

Physicochemical parameters of the gum of *Terminalia catappa* L. (almendrón)

Maritza Martínez^{1*}, Antonio Vera², Juan Parra¹, Olga Beltrán¹, María Gabriela Leal¹, Didier Le Cerf³ and Luc Picton³

¹Centro de Investigaciones en Química de los Productos Naturales, Facultad de Humanidades y Educación. Universidad del Zulia. ²Laboratorio de Ecología, Centro de Investigaciones Biológicas, Facultad de Humanidades y Educación. Universidad del Zulia. ³URA 500 du -cnrs "Polymères, byopolymères, membranes, Faculté des Sciences de l'Université de Rouen, 76134 Mont Saint Aignan Cédex, France

Recibido: 14-04-2012 Aceptado: 10-10-2012

Abstract

In Venezuela, the genus *Terminalia* (Combretaceae), is represented by thirteen (13) species. *Terminalia catappa* exudes an amber-colored gum, soluble in water. Relatively few studies exist concerning the gum of this species. The objective of this work is to determine the physicochemical parameters of the gum of *T. catappa* and to compare these parameters to those published for other gum exudates of Combretaceae. The physicochemical parameters were determined by the classic methodology for carbohydrates, size exclusion chromatography SEC-MALLS and IR spectroscopy. In general, the gum of *T. catappa* showed parameters comparable to those reported for the species of the same genus and, in general, of the sub-tribe Terminaliinae. It also exhibits characteristics analogous to those exudates from *Combretum* spp. (sub-tribe Combretinae). Greater differences were observed with the gum of *Laguncularia racemosa*, belonging to a superior taxonomic category (Tribe Laguncularieae). The physicochemical parameters constitute an important fingerprint in order to differentiate gums of diverse species and genus. The gum of *T. catappa* exhibits properties which confer it a potential technological interest.

Keywords: *Terminalia catappa*, Combretaceae, physicochemical parameters, gum exudates.

Parametros fisicoquímicos de la goma de *Terminalia catappa* L. (almendrón)

Resumen

El género *Terminalia* (Combretaceae), en Venezuela, está representado por trece especies. *Terminalia catappa* exuda una goma de color ámbar, soluble en agua. Existen relativamente pocos estudios acerca de la goma de esta especie. El objetivo de este trabajo es determinar los parámetros físico-químicos de la goma de *T. catappa* y compararlos con los publicados para otros exudados gomosos de Combretaceae. Los parámetros físico-químicos se determinaron por metodología clásica para carbohidratos, cromatografía de exclusión por tamaño SEC-

* Autor para la correspondencia: mmartinez.luz@gmail.com

MALLS y espectroscopía de IR. La goma de *T. catappa* mostró parámetros comparables a los reportados para las especies del mismo género y de la sub-tribu Terminaliinae, en general. Así mismo, exhibe características análogas a los exudados gomosos de *Combretum* (sub-tribu Combretinae). Se observaron mayores diferencias con la goma de *Laguncularia racemosa*, perteneciente a una categoría taxonómica superior (Tribu Laguncularieae). Los parámetros físico-químicos constituyen una huella dactilar importante para diferenciar gomas de diversas especies y géneros. La goma de *T. catappa* exhibe propiedades que le confieren un potencial interés tecnológico.

Palabras clave: *Terminalia catappa*, Combretaceae, parámetros físico-químicos, exudados gomosos.

Introduction

The Combretaceae family is a very complex taxon and, according to the Exell y Stace review (1) is made up of two sub-families, two tribes, and two sub-tribes. The sub-tribe Terminaliinae includes the genera *Terminalia*, *Anogeissus* y *Conocarpus*, amongst others (1, 2). This taxonomic classification corresponds with phylogenetic and DNA studies carried out subsequently (3).

The diversity and complexity of the Combretaceae family corresponds with the variability in the composition of the polysaccharides and the aminoacids of the gums resulting from the different genus and species which conform it (4).

Unlike those corresponding to the genus *Acacia*, few studies have been made on the gums of Combretaceae, with the exception of the gum exudates from *Anogeissus latifolia*, commercially known as "goma ghatti" (5), *A. schimperi* (6-8) (syn. *A. leiocarpus*), of a certain species of *Combretum* (9, 10), and of the genus *Terminalia* (*T. tomentosa*, *T. sericea*, *T. superba*, *T. argentea*) (9, 11, 12).

On the other hand, Lambert *et al.* (13), reported the gum-resin characteristics of the exudate of *Bucida buceras*, and, in Venezuela, the physicochemical parameters and structural characteristics of the gum of *La-*

guncularia racemosa (mangle blanco), have been detailed (14, 15). In contrast to these, no data have been published for gums of the genus *Conocarpus*.

In Venezuela, the genus *Terminalia* is represented by thirteen species, *T. catappa* (16), amongst these. Extensive research has been made on the use of its leaves, bark, and fruits in antidiarrheic, antipyretic, and anticoagulant purposes (17), as well as on the nutritive value of its seed (18). Nevertheless, little is known about its gum exudate.

Recently, Kumar *et al* (17) confirmed the benefit that the gum of *T. catappa* might render as an excipient, delaying the release of drugs; in addition to this, a rheological study was performed.

The objective of this research is to determine the physicochemical parameters of the gum of *T. catappa* (almendrón) and to related them to its taxonomic classification.

Materials and methods

Origin and purification of the gum

The gum of *T. catappa* (almendrón) was recollected from four samples taxonomically identified by Dr. José Grande, taxonomist botanist from la Universidad Central de Venezuela. Furrowed cuts were performed on the trunk, cuts which were removed periodically

(weekly). The gum was recollected during the dry season (January-March 2010).

General methods

To evaluate the physicochemical parameters of interest the established classic methodology for carbohydrates was used. Moisture content was determined by drying to constant weight at 105°C. Total ash content was established by ashing at 550°C (in a muffle furnace) to constant weight. The mineral ash composition was determined by atomic absorption spectroscopy (AAS) and the nitrogen percentage by the Kjeldahl method. The crude protein was calculated from the nitrogen content using the conversion factor 6.25 (9, 10). Total soluble fibre was obtained by subtraction of contents of moisture, ash and protein from 100 (20). Tannins (polyphenols) were estimated by the Folin-Ciocalteu method (19) Also, the percentage of uronic acids was determined by the Blumenkrantz-Asboe method (19), whilst the composition of neutral sugars was established by the phenol-sulfuric method (19) and was corroborated by HPLC liquid chromatography, using an amino column (Waters), at 35°C, a mixture acetonitrile: water 80:20, as mobile phase, and an index refraction detector, at 35°C. Specific rotation was determined in water (1% w/v) at 30°C in an ATAGO POLAX-D polarimeter; and the intrinsic viscosity, by the isoionic method, using an UBBEHLÖDE viscosimeter. The solubility in water (0.1% w/v, at 30°C) was evaluated as described previously (20).

Size exclusion chromatography (SEC-MALLS)

The average molar mass (M_w) and the average molar mass in number (M_n) were determined by size exclusion chromatography (SEC-MALLS). The SEC-MALLS technique has been described previously (21).

Infrared spectroscopy

The identification of the acetyl groups was performed by means of IR. spectroscopy.

The IR spectrum was recorded on a Prestige 21 (SHIMADZU) spectrometer. The lyophilized dry powder was mixed with KBr and pressed into pellets under mechanical pressure. The IR spectra were acquired after 50 scans between 4000 and 400 cm^{-1} , with the spectral resolution of 4 cm^{-1} .

Results and discussion

Physicochemical parameters of the gum of *T. catappa* and those corresponding to other gums of Combretaceae are presented in table 1. The mineral composition of the gum, object of this study, is showed in table 2.

The SEC-MALLS chromatographic profile is illustrated in Figure 1 and the IR spectrum of the gum of *T. catappais* presented in figure 2.

The moisture content of the gum of *T. catappa* (table 1), is situated within the minimum interval established by the European specifications ($\leq 15\%$) for a gum of good quality; this level of humidity prevents microorganisms proliferation (20, 22).

The total ash content of the gum in study (table 1) suggests a partial neutralization of the carboxylic groups of the uronic acids by metals (15). The mineral composition of the ash (table 2) confirms this fact and reveals that the predominant cation is calcium, such as in the gum exudate of *Combretum paniculatum* (23), (sub-tribe Combretinae). However, these results are quite different to the observed for the gum of *A. leiocarpus*, (sub-tribe Terminaliinae) which has a high content of iron and magnesium. The concentrations of aluminum and lead (toxic metals) are over the limits established by the food industry (< 2 ppm), nevertheless, an analogous value was reported for the gum of *C. paniculatum* (23). The presence of cations in the gums is associated with the mineral composition of the soil where the productive species grow (20).

Table 1
Physicochemical parameters of *T. catappa* gum exudate and from other species of Combretaceae

Parameter	Species				
	<i>T. catappa</i> ^a	<i>T. sericea</i> ^d	<i>T. superba</i> ^d	<i>C. nigricans</i> ^e	<i>L. racemosa</i> ^f
Moisture, %	9.76	9.2	12.2	10.6	18.45
Ash, % ^b	2.02	2.4	0.6	2.1	8.71.
Nitrogen, % ^b	0.45	0.46	0.18	0.32	0.06
Protein, % ^b (N x 6.25)	2.84	2.87	1.12	2.00	0.42
Total soluble fibre, %	85	nd	nd	nd	nd
Intrinsic viscosity, dl.g ^{-1b}	0.38	1.45	1.57	0.35	0.62
Molecular weight, Mw x 10 ⁵	9.8	nd	nd	4.8	nd
Solubility, % (30°C, 0,1% m/v) ^b	27	nd	nd	nd	nd
[α] _D in water, degrees ^b	-7.5	-13	+44	-53	+61
Tannins, % ^b	0.11	nd	nd	nd	nd
Hence, uronic acids, % ^{b,c}	19	10.9	10.9	11	37
Neutral sugar composition after the hydrolysis, % ^b					
Galactose	20	22	20	28	20
Arabinose	59	48	51	54	33
Mannose	1	7	9	0	0
Xylose	1	6	4	trace	0
Rhamnose	-	6	5	7	10

^aAverage of four specimens. ^bCorrected for moisture content ^cIf all acidity arises from uronic acids^dRef. 11^eRef.10^fRef.14 nd= not determined.

Table 2
Mineral composition of *T. catappa* gum exudate

Elements	Proportions, g/Kg
Calcium	12.37
Magnesium	1.02
Potassium	0.14
Sodium	0.55
Lead	0.01
Aluminum	0.02
Vanadium	.01

The content of uronic acids (table 1), is higher than that described for the gums of *T. sericea* and *T. superba* (11), but much lower than that corresponding to the gum exudate of *L. racemosa* (14, 15), belonging to a superior taxonomic category, in the tribe Laguncularieae (1, 2).

The percentages of nitrogen and of protein indicate the existence of an important proteic fraction, linked to the carbohydrate (4). These values correspond to those published for the gums of *T. sericea* (11) (Table 1) y *T. argentea* (2).

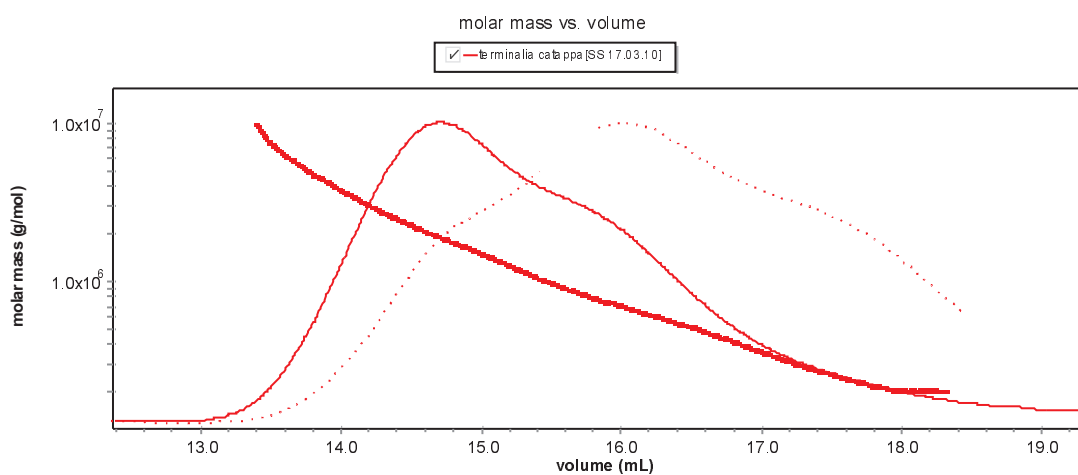


Figure 1. Size exclusion profile of the *T. catappa* gum exudate.

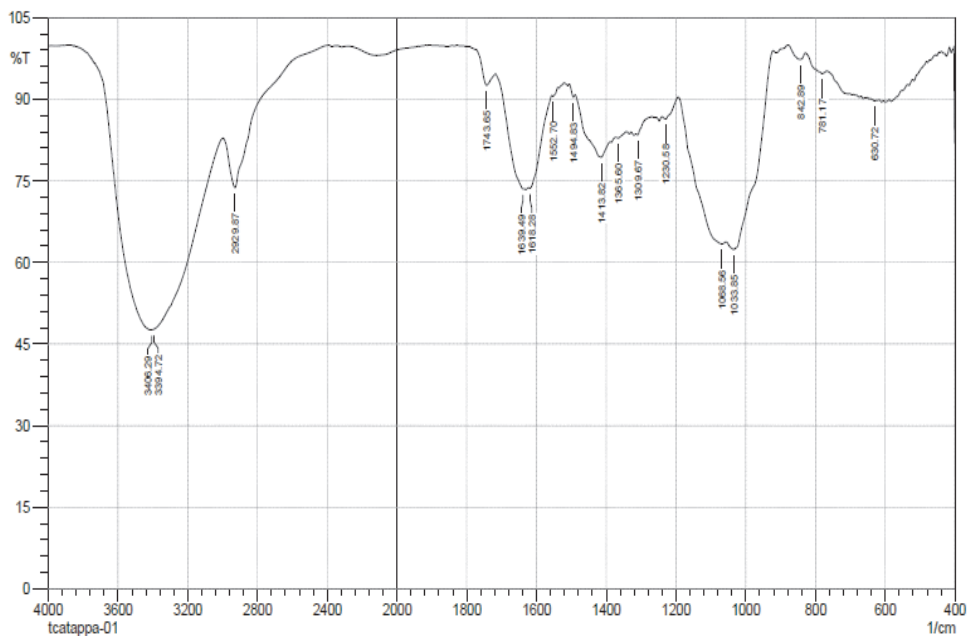


Figure 2. I.R. spectrum of *T. catappa* gum exudate.

The total soluble fibre of the studied gum, table 1, is relatively high in comparison to *A. senegal*, *A. seyal* and *A. siebarana* exudates (20), which confer it a potential nutritional value.

The specific rotation, an important parameter for determining the purity of the

gum, is low negative, suggesting a predominance of sugars in β configuration in the structure of the polymer (15), a result analogous to that obtained for the gum of *T. sericea* (11), but in contrasts with the high positive value of the gum exudate of *L. racemosa* (14, 15) (table 1).

The intrinsic viscosity of the gum object of this study (table 1) suggests the existence of a higher molecular weight polymer in the gum's chemical constitution" (20). The high viscosity is a characteristic feature of the gums of the genus *Terminalia* studied up to now, which confers them a great industrial potential (11). In fact, the SEC-MALLS chromatography of the gum of *T. catappa* revealed a polydisperse system ($I_p = 1.8$), figure 1, with an average molar mass of 9.8×10^5 g/mol and an average molar mass in number of 5.0×10^5 g/mol. Values in the order of 10^5 have been described for gums of *Combretum* (9).

In addition, *T. catappa* gum has a solubility of 27% in water (0.1% w/v), at 30°C, lower than that reported for *A. senegal*, *A. seyal* and *A. siebarana* gum exudates (20). This relative insolubility is indicative of the presence of cross linking between the polymeric chains that favors the swelling in water, without dissolving (20).

The percentage of tannins (0.11%), Table 1, is lower than that reported for gums of *Combretum paniculatum* (23) and *A. leiocarpus* (7). The presence of tannins would limit its use in the food industry.

The gum of *T. catappa* contains galactose, arabinose, mannose, and xylose. The predominance of arabinose and the presence of mannose and of xylose have been reported for gums of *Terminalia* (11) and *Combretum* (9), table 1.

The absence of rhamnose (table 1), suggests that no methyl groups exist that could act as hydrophobic poles assisting in an emulsifying process. In contrast, structural studies have proven that the gum exudates of some *Combretum* spp (9) and *L. racemosa* (14, 15) contain a high proportion of rhamnose.

However, the presence of acetyl groups, which could contribute in an emulsifying process, was confirmed by IR spectroscopy

peaks at $1,743.65 \text{ cm}^{-1}$ and $1,230.58 \text{ cm}^{-1}$ are indicative of these groups, figure 2 (24).

Conclusions

The gum of *T. catappa* showed parameters comparable to those reported for the species of the same genus and the sub-tribe Terminaliinae, in general. It also exhibits characteristics analogous to the gum exudates of *Combretum* (sub-tribe Combretiinae). Major differences were observed with the gum of *Laguncularia racemosa*, belonging to a superior taxonomic category (Tribe Laguncularieae).

The physicochemical parameters constitute, in this way, an important fingerprint to relate gums of diverse species and genus.

The gum of *T. catappa* exhibits physicochemical data that confer it a potential technological interest.

Acknowledgments

To the Consejo de Desarrollo Humanístico y Científico (CONDES) of the Universidad del Zulia, for its financial support given for the development of this project. To the Facultad Université de Rouen, France and to the de Ciencias, LUZ, for their respective contributions in the measuring of the molar masses and the recording of the infrared spectrum.

References

1. EXELL A.W., STACE C.A. *Boletim da la Sociedad Broteriana. sér 2*, 40: 5-25. 1966.
2. LOIOLA M.I.B., SALES M.F. *Arq Jard Bot Rio de Janeiro* 34(2): 174-188. 1996.
3. TAN F., SHI S., ZHONG Y., GONG X., WANG Y. *J Plant Res* 15: 475-481. 2002.
4. ANDERSON D.M.W., HOWLETT J.F., MCNAB C.G.A. *Phytochemistry* 26: 837-839. 1987.

5. KANG J.I., CUI S.W., CHEN J.I.E., PHILLIPS G. O., WU Y., WANG Q. **Food Hydrocolloid** 25: 1984-1990. 2011.
6. MC ILROY R. J. **J Chem Soc** 1918-1919. 1952.
7. AHMED S.E., MOHAMED B.E., KARAMALLA K. A. **Pak J Nutr** 8: 826-828. 2009.
8. AHMED S.E., MOHAMED B.E., KARAMALLA K. A. **Pak J Nutr** 8: 782-786. 2009.
9. ANDERSON D.M.W., BELL P. C. **Carbohydr Res** 57: 215-221. 1977.
10. ANDERSON D.M.W., STEFANIA., WEIPING W. **The International Tree Crops Journal** 6: 275-285. 1991.
11. ANDERSON D.M.W., BELL P.C. **Phytochemistry** 13: 1971-1874.1974.
12. BOFF S., GRACIOLLI G., BOARETTO A., MARQUES M. R. **Rev Bras Entomol** 52: 477-479. 2008.
13. LAMBERT J.B., WU Y., SANTIAGO-BLAY, J.A. **J Nat Proc** 68: 635-648. 2005.
14. LEÓN DE PINTO G., NAVA M., MARTÍNEZ M., RIVAS C. **Biochem Syst Ecol** 21: 463-466. 1993.
15. LEÓN DE PINTO G., GUTIÉRREZ DE GOTERA O., MARTÍNEZ M., OCANDO E., RIVAS C. **Carbohydr Polym** 35: 205-213. 1998.
16. HOKCHE O., BERRY P.E., HUBER O. **Nuevo catálogo de la flora vascular de Venezuela** Fundación Instituto Botánico de Venezuela. Caracas (Venezuela) 336-337. 2008.
17. KUMAR S.V., SASMAI D., PAIS C., AAPS. **Pharm Sci Tech** 9: 885-890. 2008.
18. GONZÁLEZ-MENDOZA M., MENDOZA F., MORA J., MENDOZA M., MARQUEZ J., BRAVO M. **Revista Facultad de Farmacia UCV** 47: 25-29. 2005.
19. ABED EL KADER D., MOLINA E., MONTERO KC., GUTIÉRREZ O., TRONCONE G. Y LEÓN DE PINTO G. **Rev Fac Agron. (LUZ)** 23: 95-108. 2008.
20. PICTON L., BATAILLE I., MULLER G. **Carbohydr Polym.** 42: 23-31. 2000.
21. YUSUF, A. K. **JORIND** 9: 10-17. 2011.
22. MARTINS E., OMOYEME I., CHRISTIANA I., OFOEFULE S., OLOBAYO K. **Afr. J Pharm Pharmacol.** 3: 265-272. 2009.
23. ANDERSON D.M.W., WEIPING D.M.W. **Phytochemistry** 29: 1193-1195. 1990.
24. VINOD V.T.P., SASHIDHAR R.B. **Indian J Nat Prod Resour.** 1: 181-192, 2010.