A Proposal of Eucalyptus Wood Identification by ^{13}C NMR

Natália Dias DE SOUZA, Heber dos Santos ABREU, Gisely de Lima OLIVEIRA, Iara Grotz MOREIRA, Tatiane Gosmes COSTA

Universidade Federal Rural do Rio de Janeiro- Departamento de Produtos Florestais- Instituto de Florestas

ABSTRACT

The trees of eucalyptus in general in tropical country have a high rate of growth. These trees also have high plasticity, straight growth, natural pruning and wood properties suitable for diverse utility. However, many questions on eucalyptus wood still need to be solved. One of these problems is wood identification with wood with high similarly. On this point of view, it was proposed an alternative way for identification, without to lance the hand of the other traditional tools. The application of Nuclear Magnetic Resonance (NMR) has shown to be one promise technique for wood identification. This has turned possible with NMR ^{13}C spectrometry. A spectral variation of cyclohexane extracts from wood of eucalyptus, permitted to observe the physiological, ecological and genetical behavior. Dada of ^{13}C NMR has shown that the cyclohexane extracts from heartwood was the most representative for the wood identification. From these data was possible to establish a common spectral profile for *E. grandis*, *E. urophylla* and *E. urograndis* clones from each anatomical wood region (sapwood, transition zone and heartwood).

Key words: Wood identification, extracts, spectral profile, ^{13}C NMR, heartwood

INTRODUCTION

The eucalyptus woods have anatomical characteristics similar among species. This take to a difficult task in the wood identification. Problems as natural occurrence of hybrids trees and tree from genetically improved, bring more difficulty for identification (González, 2002).

Techniques of systematic botany, always need of leaf and flower for identification. The knowledge about the chemistry of wood may is an interesting tool for wood identification. The occurrence of certain compounds can help in the wood identification as is used in the chemosystematic field. Many compounds in the wood work as a chemical barrier against various microorganisms, however, its applicability as resource of systematic information has been very little explored, mainly in a routine work of wood identification (Sjöström and Alén, 1998; Gullichsen and Paulapuro, 2000; Freire et al., 2002; Sun and Tomkinson, 2003; Morais et al., 2005).

We percept that the ^{13}C NMR can be a new tool to solve questions that the botanical and anatomy do not get to make in a fast time. The technique of RMN has been widely used to elucidate structures of organic compound which occur in plants (Harbone, 1994; Gottlieb and Yoshidas, 1989), applying experimental techniques of 2D (Lambert and Mazzola, 2003).

According to Cienfuegos (2000), the technique of MNR, is not destructive, hardly presents disadvantages when compared with traditional techniques. The mains advantages of NMR are: simple preparation, physical measurement, easy to operate, fast, robust, software for analysis, samples of many different shapes and sizes. The objective of this work was to map the molecular carbon of cyclohexane extract to form a data bank by mean of ^{13}C NMR toward wood identification.

MATERIAL AND METHODS

The material for analysis was obtained from the ARACRUZ FORESTAL S.A. The samples were collected from clones of trees of *E. grandis*, *E. urophylla* and the hybrid *E.* urograndis. Each species was represented by four trees selected in the two different areas with approximate 15 years old.

The samples were extracted from sapwood, transition zone and heartwood. The samples were ground in Willey mill. The method used for chemical analysis followed the ASTM norm.

16 grams of dry saw of wood was extracted for 48 hour in soxhlet extractor. The extraction has started with cyclohexane and then ethyl acetate and finished with methanol. The extracts were concentrated in a evaporator rotatory. The concentrates were transferred to a container until the complete evaporation of the solvent at room temperature.

The spectra of the extracts were obtained from a spectrometer VARIAN MERCURY PLUS (75.46 MHz), using the probe of 5 mm of internal diameter, at room temperature and pulse of 45^{o}. The chemical shifts (ppm) were referenced based on ^{13}C NMR spectrum of $CDCl_3$ (77.0 ppm). It was used the complementary APT technique (Attached Proton Test) (Brektmaeir and Voelter, 1987).

The tests were carried out at the Centre of Nuclear Magnetic Resonance of the Institute of Chemistry at the Universidade de Brasilia, Brazil.

RESULTS AND DISCUSSION

It was registered The ^{13}C NMR spectra of cyclohexane, ethyl acetate and methanol extracts, however, only the cyclohexane extract was used. It was preferred due the low complexity and high solubility in Deuterated Chloroform.

The absorptions from ^{13}C NMR were assignment in according to following class: aliphatic (0 to 55 ppm), olefinic (110 to 155 ppm) and carbonilic (155 to 220 ppm). The spectra showed high concentration of signals in the aliphatic region (C, CH, CH_2 and CH_3), with low concentration of olefinic, aromatic carbon and no signs between 80 ppm and 110 ppm. It was found a great concentration of signals in the aliphatic region. It was observed that cyclohexane extract from sapwood, transition zone and heart of *E. grandis*, *E. urophylla* and the hybrid *E. urograndis* present the some similar absorptions.

The spectra of cyclohexane extracts from sapwood showed that woods from *E. grandis* and *E. urphylla*, E. urograndis collected from area 1 and 2 present similarity as well.

It was observed that the wood of the same species remained the same spectral characteristics for each region from cyclohexane spectra. This takes us to observe that there is no change on point genetic and ecologic view.

The spectra from cyclohexane extracts of the heartwood were considered the most representative for the study of identifying the genus *Eucalyptus* wood. It due to the higher number of signals, meaning a great variety of carbons in terms of chemical constituents. These extracts showed absorption of olefinic/aromatics carbons, between 110 and 155 ppm. A little change was observed in the extract from heartwood from hybrid eucalyptus in the change between 155 to 220 ppm.

Spectra of cyclohexane extracts from heartwood of all wood provide established an identity for the genus spectrum. These signals were: 11.80-11.84; 11.93-11.96; 14.08-14.13; 18.72-18.76; 19.78-19.81; 22.65-22.69; 22.99-23.04; 24.25-24.28; 24.68-24.70; 25.97-26.03; 27.14-27.18; 28.20-28.24; 31.85-31.91; 36.09-36.13; 42.25-42.29; 45.76-45.80; 123.00-123.03; 128.76-128.82; 130.85-130.88 ppm

It was also observed that *E. Grandis, E. urophylla* and *E*. urograndis, have different spectral profiles, characterizing specific signals. These signals were for *E. grandis*: (38.09-38.13; 71.80-71.83; 122.55-122.58; 127.86-127.88), *E. urophylla*: (15.11-15.19; 23.67-23.71; 27.93-28.08; 28.72-28.75; 34.78-34.75) and *E*. urograndis: (24.85-24.87; 34.64-34.67; 37.19-37.22; 56.13-56.16; 102.71-102.78).

Spectrum of *E.* urograndis showed some signals similar when compared with the spectrum of *E. grandis* (19.36, 21.04, 31.55, 33.86, 50.07, 55.99, 56.71, 115.56, 121.71, 140.68ppm) and with spectrum of *E. urophylla* (38.67, 68.13, 130.03). *E*. urograndis is product of genetic improvement that probably results in a recombination of characters. It can to see by the signals the *E. grandis* that showed to be more representative with respect to than *E. urophylla*. This effect is correlated with the legacy or a maternal dominance, the hybrid can be called *"E. grandisuro"*.

CONCLUSIONS

• The spectroscopic data of ^{13}C NMR showed that the spectra of ciclohexane extracts from the wood of the heart, was considered the most representative for the study of the identification of timber species *E. grandis*, *E. urophylla* and *E*. urograndis, due to the number of signals found and considering that region with more stable and mature nature.

• Carbon of carbonila/acila in the range between 155 to 220 ppm was observed only in the spectra of ciclohexane extracts from the wood of the region of the heartwood of the hybrid E. urograndis.

• The absorption of ^{13}C in the spectra of extracts ciclohexânicos the transition zone confirm the status of transition between the sapwood and heartwood, as new signs were found in the heartwood.

• NMR of ^{13}C was possible to develop a model of identification since each species and the hybrid had specific spectral profiles.

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