. In many cases, resistance to decay fungi is considered synonymous to the durability of wood. The resistance of various woods to fungal attack varies, but no wood is immune. Differences are due mainly to variations in content of toxic extractives. A higher extractive content imparts a higher resistance. Two main categories of decay (rot) are recognized, brown and white. Fungi that cause brown rot consume mainly carbohydrates whereas white rot fungi may decompose both carbohydrates and lignin (Tsoumis 1991).

The objective of this paper was to evaluate the natural durability of four Argentinean species of *Prosopis* (*P. alba*, *P. nigra*, *P. kuntzei* and *P. ruscifolia*) and one of *Acacia* (*A. aroma*) in laboratory tests. The evaluation of durability was complemented by assessing the wood chemical composition of the selected species in an attempt of verify the eventual presence of any relationship between durability and chemical composition.

In the present study, a limited sample of three trees per species was used. Limited sample was necessitated by protect of some species in some provinces of Argentina. It was necessary to cut the entire tree to perform the tests since the hardness of the wood makes it difficult to take small samples from alive trees.

Materials and methods

Sampling of wood material

The species tested were: *P. alba* Griseb., *P. kuntzei* Harms., *P. nigra* (Griseb.), *P. ruscifolia* Griseb and *A. aroma* Hook et Arn. Wood sample discs 5–6 cm thick < 15 cm in diameter were obtained at breast height. All of the species came from Santiago del Estero province, República Argentina and were cut in 2006. Three trees were used for each species except for *P. ruscifolia,* for which only two trees were used. *P. alba* samples came from a plantation located at Estación experimental Fernández, in Fernández, Department of Robles. *P. nigra* and *P. kuntzei* samples came from a natural population located at Establecimiento Yanda, in Robles, Department of San Martín. *P. ruscifolia* samples came from a natural setting located at Establecimiento Agroten S.A., in Brea Pozo, Department of San Martín. *A. aroma* samples came from a natural population located at Ruta provincial n° 18, Robles, Department of San Martín (Fig. 1). Trees

Fig. 1 Map of South America showing details of Argentina and Santiago del Estero province, where specimens were sampled from. SE, Santiago del Estero Province; *filled circles* locality of Fernández (*P. alba*); *filled triangles* locality of Robles (*P. nigra*, *P. kuntzei* and *A. aroma*); *filled squares* locality of Brea Pozo (*P. ruscifolia*)

from natural populations were selected as representative of the whole population and, when possible, those with a straight trunk were chosen. The material was sampled according to standard UNI EN 350-1 (1996).

Fungal decay test in the laboratory

The methodology proposed by Bravery (1979) was followed instead of the EN 113 standard, since the quantity of material available was insufficient to follow the standard. This technique employs wood blocks measuring 30 × 10 × 5 mm. Blocks were extracted from a strip cut from the centre of the discs. Samples were selected to analyse different zones of the section (Fig. 2):

- zone A, sapwood;
- zone B, external heartwood;
- zone C, inner heartwood (near the pith).

These samples were conditioned to constant weight before the test at 20°C and 65% R.H. The wood was considered to reach an equilibrium moisture content value (e.m.c.) of 12%. Additional samples of each species (3–11 per zone depending on availability), were cut in order to calculate the theoretical oven-dry mass (103°C).

After conditioning and sterilization by gamma radiation, six replicates of each species from each zone (when the material was enough) were selected for exposure to each fungus. Each sample was placed side by side with a control sample of sapwood of *Fagus sylvatica*, as a reference species in a Petri dish, measuring 90 mm in diameter and containing approximately 20 ml of 4% malt in 2% agar medium. The fungi used in the tests were pure and certified cultures of *Gloeophyllum trabeum* (Persoon ex Fries) Murril (strain BAM Ebw. 109), *Coniophora puteana* (Schumacher ex Fries) Karsten (strain BAM Ebw. 15), *Serpula lacrymans* (Schumacher ex Fries) (strain BAM 315) and *Coriolus versicolor* (Linnaeus) Quelet (strain CTB 863 A). The incubation time was 8 weeks at 22°C and 75% R.H., after which the samples were dried at 103 ± 2°C and reweighed to determine mass loss.

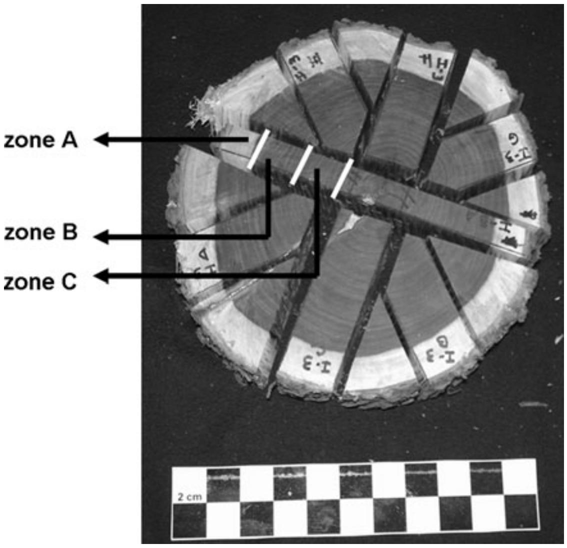

Fig. 2 Picture exemplifying the sample cutting for durability test of zones A, B and C

The natural durability of the wood of each species was classified in five categories according to the Standard UNI EN 350-1 (1996). The classes of durability were classified according to the value of the durability index "x" (x = (% average mass loss of test specimens)/(% average mass loss of reference specimens)) and were Class 1 (Very durable): $x \leq 0.15$; class 2 (Durable): $0.15 < x \leq 0.30$; class 3 (Moderately durable): $0.30 < x \leq 0.60$; class 4 (Slightly durable): $0.60 < x \leq 0.90$ and class 5 (Not durable): $x > 0.90$.

Determination of organic and aqueous extractives

Among 2–4 samples of sapwood and heartwood per species were milled in a Wiley mill (Thomas Scientific, Swedesboro, NJ) to obtain a 40–60 mesh meal (approximately 0.2–0.4 mm). No differentiation was made between external and internal heartwood.

The amount of extractives was measured using a slightly modified version of TAPPI standard, T204 (1996) for the organic samples followed by extraction in hot water (Pometti et al. 2009).

The amount of extractives was calculated as a percentage of the initial anhydrous mass.

Determination of tannic and non-tannic substances

For these analyses were used two samples of heartwood and sapwood per species.

The measurements have been carried out on approximately 20 g of milled material sieved to collect a fraction between 85 and 200 µm. The determination of tannic and non-tannic substances was made following the method described in the Standard UNI 4632 (1996) and in Bravo (1952).

Extraction of soluble phenolic compounds

Material for phenolic analysis was taken from 3 or 5 zones (depending on the availability) on the same ray of wood disk, from sapwood towards inner heartwood. From each zone, a piece 2 mm in thickness was milled in particles of 100 µm diameter. The number of samples was three per species from each zone.

Total polyphenols were estimated by a modified version of the Folin–Ciocalteu method (Boizot and Charpentier 2006). The absorbance at 735 nm was measured spectrophotometrically and the results were expressed in mg equivalent of Gallic acid per gram dry weight.

Data analysis

Means and standard deviations were calculated for mass losses due to the fungal attack and for extractive contents, tannic and non-tannic substances content and phenolic compounds. In order to investigate the existence of any relationship between durability and factors influencing decay resistance, regression analyses were carried out for durability index versus extractives content and versus wood density, and phenolic compounds versus mass loss. All statistic analyses were performed using Statistica software for Windows (STATSOFT, Inc., 2000).

Results and discussion

The weight losses indicated that *Coriolus versicolor* was generally more aggressive compared to the other three basidiomycetes used (Table 1). Although in some cases, *Coniophora puteana* and *Serpula lacrymans* caused higher mass loss (Table 1). Consequently the durability classes were determined using data regarding the maximum mass loss for each zone (Table 2). Data regarding *Gloephyllum trabeum* was not considered for the calculation of durability classes since control specimens for this fungus showed a very low mass loss; this means that the virulence against beech for *Gloeophyllum trabeum* was very low.

Table 1 Mean mass loss (%) for each zone of each species and for beech control virulence sample, for each fungus tested

Fungus: species	Mass loss (%) for each fungus			
	Gloeophyllum trabeum	*Coniophora puteana*	*Coriolus versicolor*	*Serpula lacrymans*
Acacia aroma—zone A	9.1 (1.8) N = 4	2.6 (1.5) N = 6	17.8 (8.2) N = 4	5.1 (1.5) N = 4
Acacia aroma—zone B	3.5 (0.4) N = 3		3.9 (0.5) N = 3	3.1 (0.8) N = 3
Acacia aroma—zone C	2.5 (0.1) N = 3	0.9 (0.2)[a] N = 6	2.6 (0.7) N = 3	2.1 (0.4) N = 3
Prosopis alba—zone A	6.4 (1.2) N = 3	2.0 (0.5) N = 6	6.5 (2.6) N = 3	5.8 (0.7) N = 3
Prosopis alba—zone B	0.0 (0.0) N = 6	4.5 (1.8) N = 6	4.0 (1.0) N = 6	4.3 (1.1) N = 6
Prosopis alba—zone C	0.0 (0.0) N = 6	1.3 (1.2) N = 6	2.3 (1.1) N = 6	2.1 (1.1) N = 6
Prosopis kuntzei—zone A	4.9 (0.9) N = 6	4.1 (1.3) N = 6	17.5 (9.0) N = 6	4.2 (0.9) N = 6
Prosopis kuntzei—zone B	8.2 (2.7) N = 6	6.1 (1.3) N = 6	10.5 (4.1) N = 6	9.5 (2.3) N = 5
Prosopis kuntzei—zone C	15.3 (2.1) N = 6	5.0 (0.6) N = 3	15.9 (2.1) N = 6	17.9 (2.2) N = 6
Prosopis nigra—zone A	9.1 (4.5) N = 2	9.0 (2.8) N = 6	15.1 (4.8) N = 2	12.5 (2.0) N = 2
Prosopis nigra—zone B	4.0 (4.3) N = 5	0.6 (0.0) N = 1	1.9 (0.2) N = 5	1.7 (0.3) N = 5
Prosopis nigra—zone C	4.4 (7.2) N = 6	0.8 (0.4) N = 6	3.1 (2.5) N = 6	10.7 (2.6) N = 5
Prosopis ruscifolia—zone A	6.1 (3.3) N = 4	3.6 (3.4) N = 6	16.4 (1.9) N = 4	4.4 (0.9) N = 4
Prosopis ruscifolia—zone B	2.9 (0.5) N = 5	0.4 (0.3)[a] N = 6	4.7 (4.4) N = 5	1.6 (0.7) N = 5
Prosopis ruscifolia—zone C	3.6 (3.6) N = 5		8.0 (3.9) N = 5	1.3 (0.2) N = 5
Fagus sylvatica	2.1 (0.2) N = 6	15.5 (19.4) N = 6	14.8 (11.4) N = 6	43.5 (5.5) N = 6

Standard deviation between parentheses. N = sample size. Zone A: sapwood; zone B: external heartwood; zone C: inner heartwood

[a] Indicates no distinction between zones B and C

Table 2 Durability index and durability class obtained from maximum mass loss of each zone differentiated for sapwood (S, corresponding to zone A) and heartwood (H, corresponding to zones B: external heartwood and C: inner heartwood)

Species	Durability index	Durability class
Acacia aroma S (A)	0.38	3 Mod. durable
Acacia aroma H (B)	0.12	1 Very durable
Acacia aroma H (C)	0.07	1 Very durable
Prosopis alba S (A)	0.19	2 Durable
Prosopis alba H (B)	0.38	3 Mod. durable
Prosopis alba H (C)	0.13	1 Very durable
Prosopis kuntzei S (A)	1.08	5 Not durable
Prosopis kuntzei H (B)	0.61	4 Sligh. durable
Prosopis kuntzei H (C)	1.68	5 Not durable
Prosopis nigra S (A)	0.28	2 Durable
Prosopis nigra H (B)	0.04	1 Very durable
Prosopis nigra H (C)	0.75	4 Sligh. durable
Prosopis ruscifolia S (A)	0.32	3 Mod. durable
Prosopis ruscifolia H (B)	0.10	1 Very durable
Prosopis ruscifolia H (C)	0.17	2 Durable

All the species were classified as slightly durable to very durable, except for *P. kuntzei*, which was classified as not durable to moderately durable. In all cases, heartwood was most resistant to fungal attack (Table 2). Exudates and black substances were produced by *P. kuntzei* during the fungal exposure. These exudates could be attributed to the high quantity of extractives present in this species (Table 3) and some of the mass loss could actually be extractive loss.

Generally, a higher heartwood extractive content imparts higher decay resistance (Tsoumis 1991; Onuorah 2000; Rowell et al. 2005). For all the species, sapwood (zone A) was substantially less resistant to decay than heartwood (zones B + C) (Table 1). Moreover, in some cases substantial differences on mass loss between external heartwood (zone B) and internal heartwood (zone C) could be observed, for example in *P. alba*, *P. kuntzei* and *P. nigra*. In these last two species, the differences are due to a lower mass loss in zone B (Table 1). Other authors found a similar situation and correlated this fact with the high extractives concentration in the external heartwood; hence the innermost portion of the heartwood has a lower resistance to fungal attacks as compared to its outer portions (Giordano 1988; Windeisen et al. 2002).

The amount and the type of extractives present in a particular material may provide a good indication of its durability (Schultz et al. 1995). Gérardin et al. (2004) attributed the fungal and termite resistance of *Prosopis africana* to the presence of gums which fill the cell lumens, and alter the hydrophobic character of wood cells. They support this hypothesis by noting a volumetric swelling coefficient of only 6% for this species. Sirmah et al. (2009) found that the antioxidant properties of one of the extractives of *Prosopis juliflora* could improve fungistatic properties and hence, natural durability of *P. juliflora* heartwood.

Table 3 Percentage wt/wt of the various types of extractives based on oven-dry weight

Species	Organic extractives (%)	Aqueous extractives (%)	Tannic substances (%)	Non-tannic substances (%)	Phenolic compounds (mg eq. gallic acid/g d.m.)
P. alba (S)	9.94 (2.49)	10.65 (3.33)	5.77 (0.13)	4.49 (0.23)	6.31 (–)
P. alba (H)	16.59 (2.49)	2.91 (0.92)	11.01 (2.05)	3.90 (0.16)	128.09 (3.47)
P. kuntzei (S)	5.13 (0.01)	2.24 (0.48)	0.51 (0.45)	5.05 (0.23)	9.99 (–)
P. kuntzei (H)	20.83 (0.16)	2.93 (0.06)	17.10 (2.39)	4.25 (0.47)	213.83 (0.50)
P. nigra (S)	9.11 (1.98)	5.17 (0.18)	2.70 (0.17)	5.28 (–)	10.22 (–)
P. nigra (H)	8.18 (1.52)	3.49 (0.29)	4.46 (1.15)	1.89 (0.26)	82.51 (3.58)
P. ruscifolia (S)	4.78 (0.89)	4.09 (2.81)	2.91 (0.78)	4.82 (1.39)	7.42 (–)
P. ruscifolia (H)	5.90 (0.85)	3.15 (1.45)	3.64 (1.20)	3.60 (0.40)	27.10 (6.58)
A. aroma (S)	8.68 (2.46)	6.73 (1.23)	1.69 (0.77)	4.50 (–)	10.11 (–)
A. aroma (H)	16.59 (0.32)	8.76 (0.84)	8.14 (0.37)	8.27 (0.16)	50.19 (11.36)

S sapwood, *H* heartwood; mg eq. gallic acid/g d.m. = mg equivalent of gallic acid per gram dry mass. Standard deviation between parentheses

Schultz and Nicholas (2000) have hypothesised that extractives could act both as fungicides and as free radical scavengers (antioxidants). Free radicals are not biocidal, but they can inhibit enzymatic activity.

In this work, as evidenced from the results of extractable contents (Table 3) and of durability tests (Table 1), extractives was not a good predictor of considered species: in some cases where there was a difference on total extractive content between sapwood and heartwood, there was no differences on mass loss between these two zones. This can be observed in *P. alba* and *P. kuntzei* where there was a remarked difference in organic extractive content between sapwood and heartwood that could not justify a similar mass loss in these two zones. On the other hand, *P. nigra* had a similar amount of organic extractives in sapwood and heartwood and there was a great difference in mass loss between these two zones. Similar results were found by Paes et al. (2004) studying durability of nine wood species and their aqueous extractives, especially for *Prosopis juliflora*, where the amount of aqueous extractives was poorly correlated with decay resistance.

The amount of tannic substances was higher in the heartwood for all the species (Table 2). The value obtained for *P. alba* (11.01%) is in accordance with that reported by Tortorelli (1956) of 10–12%. The comparison with durability indexes for heartwood and sapwood of all the species yields similar results to those obtained with total extractives. Not in all cases is the mass loss lower in the heartwood or is the durability of this zone higher (Tables 1, 2 and 3).

The relationship between the quality of extractives, in addition to their quantity, and the durability against fungi, was investigated considering the mass loss data coming from the experiments with *Coriolus versicolor*. This fungus was taken into consideration because of its greater aggressiveness, good availability and completeness of experimental measurements.

When the amounts of organic and aqueous extractives (Table 3) were separately compared with the durability index (Table 2), it was not possible to observe any proportionality between either the durability or the organic or the aqueous content of extractives ($R^2 = 0.031$ and 0.269, respectively; graphs not shown).

Conversely, when the mean mass loss of each specific zone was compared with the value of phenolic compounds measured in the same zone, the graph shown in Fig. 3 was obtained. It appeared evident how a clear decrease of mass loss (i.e. an increase of durability) could be observed with the increase of phenolic content in the extract for the considered wood species, except for *P. kuntzei* but including *A. aroma*, which also fitted quite well with the points of other *Prosopis* species. In particular, the relationship between mass loss and phenolic content shown in Fig. 3 was of hyperbolic type ($R^2 = 0.975$). This observed relationship confirms the very important role played by phenolic compounds. Phenolic extractives of plants are known to be the main reason for the natural durability of lignocellulosic materials, with free phenolic groups of lignin acting as antioxidants (Schultz and Nicholas 1997). However, the fact that both the blocks sampled from the heartwood of *P. kuntzei* (zones B and C) did not fit within this relationship allows to argue that these compounds could not be the only substances responsible for determining the durability of *Prosopis* species.

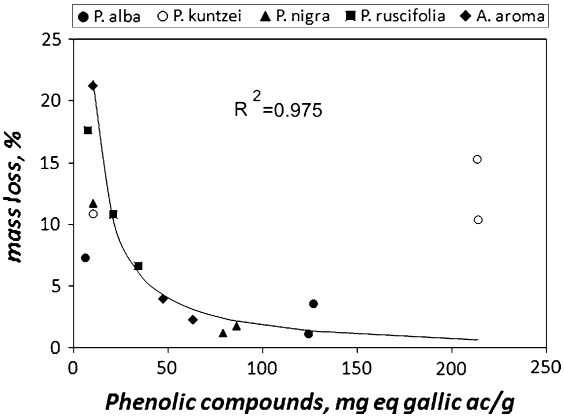

Fig. 3 Relationship between mass loss and amount of phenolic compounds of the heartwood and sapwood of five *Prosopis* and *Acacia* species

Another factor influencing decay resistance is wood specific gravity that is considered as an indicator of decay resistance in both angiosperms and gymnosperms (Panshin and de Zeeuw 1980). The species studied here have densities from 0.69 g/cm^3 for *P. alba*, to 1.11 g/cm^3 for *P. kuntzei* (Pometti et al. 2009) and there was no relationship between density and decay resistance, since the heaviest species *P. kuntzei* is moderately durable and the softest one, *P. alba* is very durable (Table 3) ($R^2 = 0.325$; graph not shown). Similar results where no relationship between density and decay resistance exists were found by Bhat et al. (2005) and Paes et al. (2004).

By taking into account all the aspects considered so far, it was not possible to find a unique and definite factor able to determine durability of all the *Prosopis* species here considered and of *A. aroma*. In a previous study (Pometti et al. 2009), the physical characteristics of the same species considered in this work were measured, and it was found that *P. kuntzei* had a similar or even lower volumetric shrinkage coefficient than other species (4.8% for *P. alba*, 5.5% for *P. kuntzei*, 7.3% for *P. nigra* and *P. ruscifolia*, 8.4% for *A. aroma*). Moreover, heartwood of *P. kuntzei* had a lower than expected specific volumetric shrinkage in comparison to its density value. Therefore, it does not seems that the durability of *Prosopis* species can be simply related to its hydrophobic character.

Prior to broad use of chemical preservatives for protection of biodeterioration, the use of naturally durable species provided the only means of ensuring long-term service of these materials in hazardous environments (Yalinkiliç et al. 1998). In recent years, naturally durable species have again gained interest due to the health risks or environmental problems associated with the application of wood preservatives (Willeitner and Peek 1997). In this sense, all the species of *Prosopis* and *Acacia* examined here may be classified as slightly durable to very durable. These findings, together with the results obtained in a previous work where these species proved to be very resistant woods (Pometti et al. 2009), determine that they could be used as external frame, fences, ships, bridge supports, furniture, floors, among others.

The amount of all the chemical extractives (organic, aqueous, tannic, phenolic) was higher in the heartwood.

With the exception of phenolic compounds, the durability of the species did not show a good relationship with extractive contents nor the wood density. Instead, it is possible that extractives could contribute to natural durability in different ways, including the effects related to the antioxidant properties of some of them, as reported. Further investigation is needed in order to verify this hypothesis; this deepening work will have to be aimed at enlarging the spectrum of mass analyses, even by using other and different techniques.

The evaluation of decay resistance of this study, although preliminary, provides a basis for validating these species and for a more efficient utilization of their wood.

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