Low field NMR study of Cumbaru seed fruit

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Abstract:
Cumbaru is a fruit from Mato Grosso in Brazil, and its seeds are commonly used in popular medicine to prevent kidney diseases. This seed is mainly constituted by starch, oil and protein. Particularly the chemical composition and structural characteristics of this starch, which is a natural polymer, is important to investigate its potential applications. In this work our aim is to obtain physico-chemical and micro-structural information about both the cumbaru seed fruit and cumbaru seed fruit starch. This information can be extremely useful to identify such applications. Low field NMR spectroscopy was used for this purpose and the results showed that this technique is a powerful tool to study the chemical composition and the structural characteristics of natural polymers, such as starches.

Resumo:
O cumbaru é uma fruta proveniente do Mato Grosso, Brasil, e as suas sementes são utilizadas na medicina popular para prevenir alguns tipos de doenças. Esta semente é constituída principalmente de amido, óleo e proteína. Conhecer a composição química e as características estruturais deste amido, um polímero natural, é importante para investigar seu potencial de aplicação. Neste trabalho nosso objetivo é obter informações físico-químicas e microestruturais tanto da semente da fruta do cumbaru e também quanto do amido proveniente desta semente. Tal informação é extremamente importante para identificar suas aplicações e benefícios. Utilizamos a espectroscopia de RMN de baixo campo, e os resultados mostraram que esta técnica é poderosa para estudar a composição química e estrutural de polímeros naturais, como é o caso dos amidos.

Introduction

Cumbaru is a fruit from Mato Grosso, Brazil. The seeds of this fruits are commonly used in popular medicine to prevent kidney diseases, like tuberculosis.

It is known that cumbaru seed is mainly constituted by starch, oil and glycoprotein. *Particularly, the chemical composition and structural characteristics of this starch, which is a natural polymer, is important to investigate its potential applications. In this work, our aim is to obtain physico-chemical and microstructural information about both the cumbaru seed fruit and cumbaru seed fruit starch; this information can be extremely useful to identify such applications.* To achieve this purpose, we used low field NMR spectroscopy, applying the following nuclear relaxation measurements: proton spin-lattice relaxation time, with a time constant, T_1, and proton spin-spin (T_2). These relaxation parameters can provide detailed information on mobility behavior, domain formation, interaction, and domain components at the molecular level.[1-4]

Experimental

All the analyses of the samples (Figure 1) were carried out on a Maran Ultra NMR spectrometer (Resonance Instruments, Oxford, UK), operating at a ^1H resonance frequency of 23 MHz. The spectrometer was equipped with a temperature control device allowing temperature regulation at ± 0.5°C. The specimens were analyzed at 27°C and 35°C.

The T_1H values were determined directly by the traditional inversion recovery pulse sequence using a range of τ varying from 0.1

to 5,000 ms, with a recycle delay at 5s, using 20 data point with 4 scans each.

The T_2H values were also determined at 35°C using a CPMG pulse sequence applying four values of τ: 30, 50, 100 and 400 μs, with 5s of recycle delay using a single pulse experiment with 9600 scans.

The relaxation parameter and relative intensities were analyzed by fitting the exponential data with the aid of the WINFIT program. Distributed exponential fittings as a plot of relaxation amplitude versus relaxation time were performed by using WINDXP software.

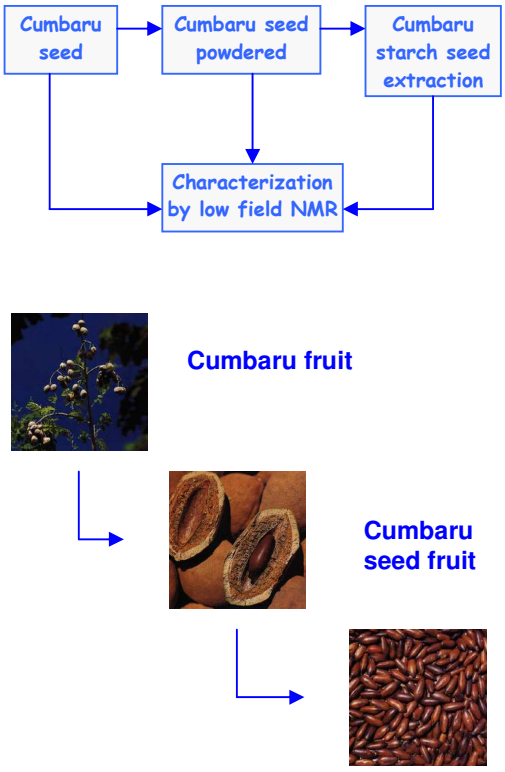

Figure 1. Flowchart of the experimental stages – samples analysed.

Results and Discussion

Tables 1 and 2 show the T_1H values for the entire and powdered cumbaru seed and for the cumbaru seed starch, respectively. The results showed that the increase in temperature can cause changes in intermolecular interactions, thus affecting the molecular mobility of the whole sample, due to changes in intermolecular interactions, as the degrees of freedom of the chains also increased. At 35°C, the starch seed presented two values of relaxation, which come from mobile (amorphous polysaccharides) and rigid domains (crystalline polysaccharides).

Table 1. T_1 H values obtained by the entire, powdered and starch seed at 27°C

Samples	T_1 H(ms)
Entire seed	10
Powdered seed	75
Starch seed	116

Table 2. T_1H values obtained by the entire, powdered, and starch seed at 35°C

Samples	T_1 H (ms)
Entire seed	108
Powdered seed	97
Starch seed	22
	173

Tables 3, 4 and 5 show T_2H values for the entire, powdered, and starch seed, respectively. Analyzing T_2H values for all samples, it is found that the increase in T_2H values with the increase in the ι usually originates from high mobility domains.

From the relaxation data listed in Tables 3, 4 and 5, it is clear that no significant difference was found in T_2 for each type of sample, when the τ parameter was varied from 30 to 400 μs. However, for high τ values T_2 increases as a consequence of high mobility domain detection (extra granular water).

Comparing the three types of samples, we find that T_2H values are lower for the seed starch, because the polysaccharides have lower molecular mobility and stronger intermolecular interactions, causing rigidity in the sample. Thus, no high mobility domain was detected for the starch seed. The starch relaxation process is controlled by a rigid domain, which is probably constituted by crystalline polysaccharides.

Table 3. T_2 H values obtained by the entire seed at 35°C for different values of ι

ι (μs)	T_2 (ms)
30	153
50	145
100	148
400	160

Table 4. T_2H values obtained by the powdered seed at 35°C for different values of ι

ι (μs)	T_2 H (ms)
30	120
50	130
100	137
400	137

Table 5. T_2 H values obtained by the starch seed at 35°C for different values of ι

ι (μs)	T_2 (ms)
30	9
50	10
100	9
400	-

Conclusions

The results showed that low field NMR is a powerful technique to study the chemical composition and the structural characteristics of natural polymers, like starches.

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