Comparison of Woods Extractives Coming from Species Commonly used in Manufactures of Wood

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ABSTRACT

Wood extractives are considered commonly of major importance for the wood toxicity. Probably the first step of illness is the penetration of toxic molecules into human corpus, so we examine and compare extractives coming from woods commonly in Morocco industry. We solvate extractives from direct wood powder in water, sodium chloride solution and ringer salt solution. Dry powder of extractives woods are then characterize by IR spectra. We found great correlation between group of IR peaks that limit the independent peaks at five, each of them being characteristics of one or more chemical bonds. Comparing the peaks intensity between the free solvent show a selectivity effect of salts against the chemical bonds present into the extracts.

Keywords : Woods extractives, water solution extraction, IR spectra characterisation.

INTRODUCTION

Wood extractives is the part of wood which is soluble into a solvent, their chemical composition depends of wood nature and experimental conditions for the extraction, the majors factors being: the wood species, the nature of the solvent, the temperature and in a minus importance the pressure of the extraction.

They have importance in many domains: green chemical industry or pharmacology for the production of molecules, winery for the maturity of wine or medicine because they are named to be responsible of illness coming from wood like asthma, skin allergy or ethmoid bone carcinogenesis

The medicals studies on wood toxicology underlined that the nature of wood exposure is determinant in the kind of damage made in human corpus [1, 2, 3, 4]. In these studies our purpose is to characterise the extractives in pure water or salted water with sodium chloride or ringer solution. These conditions are chosen because in human corpus water is present everywhere and commonly

associated with salts, sodium chlorine being the major in mass, which regulate the osmotic pressure into corpus, ringer salt is a mix which has the same osmotic pressure than the blood.

Particles of wood in contact with human corpus, especially respiratory tree, are essentially dust with a size consistent with an air transport, with a maximum size near hundred microns, below sedimentation is very efficient [5]. The more efficient machinery to produce this size band is sandpapering [6] for which particle production is very important because the small size of particles and particle pick up is difficult because their transport by air is very easy.

In this work we compare the dry extracts coming from different species of wood by the way of FTIR spectra analysis. After, we study the influence of the ionic strength on the solubility of the extractives components. Wood used was four softwoods, three hardwoods and six exotic woods, each of them currently used in European country.

MATERIALS AND METHODS

Dry extractives extraction

Our woods choice integrates a panel of common woods used in morocco. We have tested: Softwoods: Atlas cedar (*Cedrus atlantica*), cedar (*Tetraclinis articulata*), fir (*Abies alba*), pine (*Pinus nigra*) and douglas (*Pseudo tsuga menziesii*). Hardwoods: ash (*Fraxinus excelsiors*), beech (*Fagus sylvatica*) and oak (*Quercus radiata*), Exotic woods: ipe (*Lovoa trichiloides*), iroko (*Milicia excelcia*), mahogany (*Khaya ivorensis*), samba (*Malvales malvaceale*), teak (*Tectona grandis*), wenge (*Milettia laurentii*).

Each of them is sandpapered with a 120 grain band. Powder is sieved between 0-18 µm. 6g of this powder is placed in 400 ml of solution for extraction in a bath at a regulated temperature of 37°C, permanently agitate during 24 hours. Solution could be: Pure distilled water, distilled water with a concentration of 20g/l of sodium chloride or a ringer solution (NaCl 2.25 g/l, KCl 0.105 g/l, $CaCl_2$ 0.12 g/l and $NaHCO_3$ 0.05 g/l).

Solution with extractive is filtrated on a membrane of cellulose at a 0.45 µm aperture. The filtrate is then lyophilized to obtain the extracts or the mix extracts + salts before weighting. The dry product is kept in a glass flask for diminishing later atmospheric water exchange.

Infra Red Spectra

0.5 mg of dry product, that is pure extract powder with or the mix extracts and salts are mixed and compressed at 20 bars with solid KBr to do a 6 mm thick drop. The drops are then analyzed with a Perkin Elmer FTIR apparatus in transmittance. For minimizing errors, for each extracts, two drops are analyzed and for each drop we do three scans at different angle, results are meant.

Even our care, spectra present shifts in base line and intensity so we rectify in normalization at 50% of transmittance of the O-H band (3400 cm⁻¹). We choose this band because it is the brighter band of the spectra, then normalisation minimizes the correction, and this band integrates different possible water content into the different samples due to the extracts nature itself and with hygroscopic salts when presents.

RESULTS
Presentation of spectra: bands of interests

In wood extracts, the nature of organic molecules present is very important [2, 4, 6, 7, 8], but in IR we see only, their bonds and so the different group of organic function are relatively few (Fig. 1). With the aid of IR table [9] and the interpretation from [9], we can present interpreted spectra in Fig.1.

Fig.1 shows differences between the three woods extractives peaks, for example the C-H peaks at 2,925-2,850 cm⁻¹ are more evident in cedar than in beech, peak at 1,635 cm⁻¹ is different for the three woods etc… from this spectra it is not possible to specify wood family, in each of them, each band height vary with an importance for which it is not possible to differentiate the three family.

From our results, we can evidence eighteen remarkable peaks because presents in more than three times in the different spectra of woods extractives. For a peak position we consider a precision in frequency of ± 10 cm⁻¹, which seems the wide band of frequency near the maximum from
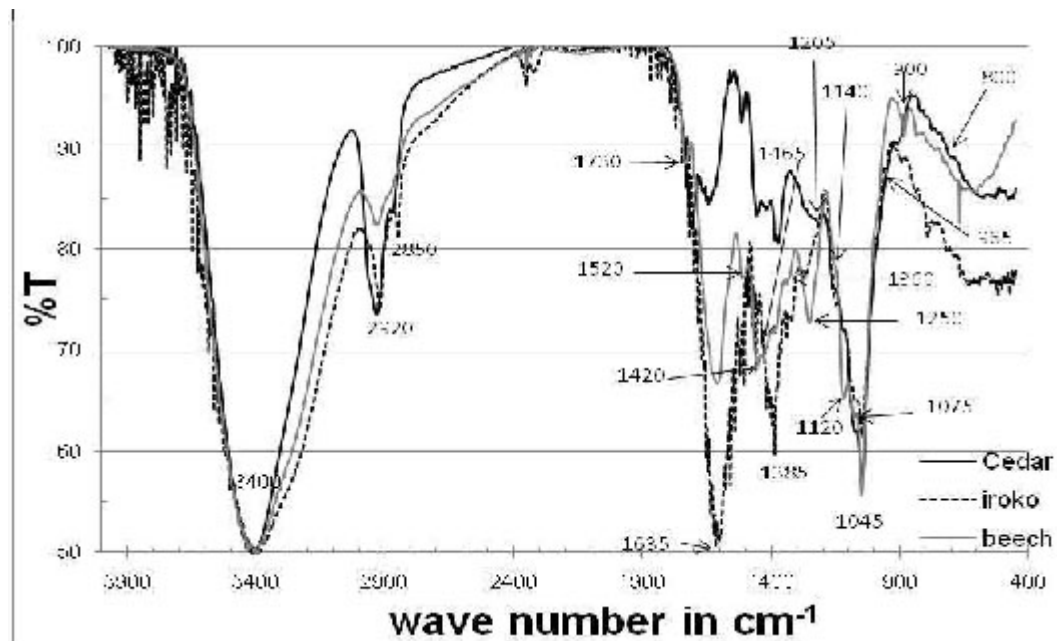
**Fig.1: examples of FTIR spectra from three chosen wood extracts
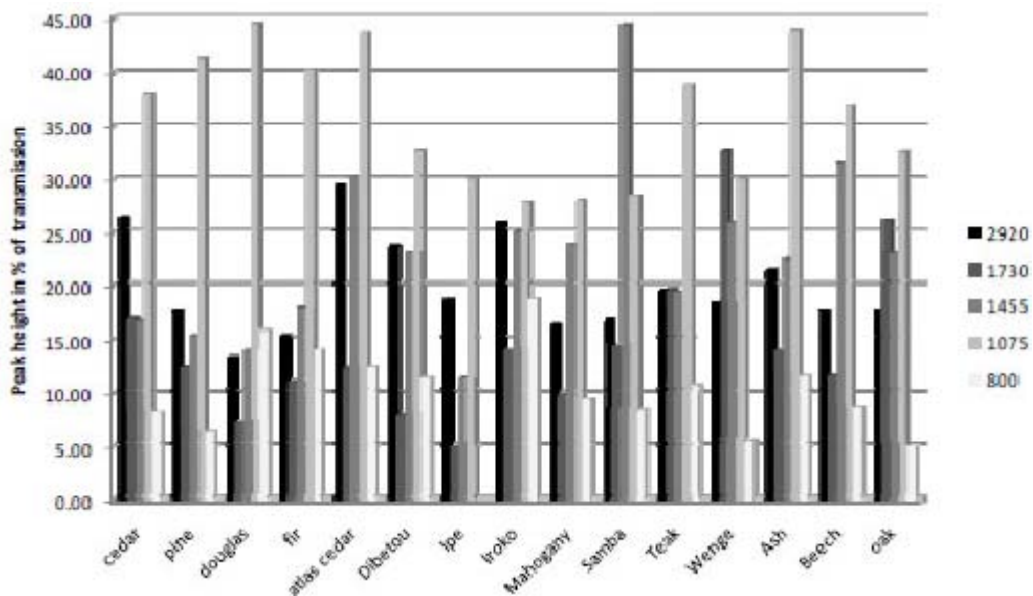and positioning of the studied peaks**

Fig. 2: five chosen band intensity obtained with wood extracts.

Table 1: bands wave number and possible organic function associated.

IR bands in cm^{-1}	Bonds attribution
2920	C-H stretching from: All alkanes, alkenes substituted
2850	C-H stretching from : All aldehydes aliphatic or aromatics
1730	C=O stretching from: All esters, aldehydes ketones and carboxylic acids
1630	C=C stretching from : All and aromatics alkenes
1520	aromatics bonds substituted or not and ionized carboxylic acids
1455	C-C from : All alkanes
1420	C -C from : All alkanes and alkenes
1385	C-C all alkanes; alkenes di substituted, naphthalene, all alcohols, carboxylic acid, aldehydes
1360	c-c alkanes, alkenes di substituted, alcohols tertiary and aromatics, carboxylic acids, aldehydes
1250	c-c alkanes tertiary butyl, aromatics ethers, aromatic alcohols, carboxylicacids, esters acrylates fumarates benzoates, aromatics ketones
1205	alkanes tertiary butyl, aromatics ethers, alcohols tertiary and aromatics,carboxylic acids, all esters, aromatics aldehydes, aliphatic ketones
1145	alkanes tertiary butyl, aromatics (di substitution ortho or meta; tri substitution all), alcohols tertiary and aromatics, all esters, aromatics ketones
1120	alkanes isopropyl, aromatics (di substitution ortho or para; tri substitution unsymmetrical) aliphatic ethers, alcohols secondary and tertiary, esters acetates and benzoates, aliphatic aldehydes, aliphatic ketones
1075	alkanes ethyl and propyl, aromatics (mono substituted, di substitution ortho or meta, tri substitution vicinal or unsymmetrical), aliphatic ether, secondary alcohols, aromatics alcohols, aliphatic aldehydes
1045	alkanes ethyl, N propyl, aromatics (mono substituted, di substitution allposition, tri substitution unsymmetrical and symmetrical), all ethers, primary alcohols, aliphatic aldehydes
965	alkenes vinyl di substitution trans, aromatics di substituted ortho, tri substituted vicinal, aromatics ethers, all aldehydes
900	alkenes vinyl mono and di sub, carboxylic acids, all aldehydes
800	alkenes di substituted cis or di substituted on same C, aromatics (disubstitution meta or para, tri substitution unsymmetrical, naphthalene)

which we consider two peaks as different from a spectra to another, this band width becomes from a possible derive of the apparatus and the derive becoming from molecular environment inside the molecules. For each peak (table 1) we could attribute one or more chemical organic function from handbook's IR charts [9]. In this attribution, we have eliminated all molecules with nitrogen because his content is very low in wood extracts [10, 11] and so his contribution appears to be negligible compare to those of C, H, O.

From table 1, we can precise the general composition of extracts, they are constituted from alkanes, alkenes, aromatics with the classical oxygen function alcohols, esters, aldehydes, acids and ethers. IR bands intensity results from two factors: Number of bonds present and intrinsic intensity response of a bond taking into account the molecular environment.

Peaks intensity in water extracts

From the analysis of the woods spectra, we found the peaks intensity for the different woods extracts (annex 1 and fig 2). We remark that twelve of them are common at all the wood species and seven are not present for every wood. In our species, when a peak is present, it is at least for a group.

Peaks intensities vary from a wood to another which means that the relative abundance

Annex 1: table of peaks extracts form our IR spectra in % of transmission. The wave numbers are given indicatively, then between the different wood, two peaks distant from minus ± 10 cm⁻¹ are considered as the same. Blank cell= no peak in the neighbourhood within ± 10 cm⁻¹.

| wave number	cedar	pine	douglas	fir	atlas cedar	Dibetou	Ipe	Iroko	Mahogany	Samba	Teak	Wenge	Ash	Beech	oak
2990	73.50	82.40	86.60	84.60	71.60	76.20	81.30	74.10	83.60	81.08	80.40	81.50	78.50	82.30	82.20
2850	81.50	80.60	87.50	86.50	71.00	82.30	17.30	81.10	80.00	87.00	86.90	86.10	84.80	81.00	87.90
1730	83.00	87.60	92.70	88.90	87.70	92.00	95.00	86.00	90.00	85.60	80.30	67.30	86.00	81.40	73.90
1630	84.70	83.50	83.80	81.20	72.00	61.00	37.10	50.50	67.40	54.90	72.00	74.00	77.80	66.80	75.20
1520	92.60	90.90	91.90	80.00	75.60								79.10	77.10	88.80
1455	83.20	84.60	86.00	82.10	69.80	77.00	88.60	75.00	76.00	55.60	80.60	74.10	77.50	66.50	77.00
1420	83.90	83.90	82.90	81.20	67.30								79.00	65.30	78.00
1385	80.60	81.90	82.20	78.50	71.50								78.10	71.70	75.00
1380	87.10	87.70	84.50	85.20	73.20	81.00	90.00	73.30	83.00	77.00	80.50	67.60	82.40	76.50	71.10
1290	83.30	80.20	82.60	73.20	71.50	84.00	86.80	78.00	78.70	73.10	74.80	74.00	73.70	71.70	74.00
1205	82.50	89.00	85.00	82.20	65.80	82.80	82.80	85.80	82.50	81.00	83.00	64.00			
1145	83.00	77.60	68.60	73.50	63.50										
1120													67.70	65.20	72.70
1075	62.00	58.80	55.50	59.70	56.30	67.30	70.00	72.20	72.00	71.60	61.30	70.00	56.10	61.20	67.40
1045	57.30	61.80	60.10	57.60	54.90	68.10	68.60	61.50	69.50	71.00	58.10	62.60	56.70	55.60	61.20
985	85.50	91.20	83.30	83.50	83.60										
900	91.40	94.90	87.80	89.40	83.70	92.60	100.00	88.60	54.10	84.60	90.40	96.00	90.70	93.00	94.30
800	91.70	93.60	84.10	86.00	87.60	88.60	100.00	81.20	90.70	91.50	89.20	94.40	88.50	91.30	95.00
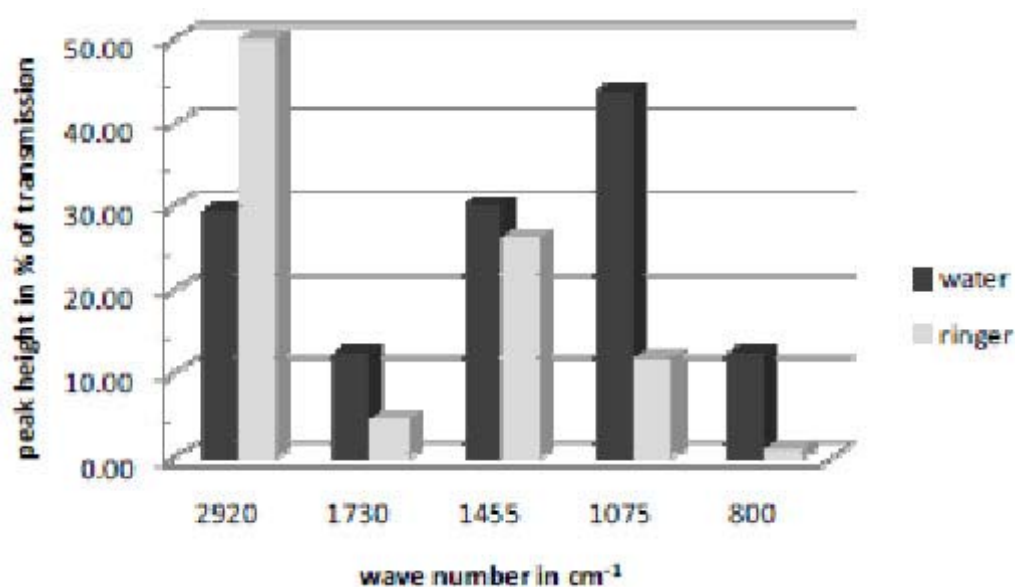
Fig. 3: comparison of peak height from Atlas cedar extraction in pure water or with a ringer solution
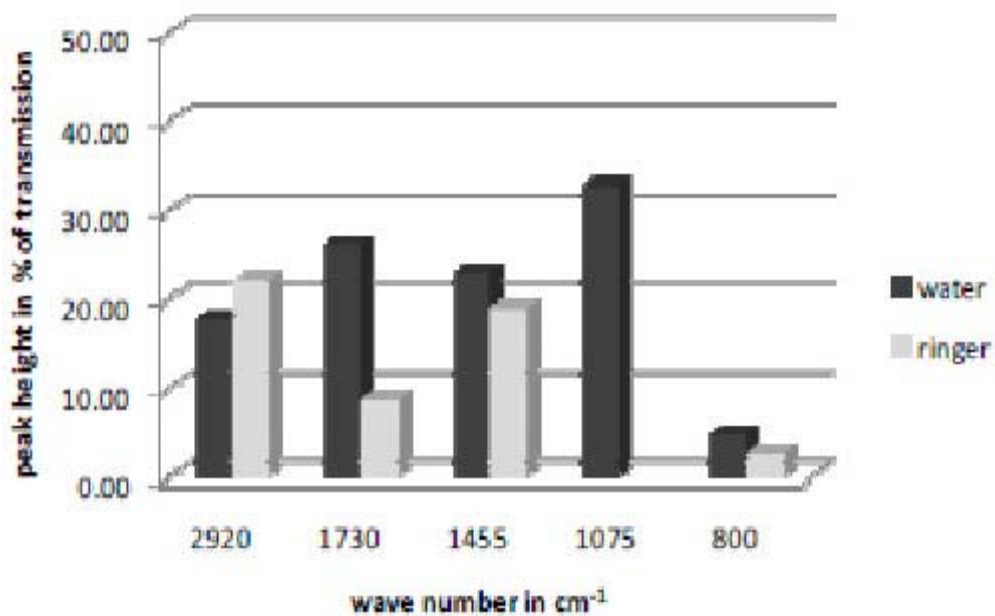
Fig. 4: comparison of peak height from oak extraction in pure water or with a ringer solution..
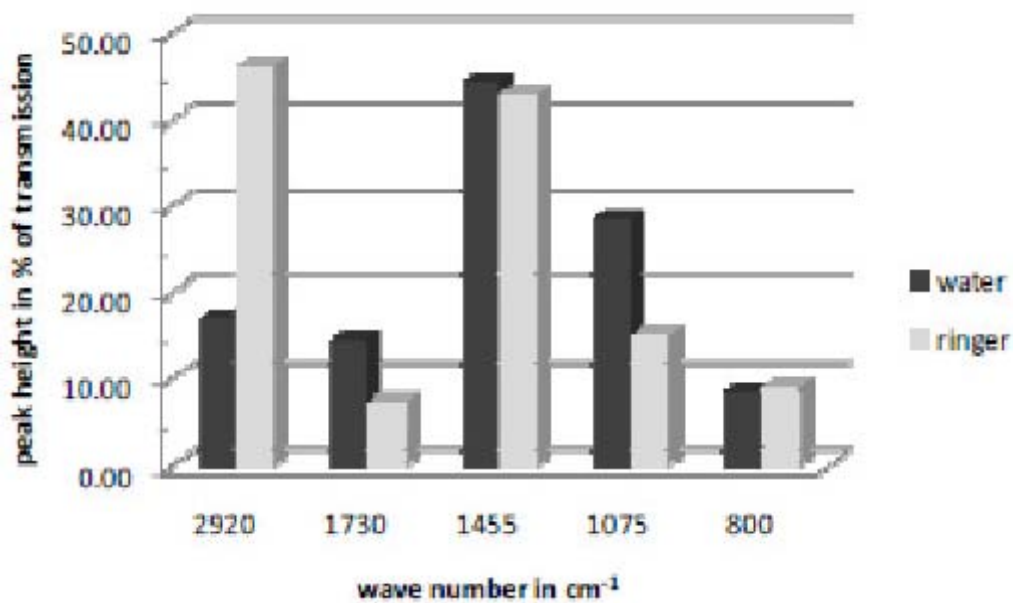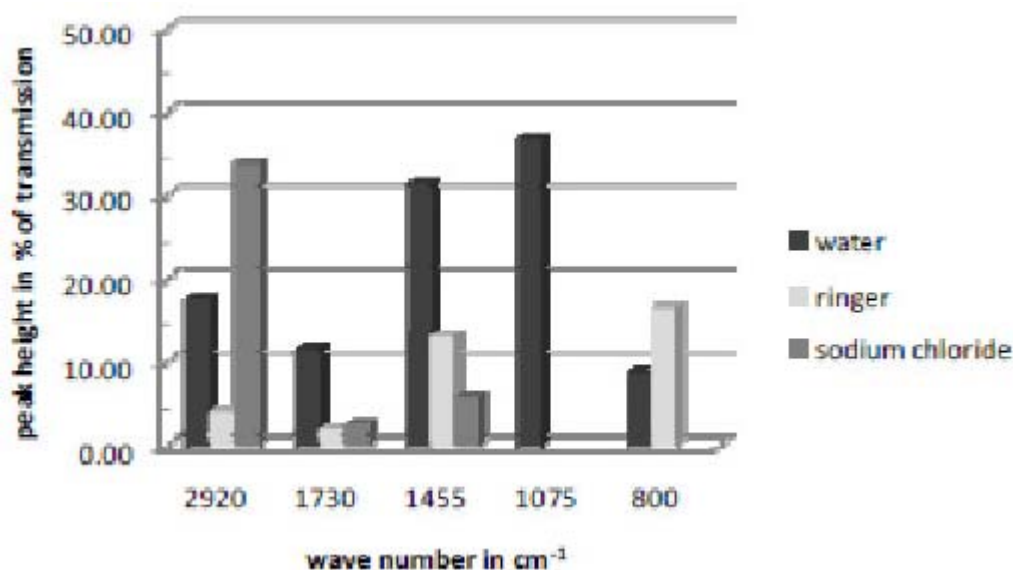

Fig. 5: comparison of peak height from samba extraction in pure water or with a ringer solution.

**Fig. 6: comparison of peak height from beech extraction in pure water,
with a ringer solution or in a sodium chloride aqueous solution.**

in the different bonds detected in the extracts is different from one to another. For example, in iroko and samba, 1630 cm^{-1} band is very important probably the result of a high content in alkenes and aromatics. At the other part for pine and wenge, the intensity of 900 cm-1 band is minus, indicating probably a globally small content in certain alkenes, carboxylic acids and aldehydes. All our results are presented in annex 1. For our research we don't take into account the peaks at 1120 and 965 cm^{-1} because there are not enough present in a sufficient number of species.

Inter band correlation in water extracts

Like our results are not specific for one or another band (Table 1), it becomes of interest to evidenced correlation between bands because it signifies that one or more kind of bonds give the major part of the intensity and so their bonds are minus. For looking at inter band correlation we have represent the linear regression between all bands and the other. We have compared the r² obtained with the value into Bravais-Pearson coefficient table for a degree of significance of 99% or 95%, these two values represent the strength of the links. The results are shown in Table 2.

We can cut the table 2 in independent parts:
- Group 1 constituted by 2920 and 2850 cm-1, these two bands are not in relation without any other. Their mutual coefficient of regression is very significant.
- Group 2 constituted by the band 1730 cm^{-1} for which exists a strong correlation with the band 1360 cm^{-1} and a less with the band 1205 cm^{-1} and 800 cm^{-1} but these two bands are more significant with other bands which not correlate with 1730 and then 1730 cm^{-1} could not be in strong relation with the other.
- Group 3 with 1630, 1520, 1455, 1420, 1385, 1360, 1250, 1205, 1145 cm-1 for which correlation are generally at 60% of them at 99% and at 16% of them not significant.
- Group 4 is the pair 1075, 1045 cm^{-1}, for which the correlation is significant at 99%.
- Group 5 with 900 and 800 cm^{-1} for which coefficient is similar to precedent.

From these six groups, we can isolate six different and independent wave number from which we can characterize each wood extracts. Arbitrary we choose 2920, 1730, 1455, 1075 and 800 cm^{-1} because they are the most important into their own group.

Table 2: Coefficient of linear regression, between the IR bands R. cell full in dark grey = coefficient significant at 99%, in light grey = coefficient significant at 95%, in white coefficient non significant (R above value for signification at 95%).

R for 99%	0.64	0.64	0.64	0.64	0.83	0.64	0.83	0.83	0.64	0.64	0.71	0.64	0.64	0.66	0.66
R for 95%	0.51	0.51	0.51	0.51	0.71	0.51	0.71	0.71	0.51	0.51	0.58	0.51	0.51	0.53	0.53
wave number	2920	2850	1730	1630	1520	1455	1420	1385	1360	1250	1205	1075	1045	900	800
2920	1.00	0.87	0.03	0.25	0.26	0.12	0.41	0.38	0.17	0.00	0.32	0.05	0.29	0.09	0.21
2850	0.87	1.00	-0.07	0.29	0.35	0.17	0.41	0.33	0.23	0.05	0.43	0.11	0.21	0.28	0.44
1730	0.03	-0.07	1.00	0.06	-0.20	0.21	-0.02	0.23	0.71	0.49	0.58	-0.19	0.16	-0.46	-0.57
1630	0.25	0.29	0.06	1.00	0.75	0.75	0.93	0.96	0.58	0.28	0.03	-0.56	-0.39	0.27	0.27
1520	0.26	0.35	-0.20	0.75	1.00	0.79	0.78	0.76	0.42	0.90	0.77	0.15	0.77	0.14	0.22
1455	0.12	0.17	0.21	0.75	0.79	1.00	0.97	0.97	0.62	0.58	0.36	-0.33	-0.35	0.24	-0.16
1420	0.41	0.41	-0.02	0.93	0.78	0.97	1.00	0.96	0.74	0.76	0.97	-0.05	0.68	0.00	0.02
1385	0.38	0.33	0.23	0.96	0.76	0.97	0.96	1.00	0.84	0.83	0.97	-0.31	0.62	-0.14	-0.15
1360	0.17	0.23	0.71	0.58	0.42	0.62	0.74	0.84	1.00	0.64	0.67	-0.33	0.05	-0.17	-0.17
1250	0.00	0.05	0.49	0.28	0.90	0.58	0.76	0.83	0.64	1.00	0.55	0.18	0.36	0.02	-0.14
1205	0.32	0.43	0.58	0.03	0.77	0.36	0.97	0.97	0.67	0.55	1.00	0.01	0.22	-0.24	-0.27
1075	0.05	0.11	-0.19	-0.56	0.15	-0.33	-0.05	-0.31	-0.33	0.18	0.01	1.00	0.71	0.19	0.19
1045	0.29	0.21	0.16	-0.39	0.77	-0.35	0.68	0.62	0.05	0.36	0.22	0.71	1.00	-0.10	0.19
900	0.09	0.28	-0.46	0.27	0.14	0.24	0.00	-0.14	-0.17	0.02	-0.24	0.19	-0.10	1.00	0.70
800	0.21	0.44	-0.57	0.27	0.22	-0.16	0.02	-0.15	-0.17	-0.14	-0.27	0.19	0.19	0.70	1.00

Influence of salts on peak intensity

The presence of sodium chloride (fig 6) or ringer salt (fig 3, 4, 5, 6) in water changes the peak height comparing to water extraction.

DISCUSSION

Water extracts

Water is a polar solvent and so it solubilises molecules with polar function. In wood extracts these molecules are sugars and polyphenol essentially[2,4,6,7,8]. This remark is seen from the nature of organic functions represented into table 2: The most part of bands are attributed to alcohol, ketones, esters functions which are with dipolar momentum. The other function like aliphatic or aromatic group is present because associated with a polar function[12,13].

If we refer to table 1 and 2, we found the explanation from the group existence; the same chemical functions are present inner a group. So we can characterise each of them by a chemical function

- Group 1 characterises the C-H function, wave number associated 2920 cm^{-1}.

- Group 2 characterises the entire C=O functions at a wave number associated 1730 cm^{-1}.

- Group 3 C=C and C-C vibrations functions with a wave number associated 1455 cm^{-1}.

- Group 4 aromatics and ethers wave number associated 1075 cm^{-1}.

- Group 5 alkenes and aromatics, wave number associated 800 cm^{-1}.

Intensity of group 1 stays relatively constant at 18±1.1 % of transmission except for cedar, Atlas cedar and iroko which are very greater, near 27 %
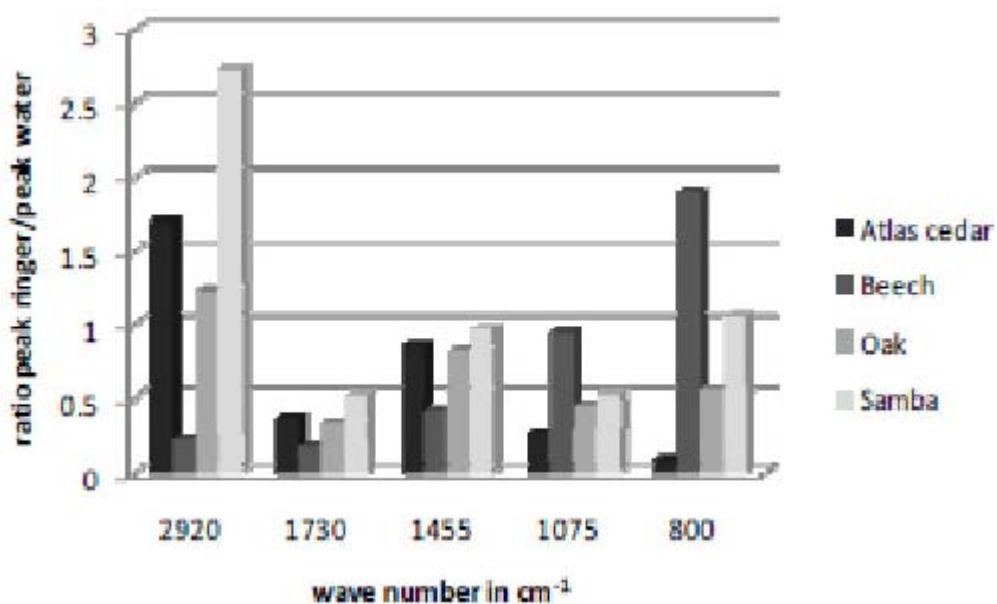
Fig. 7: Influence of a ringer solution on extractives composition for five woods. In ordinate we represent the ratio of the peak height for a wood in a ringer solution on that of the same peak in water extraction.
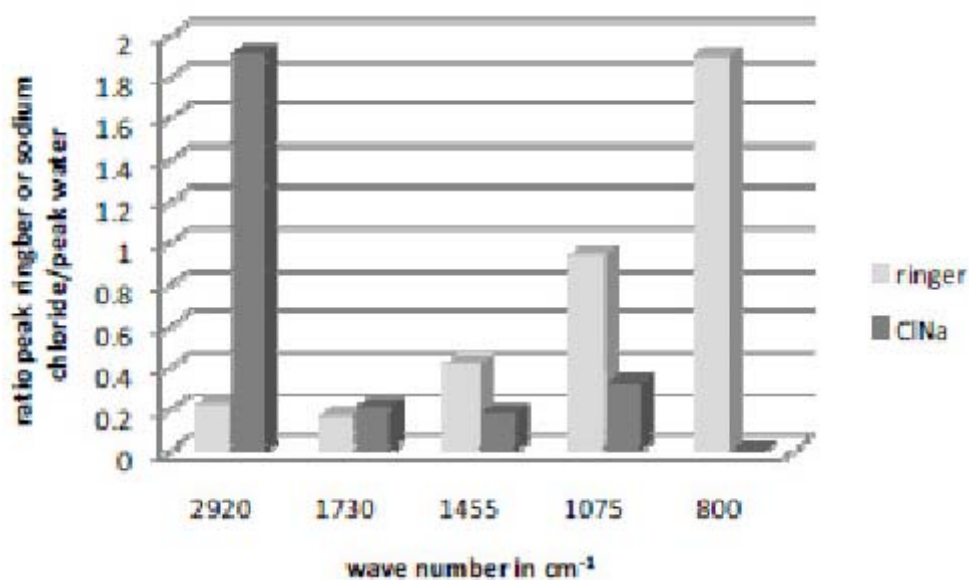

Fig. 8: Comparison of ringer – sodium chloride water extraction for beech. Ordinate is the ratio between ringer peak height on sodium chloride peak height.

of transmission, and fir and douglas which are fewer, near 14% of transmission. For group 4 all woods keep a peak height near the arithmetic mean at 36 % ± 6 of transmission. For the other group, peaks heights vary without any logic from a wood to another. So we can conclude that the C-H and aromatic content in extractives seems to be stable from the studied wood but not the other bonds.

A corollary of this conclusion concern the potential toxicity of the extractives: the global aromatic content could not be representative of their toxicity in accord with [2, 4, 6, 7, 8].

Salted water solutions extract

In a ringer solution, pH is a little basic at 7.3-7.4 as the major part of organic alcohols present in the extracts have pKa near 10, near 17 for aldehydes and near 20 for ketones so their basic forms are not present in ringer solution contrarily with organic acids which are probably in basic forms (pKa near 3-4).

In fig. 7 we enhance that for the groups 2, 3, 4 the bar height for the ringer's extractives are less concentrated in C=0 (1730 cm^{-1}), C=C and C-C (1455 cm^{-1}) and aromatics + ethers (1075 cm^{-1}) than those of water. The presence of salts in water has diminished the solubility of polar bonds, like C=O in all forms except the minor amount of organic acids. These last could react with the amphoteric salt of $NaHCO_3$ present in ringer solution and so could solubilise a part of them.

For the C-H group (2920 cm^{-1}), extraction is greater except for beech for which the extraction is very fewer (~1/5). The salts present in ringer solution are not able to change the degradation of organic macromolecules, if C-H solubilisation growth it could be assigned to the solubilisation of organic acids which react with the basic $NaHCO_3$, favouring the dissociation and the solubility.

For the di-substituted alkenes group (800 cm^{-1}), the extraction is better for beech, lesser for samba and Atlas cedar and the same for oak. Beech could have particular extract molecules in regards to the other chosen woods which present many double bonds.

In Fig. 8 we compare the extraction with a ringer solution and those of sodium chloride. If ringer solution enhances the extraction of groups 1455 and 1075 cm^{-1} and 800 cm^{-1} (C=C + C-C; aromatics + ethers and alkenes and aromatics) it diminishes the solubility for 2920 cm^{-1}, (C-H) and do not influence the peak 1730 cm^{-1} intensity in respect to sodium chloride. it seems that the sodium chloride enhance the aliphatic extraction of molecules.

CONCLUSION

Water extracts from woods could be characterised with only five independent wave number bands each of them could be associated with type of bands : 2920 cm^{-1} = C-H; 1730 cm^{-1} = C=O; 1455 cm^{-1}=C=C; 1075 cm^{-1} = aromatics + ethers and 800 cm^{-1}=alkenes and aromatics. In water, the band intensity depends with wood and eventually soluble salt presence nature.

The presences of $NaHCO_3$ in a buffer solution enhance the solubility of carboxylic acids but reduce the solubilisation of other polar molecules present in extracts especially the aromatic molecules, the ether and C=O containing molecules. Doing so, the presence of ringer salt into water diminishes the diversity of solvated molecules.

From a sanity point of view, the effects of extracts on human corpus could be decomposed into successive phases:
- Deposition on skin or on inner tissues.
- Solubilisation of extractives molecules in skin humidity or inner fluids.
- Transport and diffusion of extractives into living cells.

Our research seems to show that the inner fluids into the human corpus act as sfilter in regard to the diversity of extractives molecules and doing so, these fluids could be considered as the first protective barrier, hiding or smoothing the action of woods. It is so normal that previous study have difficulties to link the toxically effect established for woods and the molecular content of extracts.

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