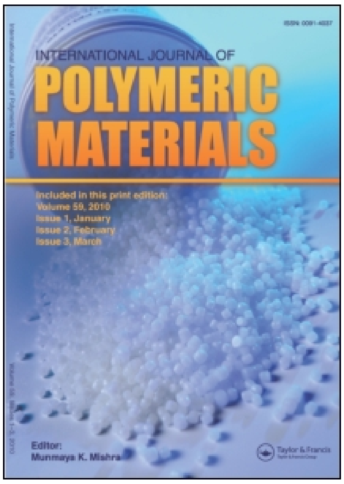

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Solid State NMR Study of *Couma utilis* Seeds

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This article studies the seed of sorva (Couma utilis) *that is a native fruit of Amazons State, in Brazil. Sorva seed components were analyzed by ^{1}H and ^{13}C using solid state high resolution nuclear magnetic resonance (NMR) spectroscopy, because they are important nuclei to be used to evaluate plant seeds. High resolution ^{1}H NMR (^{1}H HRMAS) with magic angle sample spinning (MAS), and ^{13}C NMR using MAS and particularly ^{13}C NMR with cross-polarization (CP) and MAS are techniques that allow the evaluation of the seed in detail. The variable contact–time (VCT) experiment is another useful technique that can be used to measure a proton spin-lattice relaxation time in the rotating frame, which is a parameter that gives response on the intermolecular interaction and is related to the sample spatial homogeneity. From the NMR results it was found that the sorva seeds are mainly constituted of polysaccharides, glycoproteins, and triacylglycerides.*

Keywords: *Couma utilis* seed, NMR, solid state

INTRODUCTION

Humanity's strining to improve the quality of food drives the research expressed in many types of studies. Fruit seeds have been a subject of

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studies, because they are very useful in improving the quality of human life [1–4]. Thus, some heterogeneous characteristics, encompassing different elements are: organoleptic quality; nutritional and health quality; facility of its processing and conservation; nutritional value; digestibility or indigestibility of products. The selection of fruit variety influences the final quality of the product. Generally the quality of the seed or the fruit is strongly influenced by environmental conditions.

Seeds constitute an essential part of cereal and their oil is a valuable manufacturing product for cosmetics and other industries. Seed quality is a major criterion in food product development. Quality criteria vary according to the use and demand. The first dependence is based on seed composition. It also depends on the digestibility of seed constituents and on the histology of the seed.

Fruit seed can be analyzed by several methods, which includes spectroscopy analyses. Nuclear magnetic resonance (NMR) is one of the best spectroscopies to be used to analyze the sample in nature, applying solid state techniques [3–12]. ^{1}H and ^{13}C High resolution NMR spectroscopy are the most important nuclei applied to plant seeds because it is a nondestructive analysis, and permits to evaluate the seeds' molecular behavior. The combination of high resolution ^{1}H NMR with magic angle sample spinning, and ^{13}C NMR using MAS and particularly ^{1}H–^{13}C cross-polarization with MAS allow the evaluation of the seed in detail, as well as the variable contact—time [8–9] from which proton spin-lattice relaxation time in the rotating frame is measured.

The objective of the present research consists in evaluating the chemical behavior of the sorva seed applying solid state NMR techniques, focusing on the chemical constituents.

EXPERIMENTAL

Preparation of Samples

Samples of sorva used in this study were collected in Amazon, Brazil. The seeds of unripe fruit were extracted mechanically, ground and dried in an oven at 50°C for 3 days, to obtain the entire seed without any modification. After that they were analyzed by solid state NMR techniques.

NMR SPECTROSCOPY

Solid State Measurements

All ^{13}C NMR spectra were collected at 9.4 T using a Varian Mercury 400 MHz spectrometer, operating at 100.2 MHz for ^{13}C. All measurements were acquired using MAS at a spinning rate 6.4 kHz. The MAS technique was used with short recycle delay to observe only the mobile region. The CPMAS and VCT were also registered at the same spinning rate, using a recycle delay of 2 s, for the VCT with a range of contact varying from 0.5 to 7 ms.

^{1}H High Resolution

The ^{1}H HRMAS spectrum was obtained on a BRUKER DRX 400 spectrometer operating at these conditions: spectral width: 5668.9 Hz; acquisition time: 1.8 s; pulse width: 45°; recycle delay: 1 s; and number of transients: 128. The type of processing was zero filling and line broadening: 0.

RESULTS AND DISCUSSION

The ^{13}C MAS (Figure 1a), obtained with short recycle delay between 90° pulses, showed only signals from the triacylglycerols, which are the more mobile component of the seed. The signals reveal that the chains of the triacylglycerols are long, probably stearic, oleic, and linoleic. This seed oil was analyzed by solution ^{13}C NMR and the

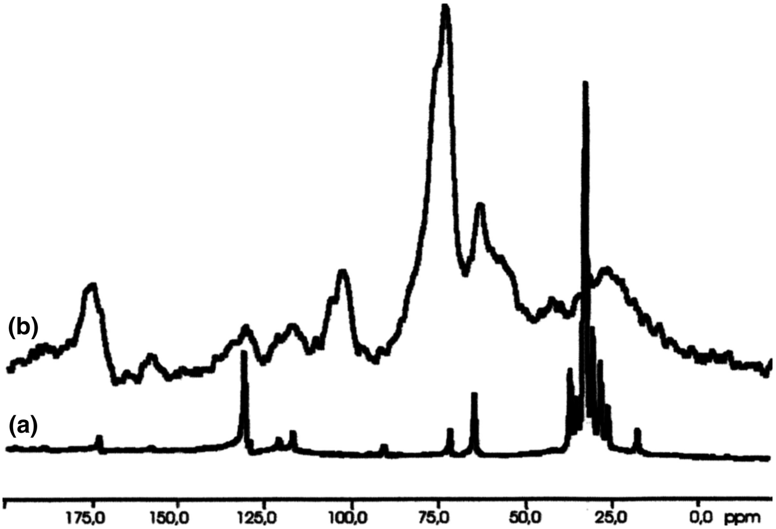

FIGURE 1 Solid-state ^{13}C NMR spectra of seeds of *Couma utilis* acquires on a Varian Mercury 400 spectrometer, operating at 100.2 MHz for ^{13}C: (a) MAS and (b) CPMAS.

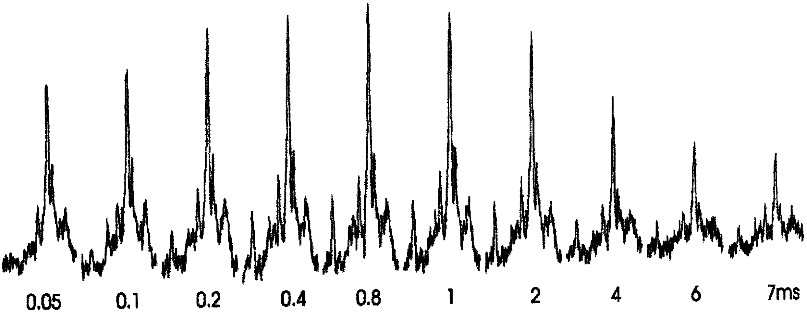

FIGURE 2 The VCT decay for the unripe sorva seed.

composition determined confirms that the oil constitutes basically palmitic, oleic, and linoleic chains.

The ^{13}C CPMAS (Figure 1b) shows a typical pattern of starch signals located at 62 ppm, 76 ppm, and 104 ppm, which are derived from the mix of amylose and amylopectin. However, four large signals located at 25 ppm (CH_2), 110 ppm (C=C or C–O), 130 ppm (C=C), and 175 ppm (C=O) were also detected and these signals can be attributed to glycoproteins.

The comparison of both MAS and CPMAS spectra shows that the techniques used identified the major components present in the seed phases that possess different molecular mobilities. In the CPMAS spectrum (Figure 1b), which shows the rigid phase signals are presented from starch (amylase and amylopectin), glycolipids and glycoproteins, In the MAS spectrum (Figure 1a) only the triacylglycerides was detected, because they constituted the mobile domain.

The VCT experiment showed ^{13}C CPMAS decay along of rotating frame with increasing contact-time (Figure 2). VCT decay exhibits a first response of the sample heterogeneity and rigidity. From this experiment the spin-lattice relaxation time in the rotating frame can also be measured, T_1H_ρ, for each type of resolved carbon (Table 1).

TABLE 1 Proton Spin-Lattice Relaxation Time in the Rotating Frame for the Entire Seed, as a Function of Chemical Shift, Obtained by VCT

Peak	δ (ppm)	T_1H_ρ (ms)
1	101.5	2.6
2	71.7	3.4
3	29.6	5.4

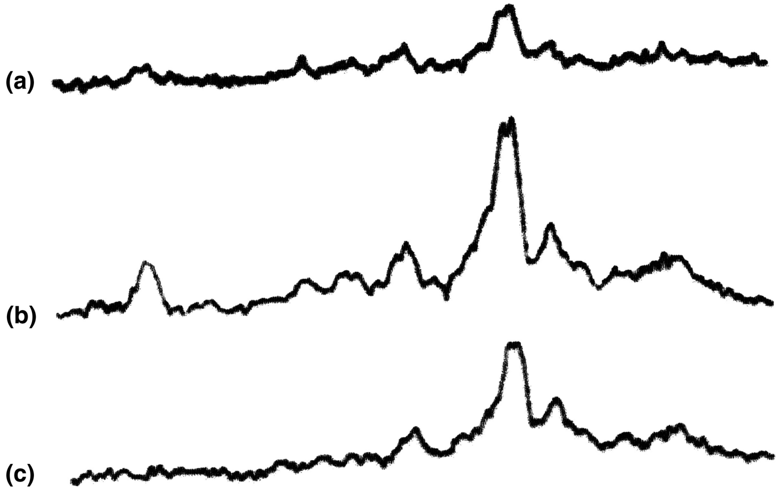

FIGURE 3 (a) ^{13}C CPMAS spectrum with the lowest contact time (0.05 ms); (b) ^{13}C CPMAS spectrum with the optimum contact time (0.8 ms), and (c) ^{13}C CPMAS spectrum with the highest contact time (7 ms).

T_1H_ρ depends on the extent of dipolar interaction that is dominated by near neighbor spin diffusion.

From VCT a comparison among the different contact times permits the evaluation of the dynamic behavior of the seed starch. Three ^{13}C CPMAS NMR spectra with contact times are shown in Figure 3, (a) ^{13}C CPMAS spectrum with the lowest contact time (0.05 ms); (b) ^{13}C CPMAS spectrum with the optimum contact time (0.8 ms), and (c)

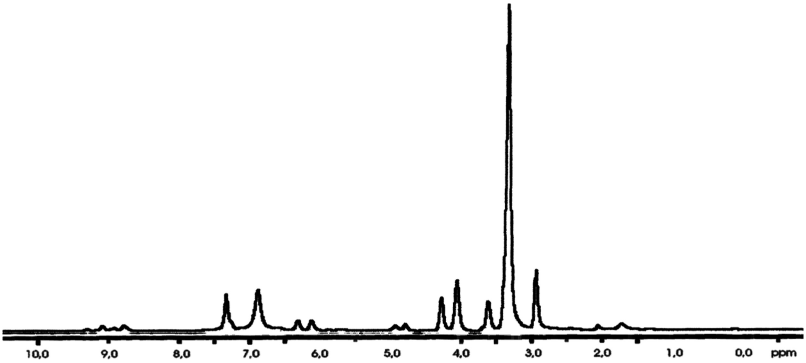

FIGURE 4 ^{1}H HRMAS of the unripe entire sorva seed.

^{13}C CPMAS spectrum with the highest contact time (7 ms). Observing these spectra, changes in the signals' form, intensity, and resolution can be detected with the increasing contact-time, showing that the starch seed is a heterogeneous rigid sample, mainly constitutes of polysaccharides, proteins, and lipids.

To confirm the seed components, an NMR analysis using ^{1}H HRMAS was carried out. Figure 4 shows the ^{1}H HRMAS of the unripe entire sorva seed; in this spectrum the identified signals belong to triacylglycerols.

CONCLUSION

The use of solid state NMR techniques provided very useful information on molecular dynamic of sorva seed starch and it was possible to characterize its main chemical components without making any modification in the sample.

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