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Cashew Tree Gum: A Scientific and Technological Review

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Abstract— *Cashew gum can be obtained from the exudate released from the stem of the species "Anacardium occidentale", commonly called cashew tree, a tree typical of Brazil and subtropical countries. It is a heteropolysaccharide complex that after hydrolysis presents a high content of monosaccharides with a varied composition depending on its origin. Due to its biological origin, the ability to form gels and the fact that it has properties similar to synthetic polymers, it is a great option for the application in several sectors of industry. In the food industry it can be used as a thickener and a stabilizer for juices, an emulsifier in salad sauces, a stabilizer in the emulsions of meats such as sausage, and in food compositions containing chocolate. In the manufacture of pharmaceuticals it may be used as an agent for suspending, emulsifying, disintegrating, binding, gelling, tabletting drugs with release control and also as a mucoadhesive agent. In medicine, studies also indicate a phytotherapeutic potential in the reduction of blood pressure and even in some types of cancer.*
Keywords— ***Anacardium occidentale, cashew gum, food industry, phytotherapy, polysaccharide.***

I. INTRODUCTION OF THE SPECIES *ANACARDIUM OCCIDENTALE*

The *Anacardium* word is a Greek word meaning inverted heart, in reference to the format of the fruit. Cashew is a fruit of high nutritional value with high levels of vitamin C, minerals, Ca, Fe, Zn [1].

The fleshy part, edible in natura, is a pseudofruit, and the chestnut cashew, consisting of a shell, almond and pellicule, is the true fruit of the cashew tree. The shell contains the cashew nut shell liquid (CNSL), a phenolic compound which can be used as a source of phenols in the industry of plastic, paints, varnishes, in the manufacture of auto parts and others. The roasted almond without the shell can be consumed as food and it is rich in high quality oils [1].

Anacardium occidentale is the scientific name of the cashew tree, a tree native to Brazil known to the indigenous inhabitants of northeastern Brazil in 1500 who used their fruit, the cashew, as one of the most complete and important foods. The nuts were toasted over the fire to remove the CNSL (cashew nut shell liquid) and used as food. The cashew pulp was squeezed to release the juice, which in turn was fermented for the production of wine. The cashew trees were also used to establish the boundaries of the territories and to provide shade. The name of the fruit itself is due to the Indians since it comes from Tupi, "acaiu". When fruiting cashew, the tribes that descended from the interior had to fight the tribes of the coast in order to own the cashew plantations. These fights became known as "cashew wars" and are supposed to explain how the cashew tree (which is not very demanding in terms of availability of water and soil) has spread throughout the northeastern interior of dry and arid lands. The words "acaiu" (nut that is produced) and "yu" (yellow) probably formed the word “caju” (cashew in Portuguese) [2,3,4,5].

In the 16th century the cashew trees became very popular among settlers. The naturalist monk Thevet, on a visit to Brazil in 1558, was the first to draw a cashew by showing how Indians harvested fruits and squeezed the pulp into a pot. Later, in 1576, the book "History of the Province of Santa Cruz" by Pero de Magalhães Gandavo was published, where a scientific description of the geography, fauna and flora of the Brazilian coast was written. In this publication Gandavo described the cashew tree as having the size of an apple tree and pear tree, and the cashew nut looking like a bean, being as tasty as the almond [4,6]. The cashew trees were brought in the first half of the century by the Portuguese to Goa in India, where they easily adapted to the region and were planted for the production of wines, cognacs and liqueurs. From India they were taken to other Asian countries, then to Mozambique and Angola, and later to Nigeria, Kenya, the Philippines, and Ceylon so that by the end of the eighteenth century there were already cashew trees scattered throughout the Indian Ocean region [2, 3, 5, 7, 8]. Meanwhile, in Brazil, the cashew trees were being replaced by sugarcane plantations.

At the beginning of the 20th century, India dominated the trade in cashew nuts [2]. During World War II the cashew agroindustry began in Brazil, due to high external demand for cashew nut shell liquid (CNSL) used in the manufacture of high voltage cables. The United States was the main consumer in the world and the crop was explored in an extractive way, and chestnuts were used exclusively as raw material for the manufacture of CNSL [9].

In the 1960s, with tax incentives from the Northeast Development Superintendency (SUDENE), Brazil was the country with the largest planted area of cashew trees and an industry for processing the production of nuts, with emphasis on the state of Ceará [9]. In the 1970s, SUDENE once again financed the implementation of large plantations. In the 1980s, Embrapa's National Center for Tropical Agroindustry was implemented with the participation of the Agricultural Research Company of Ceará (EPACE), where large researches were carried out with several generations of clones of precocious dwarf cashews of expressive productivity and high genetic quality, which contributed significantly to the increase in cashew planted areas and cashew production not only in Ceará but all over Brazil [10].

Since its production is focused on countries considered as underdeveloped or developing, cashew is considered a product of great socio-economic importance worldwide. According to data from Companhia Nacional de Abastecimento (CONAB), Brazil produced, in 2015, about 102,000 tons of cashew nuts, where 12,957 tons were exported mainly to the Netherlands, Canada and the United States.

According to data from the Food and Agriculture Organization of the United Nations (FAO), Brazil was the eleventh largest producer of cashew nuts in 2013, with a production of 109,679 tons. Vietnam, Nigeria, India and Côte d'Ivoire were the largest producers with productions of 1,110,800; 950,000; 753,000 and 450,000 tons. The following figure shows the evolution of the world production of cashew nuts between the years 2000 and 2013.

It is possible to note that Nigeria, India and Côte d'Ivoire increased their production while Brazil has kept its production stagnated in recent years.

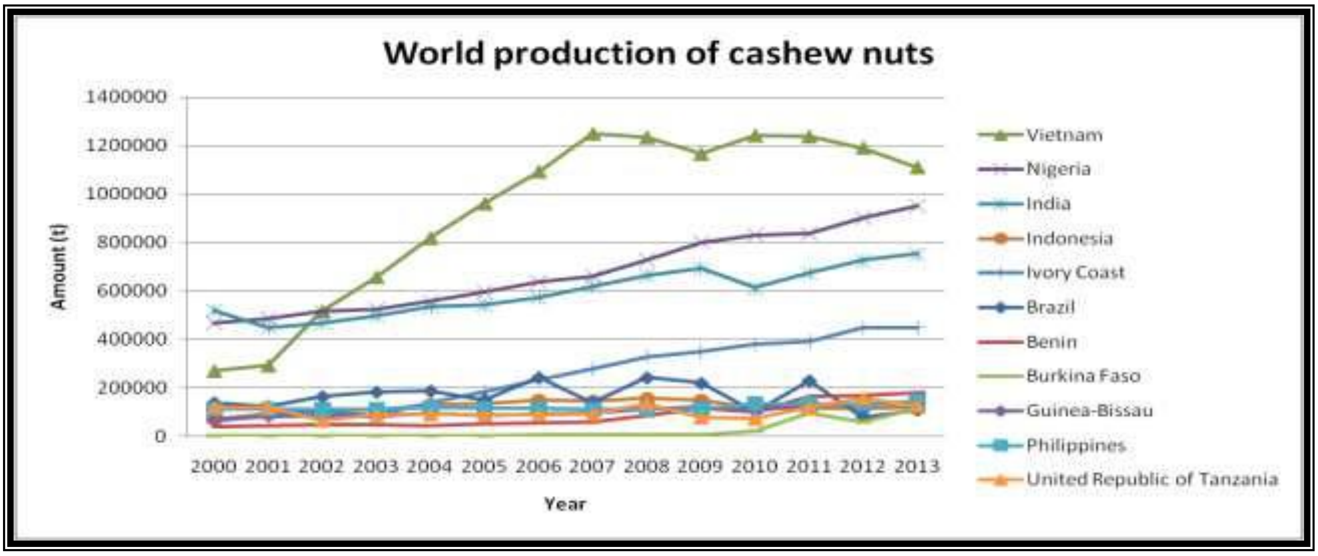

Fig. 1: World production of cashew nuts

II. CASHEW GUM

The term "gum" is generally used to characterize high molecular weight compounds capable of forming gels in the presence of suitable solvents and forming suspensions or solutions with high viscosity even at low concentrations. According to this definition, some hydrophobic substances such as high molecular weight hydrocarbons derived from petroleum, many resins and proteins, some synthetic polymers may also be referred to as gums. However, it is common to refer to polysaccharides of vegetable or microbial origin as gums, and they dissolve integrally or partially in hot or cold water producing viscous solutions or suspensions. Thus, these substances are also called hydrocolloids [11].

When the cashew stem undergoes any sort of environmental aggression, it releases an exudate, which is a resin that varies in color from yellow and brown, and after going through a purification process, it becomes a gum rich in polysaccharides [1]. The resin is produced in the epithelial cells located in the outer channels of the plant. The gum encapsulating cells pass through the cell wall into the channels, carrying the lysed cell material therein. When the flowable resin reaches the outer surface of the plant through a cut, the resin dries by evaporation [1].

Table.1: Cashew gum compositions

Monosaccharide	Cashew gum composition in differents regions (%)					
	Brazil [15, 16]	Brazil [17]	Brazil [14]	India [18]	Papua [18]	Venezuela [19]
galactose	72 - 73	81.7	69.78	61	63	49
arabinose	4.6 - 5	1.9	11.84	14	16	31
mannose	0 - 1	-	0.97	2	1	4
xylose	-	-	1.29	2	-	1
rhammose	3.2 - 4	1.9	2.28	7	7	7
glucose	11 - 14	9.5	9.78	8	9	-
glucuronic acid	4.5 - 6.3	5	0.52	6.2	5.7	8

According to Tiomno (1946) [12]; Mothé & Rao (2000) [13], cashew gum resembles gum arabic and may be used in the pharmaceutical industry, in cosmetics, and adhesive industry. It can also be used in food industry as emulsifiers or stabilizers since it is not toxic nor presents odor or taste.

Thus, the gum can add more value to cashew agrobusiness, minimizing Brazil's imports of gum arabic and then exporting to other countries.

III. CASHEW GUM CHARACTERIZATION

According to Botelho (1999) [14], cashew gum is considered a heteropolysaccharide of molar mass (Mw) 1.5 x 10^4 and a polydispersity index of approximately 1.49 (values obtained by size-exclusion chromatography). It is usually composed of galactose, arabinose, glucose, rhamnose, mannose and glucuronic acid, whose concentrations vary depending on the source of the gum.

The following table 1 shows the composition of cashew gum in different countries.

It can be observed that the gum has large quantities of galactose in relation to other monosaccharides. The gum from Brazil has larger amounts of galactose and glucose compared to the gums from other countries. Xylose was observed in small amounts only in the gums in India, Venezuela and Brazil, studied by Botelho (1999) [14].

The gum of the cashew tree has connections (1 $\rightarrow$ 3) which guarantee a lower symmetry of molecule contributing to improve its solubility. These leads are interspersed by glycosidic linkages (1 $\rightarrow$ 6), which contribute to increase the solubility of the molecule [1].

Anderson & Bell (1975) [18] proposed a possible structural fragment of the cashew gum, presented in the figure below, where R is D-mannose, D-xylose, L-ramanose, L-arabinose and R" is D-glucose or glucuronic acid.

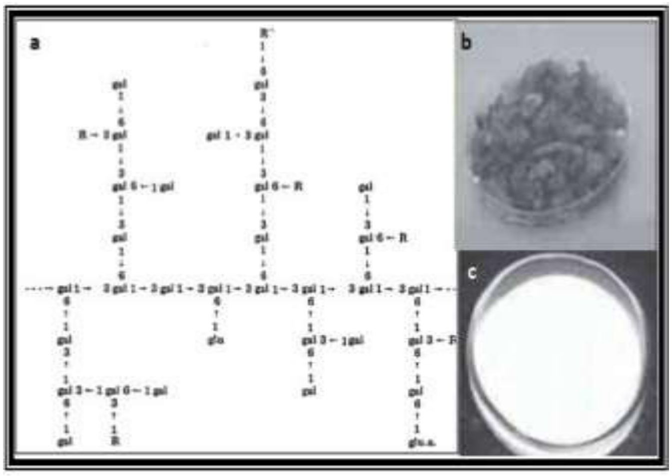

Fig.2: (a) Possible structural fragment of the cashew gum [18]; (B) Exudate of the cashew tree (c) Purified cashew tree gum [1]

IV. CASHEW GUM EXTRACTION AND PURIFICATION PROCESSES

Costa et al (1996) [20] studied a purifying method consisting of the steps of grinding, dissolution in water (4% in water) in an NaOH enviroment, filtration and precipitation with ethanol. The obtained precipitate is washed with ethanol and acetone and dried in aqueous medium, thus obtaining the isolated gum. Isolated gum suffers a first purification process which aims to remove the cations present in the gum. This first purification of the isolated gum consists of the steps of obtaining isolated gum in the dissolution step being carried out with water (4% in water) in a NaCl environment. To remove NaCl precipitate excess, a second purification method is carried out, which differs from the first only in the dissolution step, which is performed with 3% in water and NaCl.

Mothe & Freitas (2013) [21] performed the purification of cashew gum through grinding, solubilization, centrifugation, precipitation with alcohol and vacuum drying. The presence of total sugars was analyzed by the UV-Visible spectrophotometer method. The characterization on the purified sample of the gum was performed by GC-MS, and the following proportion was found: 56.7% Galactose; Arabinose 10.6%; Glucose 19.7% and 13% Rhamnose. The uronic acid was not quantified.

In a publication made by Tiomno (1946) apud Mothe et al (2006) [1], a qualitative analysis of the ashes of the cashew gum was made, and the presence of potassium, silicon, magnesium, calcium, aluminum and iron was found, as well as traces of sodium and manganese. Mothe et al, 2002 [22] after performing X-ray fluorescence analysis of cashew gum ashes, found that the calcium content was lower than 1%, and also found traces of manganese, potassium and iron.

The rheological behavior of aqueous dispersions of cashew gum and gum arabic was studied by Mothe & RAO (1999) [23] and it was concluded that both gums show a pseudoplastic, non-Newtonian behavior in concentrations of 4 to 50%. This result confirmed the study by Zaccaria & RAHMAN (1996) [24] who had observed the same behavior for the cashew gum.

A comparison of thermal behavior of gum arabic and cashew gum was performed by Mothe & RAO (2000) [13]. Thermogravimetric curves (TG) of cashew gum were performed at different concentrations (w / w) at temperatures of 0 to 800 ° C in nitrogen atmosphere. Two stages of decomposition were observed, the main one at 252º C. In this study, it was found that cashew gum and gum arabic have similar thermal behavior, so in terms of thermal stability, the gum arabic can be replaced by the cashew gum in various applications.

V. STUDIES OF CASHEW GUM BLENDS

Table 2: Cashew gum blends with other polymers

Blends of Cashew gum with other polymers		
Polymers	Purpose	References
Acrylamide	Graft copolymerisation of acrylamide onto cashew gum	Silva et al, 2007 [25]
Alginate (ALG)	Floating bead as a matrix for larvicide release	Paula et al, 2012 [26]
Alginate (ALG)	Nanoparticles for essential oil encapsulation	Oliveira et al, 2014 [27]
Carboxymethylcellulose (CMC)	Formulations as protective coatings on intact and cut red guavas	Forato et al, 2015 [28]
Cassava starch Carnauba waxe	Influence of cassava starch and carnauba waxe on physical properties of cashew tree gum based films	Rodrigues et al, 2014 [29]
Chitosan	Synthesis and thermal stability of chitosan/carboxymethyl cashew gum polyelectrolyte complex	Maciel et al, 2005 [30]
Chitosan	Chitosan/cashew gum nanogels for essential oil encapsulation	Abreu et al, 2012 [31]
Chitosan	Development and characterization of hydrogels of policaju and chitosan	Soares et al, 2014 [32]
Chitosan	Assess effect on the swelling and BSA release from CHI/CMCG MIC	Magalhães et al, 2009 [33]
Chitosan	Polysaccharide-based nanoparticles formation by polyeletrolyte complexation of carboxymethylated cashew gum and chitosan	Silva et al, 2010 [34]
Metallic phthalocyanines Polyallylamine hydrochloride	Nanobiomedical devices	Araújo et al, 2012 [35]
Polyaniline	Multilayer films electrodes for dopamine determination	Barros et al, 2012 [36]
Polyvinyl alcohol (PVA)	Bioactive film for wound dressing aplication	Moreira et al, 2015 [37]
Polyvinyl alcohol (PVA)	Stimuli-responsive and bioactive film	Silva et al, 2016 [38]
Polyvinyl alcohol (PVA)	Film for fungal growth inhibition	Silva et al, 2012 [39]

An important application of cashew gum is in the formulation of blends or mixtures. The gum may be associated with other polymers giving good filmogenic features which provide new industrial applications for the same. Table 2 below presents a list of published works associating cashew gum with other polymers such as Acrylamide [25], Alginate [26, 27], Carboxymethylcellulose [28], Cassava starch and Carnaubawaxe [29], Chitosan [30, 31, 32, 33, 34]; Metallicphthalocyanines, polyallylamine, hydrochloride [35].

Studies of cashew rubber blends with polyvinyl alcohol (PVA) have presented several applications in the formulation of films. Moreira et al (2015) [37] and Silva et al (2016) [38] produced bioactive films for use in dressings. Silva et al (2012) [39] studied a bioactive film inhibitor of fungal growth.

VI. CASHEW GUM APPLICATION

By having a biological origin, the ability to form gels and because it has properties similar to synthetic polymers, gums are an excellent choice for the use in several sectors of industry [40]. Depending on the size and molecular orientation, particle size, temperature, concentration, ionic and hydrogen bonds, the functional properties of the gums are affected.

In the food industry, it is possible to apply the cashew hum as a thickener and stabilizer for juices, as an emulsifier in sauces [22] and emulsions of meats such as sausage [41]. Recently, Mothe & Lannes (2015) [42] developed chocolate formulations containing cashew gum in candy bars, studying their thermal, rheological and sensorial properties.

In the pharmaceutical industry it may be an agent for suspending, emulsifying, disintegrating, binding, tabletting drugs with release control and also as a mucoadhesive and gelling agent.

Mothé & Silva, 2005 [44] studied the use of cashew gum in the reduction of blood pressure in spontaneously hypertensive rats. Blood pressure reduction was observed in up to 20% of the rats that were fed with cashew gum. There was also a 4% decrease in the ratio of left ventricular mass and heart mass of the rats treated with the gum. This indicates that cashew gum may have contributed as a promoter of cardiac cells, retarding their hypertrophy.

In the area of neoplasia, the effect of cashew gum was studied in mice with induced sarcoma 180, where antitumor activity was observed after the use of the gum, as well as a significant reduction of tumors [45].

Anti-diarrhea properties of cashew gum in rodents were also observed by Araújo (2015) [46].

Another application of cashew gum was in the flotation of minerals, where its use was studied as a depressor agent in the flotation process of the tailings of marble and granite industries. The benefit of this application is the fact that cashew gum is of organic origin and therefore it is non-polluting, unlike the generally used depressants, of inorganic origin [47].

VII. TECHNOLOGICAL MONITORING OF CASHEW GUM

In order to get an overview of technological and scientific development related to application of cashew gum, a technological prospection was carried out, with a database of patents and articles.

The prospection of patent applications was carried out in the period between 1976 and September 2016, a total of 40 years, and the databases of the Institute of Industrial Property (INPI), United States Patent and Trademark Office (USPTO) and World Intellectual Organization (WIPO) were used. The following terms were used as keywords: Anacardium occidentale and cashew gum. The following table 3 shows the number of patents found per database and application.

Table.3: Number of patents found per research base

Application	Reserch source			
	INPI until set 2016	USPTO (1976 to set 2016)	WIPO (1978 to set 2016)	TOTAL
Personal hygiene & Cosmetics	2	0	4	6
Flotation of calcareous minerals	1	0	0	1
Hydrogels manufacture	1	0	0	1
Pharmaceuticals	3	0	13	16
Food	5	0	22	27
Plastics industry	1	0	1	2
Production process of cashew gum	2	0	3	5
DNA sequencing	0	3	2	5
Effluent and water treatment	1	0	0	1
TOTAL	**16**	**3**	**45**	**64**

It is noteworthy that 13 patent applications found in the INPI database were also found in the WIPO database and 2 patent applications found in the USPTO were also found in the WIPO database.

The most found patent applications have applications in the pharmaceutical and food industries, which shows the importance of the cashew agribusiness in these industry segments.

Although literature has a large number of cashew gum applications, only 5 patent applications on this subject were found in the INPI database, 2 of the production process or isolation of gum, one on its use as a depressant in calcareous mineral flotation, another as a flocculant for water and wastewater treatment and another on the production of superabsorbent hydrogels.

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For the technological prospection of articles, the Web of science database was used with the keywords "cashew gum". The search period was from 1900 to September 2016, a total of 116 years. 71 records of publications were found.

Figure 3 below shows the progress per year of publications found.

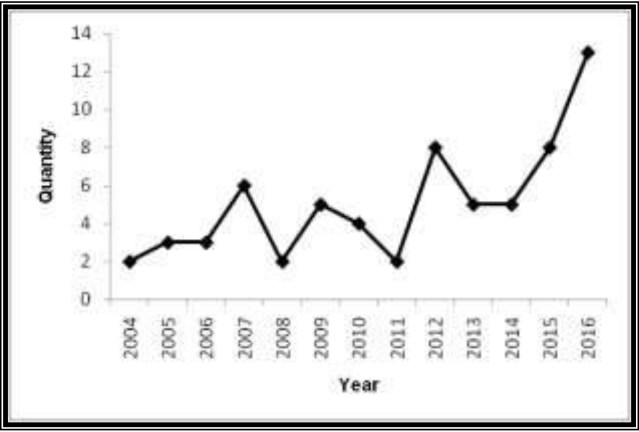

Fig.3: Evolution of publications on cashew tree gum (using data from the Web of Science)

It is possible to observe a significant increase of publications on cashew gum in recent years. In 2016, up to September, 13 publications were found.

The next graph shows the percentage of publications found, by country.

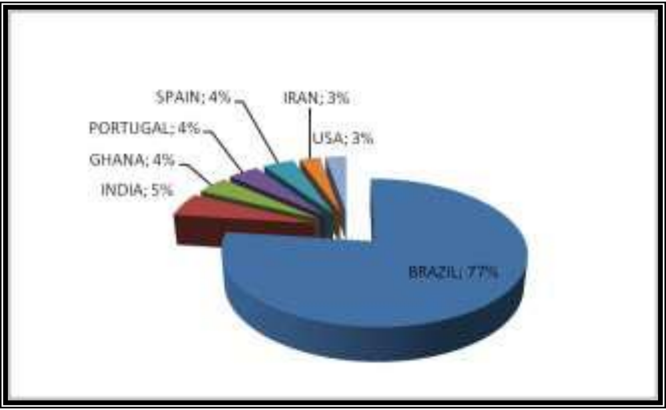

Fig.4: Publications on cashew tree gum by country (Own elaboration from Web of Science data)

It is possible to observe that Brazil is the country that has published the most about gum cashew, with 77% of publications found. India, Ghana, Portugal, Spain, Iran and the United States made publications, but in small quantities, varying from 3 to 5%.

An analysis of publications was also performed by field of study, which is presented in figure 5 below.

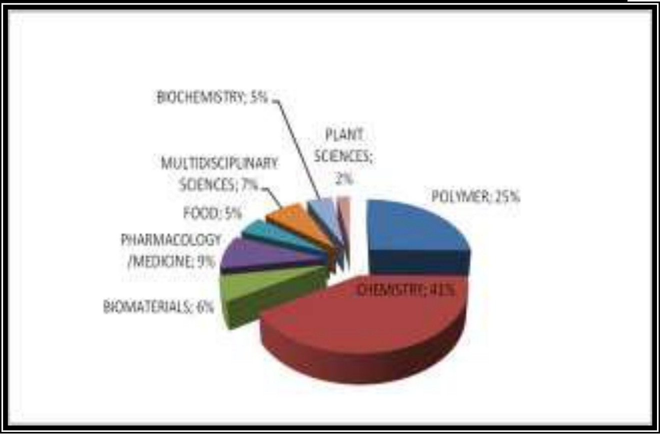

Fig.5: Publications on cashew tree gum by field of study

Most publications found, 41%, referred to the chemistry field in general. The polymer field is second with 25% of the publications, then the fields of pharmacology / medicine, with 9% of the publications.

VIII. CONCLUSION

In cashew agribusiness, there is still interest in the production of nuts and the pseudo fruit (cashew), besides of the cashew nut shell liquid (CNSL). The exudate has been considered as a solid residue, that is, with great potentiality. The perspective of the production and availability of cashew gum in Brazil, associated with recent publications on its properties and performance, such as lowering blood pressure and antitumor properties against sarcoma 180, makes this polysaccharide an excellent choice of raw material to be explored or used by the pharmaceutical industry and especially by the food industry, in the development of functional foods.

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