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CHARACTERIZATION OF WOOD FOR MUSICAL INSTRUMENTS BY DSC-ANALYSIS

U. Reh and G. Kraepelin

Institut für Biochemie und Molekulare Biologie, Technische Universität Berlin, Franklinstr.29, D-1000 Berlin 10.

INTRODUCTION

The particularly fine sound of some historical music instruments gave rise to various speculations. Among others, one theory postulates that rafting and storing of wood in water accompanied by the decay of hemicellulose by bacteria and fungi leads to the desired high quality of wood.

On the other hand, untreated spruce wood with narrow annual rings i.e. low annual increase in diameter is often preferred for violin making. In the following the contribution of rinsing and of microbial degradation to the desired loss of hemicellulose or other soluble components was investigated by chemical analysis and differential scanning calorimetry and compared with the influence of annual ring size in untreated woods.

MATERIALS AND METHODS

Untreated wood chips of spruce (*Picea abies*) and birch (*Betula sp.*) were incubated in tap water (10 g in 250 ml) for up to four months.The alterations in the constitution of chips by a random microbial population as well as by purely physical rinsing effects in autoclaved chips was measured by chemical analysis of the main components of wood (holocellulose and lignin) and by differential scanning calorimetry (DSC, DuPont, type 910, Series 99).

Experimental conditions for all DSC runs were as follows: sample size, 3 mg; heating rate, 10°C/min; initial temperature, 100°C; final temperature, 600°C.The identification of peaks is discribed elsewhere (refs. 2,3). Assuming that the total area of a thermogram corresponds to the sum of superimposing peaks differentiable by means of geometry, peak areas of individual components were determined planimetrically.

For chemical analysis all samples were ground (size 0.25 mm), extracted with ethanol-toluene (ref. 5/toluene instead of benzene). Insoluble lignin was determined as Klason lignin (ref. 4) and soluble lignin was measured following reference 6. Holocellu-

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lose was determined as total carbohydrates with the anthrone-reagent (ref. 7).Total carbohydrates and soluble lignin were also measured in the supernatant of soaked samples.

The cell number (colony forming units/ml) of the microbial population was determined by plating aliquots of the supernatant on malt extract (30 g/l; pH 5) and NB-agar (peptone, 10 g/l; NaCl, 5 g/l; $MgSO_4$, 0.25 g/l; pH 7).

An artificially matured spruce wood and six commercial spruce woods provided for violin making with different densities of the annual rings were also analyzed and compared with the soaked samples.

RESULTS AND DISCUSSION

The soaking of wood chips led to characteristic changes in the DSC thermograms. As seen in Fig. 1 the maximum of the lignin peak was shifted towards lower temperatures and the heat released per gram of the lignin component increased by the soaking treatment. The portion of the total heat released from holocellulose decreased simultaneously (difference between the lignin peak area and 100%).

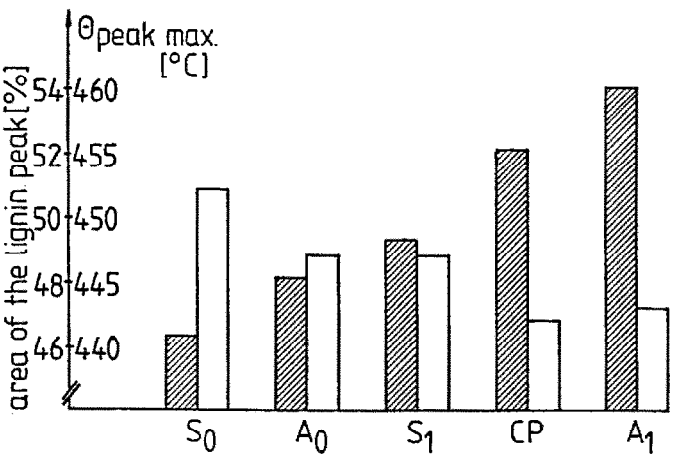

Fig.1. Energy content of spruce lignin and temperature of peak maximum in relation to soaking treatments.
Area of the lignin peak in % of the total area (total heat released; hatched columms).
Peak maximum in °C (blank columms).

S_0	soaked wood at time zero,
S_1	same after 1 month,
A_0	autoclaved and soaked wood at time zero,
A_1	same after 1 month,
CP	crushed wood particles from S_1

The decrease of the holocellulose peak area and the increase of the lignin peak area could both reflect a change of mass and/or energy content (heat released). In the case of lignin the shift of the peak towards lower temperatures could be caused by alteration towards a more oxidated state (as known for brown rot lignin/ ref. 2). Sequencing the samples by increasing energy content of their lignin component (Fig. 1) shows that microbial activity had no essential influence on the composition of soaked wood but physical rinsing effects did.

These mentioned tendencies were observed in spruce as well as in birch wood (not shown) characterized by a remarkably high amount of hemicellulose (35% xylane). In both cases the effects were intensified by autoclaving (20 min, 121°C). A decrease of total carbohydrates could not be found in the chemical analysis of the wood chips. Remarkably, quite the reverse was observed (s.sequence of carbohydrate values in wood chips from 0 to 4 month) as seen in the following table:

TABLE 1
Chemical analysis of soaked wood chips from spruce.
Values in % of dry weight.

	Autoclaved (20 min,121°C)			With microbial flora		
incubation time (month)	0	1	4	0	1	4
wood chips						
carbohydrates	52.4	52.3	60.0	52.3	53.1	59.2
soluble lignin	0.48	0.88	0.67	0.57	0.79	0.69
insol. lignin	29.43	29.83	28.10	29.0	28.78	27.65
nitrogen	0.148	0.079	0.079	0.110	0.068	0.075
supernatant						
carbohydrates	1.91	0.73	0.74	0.81	0.048	0.044
soluble lignin	0.85	5.88	2.19	0.19	0.17	0.09
total	85.22	89.70	91.78	82.98	82.96	87.75

The holocellulose within the chips detected by the anthrone-reagent increased the more the rinsing process proceeded presumably by improving accessibility. This suggests that the reduction of the holocellulose peak in the thermograms (not shown) is rather caused by a decrease in energy content than by a mass loss. The inverse may apply to lignin: Following chemical analysis the content of insoluble lignin decreased slightly (Tab. 1) while the peak area (Fig. 1) increased with incubation time. Thus, the alteration in the thermogram should be caused by an increase of energy content, although the peak maximum shifted to

lower temperatures (interpreted as oxidation). This contradiction should be investigated further by combined DSC/DTG analysis.

In the presence of a random microbial population (up to 1.6 x 10^8 CFU/ml, mainly bacteria) an increased crushing of the chips was stated. Thermograms of these crushed wood particles also revealed a holocellulose of lowered and a lignin of increased energy content, respectively. The lignin peak maximum was shifted to lower temperatures as in the wood chips (Fig. 1, CP) and the carbohydrates in the rinsing water had nearly disappeared (Tab. 1). The bacteria degraded solubilized carbohydrates but their effect on the wood chips was negligible as compared to physical effects of soaking and autoclaving (Fig. 1, A_1). Therefore, the above mentioned theory that microorganisms lead to considerable alterations in soaked wood could not be confirmed.

Spruce wood with annual rings of high density, for example from Mittenwald/Bavaria, is often preferred for violin making. In such a wood more lignin is deposited on a dry weight basis.

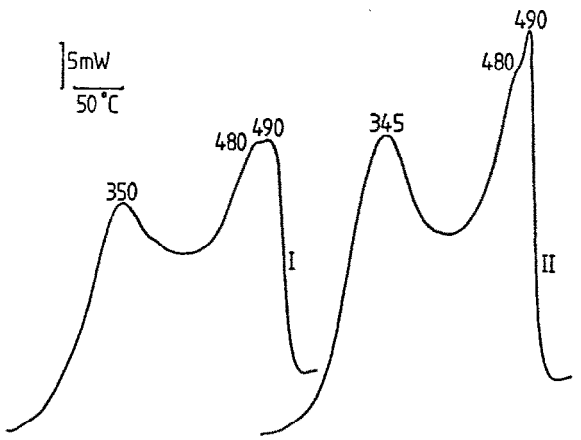

Fig.2. Thermograms of untreated spruce woods with a mean of 5.5 (I) and with a mean of 22 (II) annual rings per cm radius. **Thermogram I:** Total heat released, 8.22 kJ/g dry weight; holocellulose peak, 51.6%; additional peak (480°C), 16.7%; lignin peak (490°C), 32.0% of total. Klason lignin content from chemical analysis, 28.2%. **Thermogram II:** Total heat released, 9.74 kJ/g dry weight; holocellulose peak, 53.7%; additional peak (480°C), 13.4%; lignin peak (490°C), 33.7% of total. Klason lignin content from chemical analysis, 28.8%.

Thus, it seems reasonable to assume that the DSC-thermograms of soaked wood and of wood with a high density of annual rings may show similiar characteristics.

Actually, an increase of the total energy content of wood and of the lignin component after soaking as shown in Figure 1 was also observed in unsoaked wood samples of high density of annual rings as shown for the two examples in Figure 2.

An artificially aged commercial spruce wood, prepared by partially extracting hemicellulose (unknown procedure) showed a thermogram (Fig. 3) similar to that of soaked wood (Fig. 4). In both cases, the peak maximum of the lignin component was shifted to a lower temperature as compared to the maximum at 490°C in untreated spruce wood.

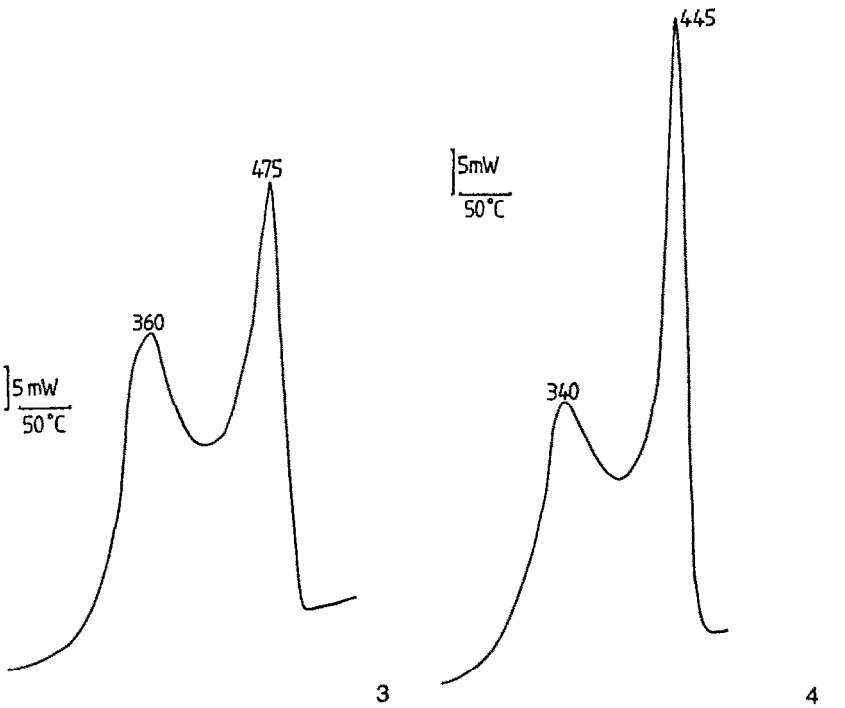

Fig. 3. Thermogram of an artificially aged spruce wood (experimental wood for violin making). Total heat released, 10.15 kJ/g; holocellulose peak, 51.1%; lignin peak, 49.0% of total. Lignin content 43.0% (chemical analysis).

Fig. 4. Thermogram of an autoclaved and soaked (for one month) spruce wood. Total heat released, 9.28 kJ/g; holocellulose peak, 44.8%; lignin peak, 54.7% of total. Lignin content, 30.3% (chemical analysis).

An increase of the total energy content of wood and of the lignin components after soaking as shown in Figure 1 was also observed in unsoaked wood samples of high density of annual rings (Fig. 2).The total heat released increased from 8.2 to 9.7 kJ/g dw by increasing the density of annual rings from 5.5 to 22 annual rings/cm, from 9.1 (soaked wood at zero time) to 9.3 kJ/g dw in autoclaved and soaked (for 1 month) wood chips and to 10.2 kJ/g dw in artificially aged wood. The heat released from the lignin compound also increased, from 32.0% to 33.7% of the total area by increasing the density of annual rings, from 46.3% (soaked wood at zero time) to 54.7% in autoclaved and soaked (for 1 month) wood chips and to 49.0% in artificially aged wood.

In contrast to the soaked samples, the energy content of the holocellulose was also increased in samples of increased density of annual rings. Remarkably, the masses determinated by chemical analysis were nearly identical (28.2% and 28.8% lignin). A simultaneous shift of the lignin peak temperature could not be detected.

The higher energy content of holocellulose in wood samples of a high density of annual rings could be explained by assuming an accumulation of crystalline at the expense of amorphous cellulose. This ecologically mediated structural shift may produce a similiar effect referring to instrumental sound quality as secondary rinsing out of some soluble carbohydrates from a fast grown wood. An enrichment of crystalline cellulose components is still speculative and needs verification. Further work on this line is in progress.

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