Isolation, Chemical Structure Elucidation and Bioactivities of *Argania spinosa* Cell Wall Polysaccharides: A Review

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ABSTRACT

The polysaccharides obtained from *A. spinosa* benefit from promising prospects in a number of different directions, thanks to their huge structural heterogeneity, reflected by the large number of diverse uses as the food, pharmaceutical, cosmetics, paper and textile industries, as well as water depollution, catalysis, membranes and others. This paper reviews the methods of separation, purification, structural elucidation and valorization in different fields of *A. spinosa* cell wall polysaccharides. This review is a useful synthesis for further research and improvement of various properties of *A. spinosa* cell wall polysaccharides.

Keywords : Argan tree, polysaccharide, extraction, structural characterization, valorization.

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INTRODUCTION

Polysaccharides constitute a class of natural products which is characterized by a large variety of structures and physicochemical properties that justify their diverse uses in food, pharmaceutical, cosmetic, paper industries, as well as in oil extraction¹. More recently, the study of polysaccharides as bioactive agents has gained increased favored their biocompatibility, interest. by biodegradability and their absence of toxicity^{2,3}. The isolation, purification and use of polysaccharides depend on their structural characteristics but also on the biological matrices in which they are naturally present. Structural analysis can provide valuable information for the understanding of the biological functions of polysaccharides, but the diversity and the aperiodic arrangement of the chains make it difficult to uncover the links between structure and function^{4,5}.

The Algerian Sahara has a diffuse and sparse vegetation⁶. Some species have bioactive properties that make them of interest in various fields⁷. One of these species, the Argan tree -Argania spinosa (L.) Skeels (synonyms Argania sideroxylon Roem. & Schult., Sideroxylon spinosum L.) - is, in Algeria and Morocco, the only representative of the tropical family Sapotaceae, which otherwise includes nearly 600 species^{8,9}. It is a very hard wood tree, which is recognizable with a short and tormented trunk topped by a very large crown; its life expectancy lies between 150 -200 years. The Argan tree is perfectly adapted to the arid saharan bioclimatic context thanks to the mechanisms that regulate the simultaneous variations of foliar water potential and transpiration¹⁰. Owing to its strong and deep root system, this species ensures the ecological balance of its habitat, protecting the soil from both water and wind erosion¹¹.

To the best of our knowledge, either the extraction and purification methods or the structural characteristics of the polysaccharides of *A. spinosa* have not been reviewed yet. Therefore, in order to better understand these macromolecules, this review seemed appropriate, the aim being to give an overview of the techniques used for the study of *A. spinosa* polysaccharides, and more especially their structure and their biological activities.

EXTRACTION, PURIFICATION AND CHARACTERIZATION METHODS OF ARGANIA SPINOSA POLYSACCHARIDES

Extraction of Argania spinosa polysaccharides

The main problem encountered by the experimenter is the chemical richness of the plant cell wall, which is reflected by a large structural diversity of macromolecules, essentially the polysaccharides. If the protocols to be used must be sufficiently selective to extract a precise category of macromolecules, they also must ensure that the molecular structures are subjected to the least possible damage^{12,13}. A detailed review of the literature in the field of polysaccharide extraction indicates that there exist a large number of classical protocols for the extraction of the different groups of polysaccharides^{14,15}. Hot water extraction of polysaccharides from the argan tree is the most widely used method for the isolation of high methyl pectins, pectic acids or their pectate salts, owing to their high affinity for water^{16,17}. On the other hand, low-methyl pectins, which are present in the wall as calcium-pectin complexes, can be extracted with solutions of calciumchelating agents such as EDTA^{16,17,18} and CDTA¹⁹. These compounds lead to the formation of pectates which are easily dissolved in hot water together with pectins²⁰.

Hemicelluloses as a whole represent the largest polysaccharide fraction of argan, as in all dicots. They are usually extracted with increasing concentrations of alcalis²¹. In their native state, hemicelluloses are more or less extensively acetylated at the *O*-2 or *O*-3 positions and are intimately bound to other parietal polysaccharides by hydrogen bonds. Thus, during alkaline extractions, saponification of these acetyl ester functions, and the breaking of hydrogen bonds contribute to the

solubilisation of hemicelluloses 22 . Alkali concentrations used range from 0.17 to 6 $M^{18,23,24,25,19,26,27}.$ The general

extraction procedures of *A. spinosa* polysaccharides are summarized in Table 1.

Polysaccharides	Argania	Argania origin	Chemical Isolation	Type of polysaccharide	References
names	organ				
AFRG-I and	Fruit pulp	Southern	0.05 M CDTA	Chelate-soluble pectin	Aboughe-Angone et
AFRG-II		Morocco			al. ¹⁹
AF10H and			1 M and 4 M KOH	Alkali-soluble	
AF4OH				hemicellulose	
P ₁ -H ₂ O	Pericarp	Stidia region,	Distilled water at 100° C	Water soluble pectin	Hachem et al. ¹⁸
P2-EDTA	fruit	west coast of	1% EDTA	Chelate-soluble pectin	
H ₁ -KOH 1M and		northern Algeria	1 and 4 M KOH	Alkali-soluble	
H ₂ -KOH 4M				hemicellulose	
ALT-WSP	Leaves	Tindouf region,	Distilled water at 100° C	Water-soluble pectin	Hachem et al. ¹⁷
ALT-CSP		Southwest	1% EDTA		
		Algeria		Chelate-soluble pectin	
ALS-WSP	Leaves	Stidia region,	Distilled water at 100° C	Water-soluble pectin	Hachem et al. ¹⁶
ALS-CSP		west coast of	1% EDTA		
		northern Algeria		Chelate-soluble pectin	
A10H and A40H	Leaves	Souss region,	1 and 4 M KOH	Alkali-soluble	Ray et al. ²⁷
B10H and B40H		south of Morocco		hemicellulose	
PWSF-I, PWSF-II	Seed	Essaouira region,	0.5, 1, and 2 M NaOH	Water soluble	Habibi and Vignon ²⁶
and PWSF-III	pericarp of	Morocco		hemicellulose	
PWIF-I, PWIF-II	fruit			Water insoluble	
and				hemicellulose	
PWIF-III					
HX	Fruit	Ait Amira region,	4,3M KOH	Alkali-soluble	Barbat ²⁵
MGX A	pericarp	Morocco		hemicellulose	
FI KOH and FIII					
КОН	Leaves	Tindouf region,	24% KOH	Alkali-soluble	Hachem et al. ²³ ;
FI NaOH and FIII		Southwest		hemicellulose	Hachem et al. ²⁴
NaOH		Algeria	4.3 M NaOH		

Table 1. Polysaccharides isolated from A. spinosa

Purification and characterization methods

Argania spinosa polysaccharide purification methods used size-exclusion chromatography on DEAE-Trisacryl M, Sepharose CL-4B, Biogel P6 and Biogel P2, which are generally associated with other techniques, such as alcoholic precipitation followed by centrifugation²⁸, enzymatic²⁹ and or acid³⁰ treatment. As a result of these purifications, various polysaccharides were isolated, and

their structural characteristics were further defined by the following methods: infrared (IR) spectroscopy, gas chromatography (GC), high performance anion exchangepulse amperometric detection-chromatography (HPAE-PAD-chromatography), matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS) and nuclear magnetic resonance (NMR), as shown in Table 2.

Table 2.	Techniques used	in the study	of A. spinosa	polysaccharides
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Polysaccharide fraction	Separation and/or Purification methods	Hydrolysis method	Polysaccharide	Characterizatio n methods	References
AFRG-I	Acidification	Endopolygalacturonase	Rhamnogalacturonan-I	GC	Aboughe-
AFRG-II	(AcOH, pH 6)		Rhamnogalacturonan-II	GC-MS MALDI-TOF	Angone et al. ¹⁹
AF10H and AF40H	Precipitation (80% EtOH)/ Centrifugation	β -1,4-endoglucanase	Xyloglucans		
P ₁ -H ₂ O P ₂ -EDTA H ₁ -KOH 1M	Precipitation (EtOH)/ Centrifugation Acidification (20%	2M TFA	Homogalacturonan Rhamnogalacturonan-I * Rhamnogalacturonan-II Homoxylan	GC FT-IR	Hachem et al. ¹⁸
and H2-KOH 4M	AcOH)		Xyloglucans Arabinoglucuronoxylans		
ALT-WSP ALT-CSP	DEAE-Trisacryl M column	2M TFA	Rhamnogalacturonan-I Homogalacturonan Rhamnogalacturonan-I*	GC GC-MS ¹³ C NMR	Hachem et al. ¹⁷

ALS-WSP	DEAE-Trisacryl M	2M TFA	Homogalacturonan,	GC	Hachem et al. ¹⁶
	column		Rhamnogalacturonan-I*	GC-MS	
ALS-CSP			Homogalacturonan	¹ H NMR	
			Rhamnogalacturonan-I*	¹³ C NMR	
A10H and	Sephadex G-15	Endo- $(1 \rightarrow 4)$ - β -D –	Glucuronoxylan	GC	
A40H	column	xylanase		GC-MS	Ray et al. ²⁷
B10H and		Endo- $(1 \rightarrow 4)$ - β -D -	Xyloglucans	MALDI-TOF MS	
B40H	HPAE-PAD-	glucanase		¹ H NMR	
	chromatography				
DIVIOR I					
PWSF-I,	Biogel P6 column	H ₂ SO ₄	Glucuronoxylan	GLC	
PWSF-II and				¹ H NMK 13C NMD	Uabibi and
PWSF-III	-		Homenulan	¹³ C NMK	Vignon ²⁶
PWIF-I, PWIF-			пошохутан		Vigiton20
НХ	Dowey 1x2	Autohydrolyse	Homoxylans	GC	Barhat ²⁵
MGX A	chloride form	Thatony arony se	Glucuronoxylans	MALDI-TOF MS	Durbut
Maxin	column		Gracaronoxyrans	NMR ¹ H	
	Biogel P2				
	0				
FI KOH and	Sepharose CL-4B		Arabinoglucuronoxylans	GLC	
FIII KOH	column	Endo- β -(1 \rightarrow 4)-xylanase		FT-IR	Hachem et al. ²⁴
				MALDI-TOF MS	
	Biogel P2				
FI NaOH and		2 M HCl	Glucuronoxylans	GLC	Hachem et al. ²³
FIII NaOH			Rhamnogalacturonans	MALDI-TOF MS	

The five polysaccharide fractions of pectic nature (AFP, AL-WSP, AL-CSP, ALS-WSP and ALS-CSP) can be considered as models of the structure of pectins secreted into the cell walls of the argan tree. The fractions contents have similar structures and correspond to homogalacturonan, rhamnogalacturonan-I, rhamnogalacturonan-II with prevalence of rhamnogalacturonan-I^{16,17,19}.

The alkali-soluble fraction extracted showed that it is composed of a polysaccharide of hemicellulosic nature. Unsubstituted linear xylans (PWIF-I, PWIF-II and PWIF- III) ²⁶, xylans (A1OH, A4OH, PWSF-I, PWSF-II, PWSF-III, FI KOH, FIII KOH, FI NaOH and FIII NaOH) substituted to a greater or lesser extent by 4-0-methylglucuronic acid ^{23,24,26,27} and xylogucans (XXGG, XXXG, XXLG, XLLG, XXFG, XLXG/XXLG, XLFG and XUFG) as is the case in the primary walls of dicotyledons^{19,27}.

Structural Features of the oligosaccharides generated Detailed data on the monosaccharide compositions and chemical structures of the repeating units generated from the polysaccharides of *A. spinosa* are listed in Table 3.

Table 3. Structural Features of oligosaccharides generated from A. spinosa polysaccharides
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Polysaccharide fractions	Monosaccharide composition	Repeating units	References
AFRG-I	Rha, Ara, Xyl, Glc, Gal, Gal A, Glc A, 2- <i>O</i> -Me-Fuc, 2- <i>O</i> -Me-Xyl in the ratios 12:60:1:1:21:3:3 ª	nd	Aboughe- Angone et al. ¹⁹
AFRG-II	Rha, Fuc, Ara, Xyl, Man, Glc, Gal, Gal A, Glc A, Api, 2- <i>O</i> -Me-Fuc, 2- <i>O</i> -Me-Xyl in the ratios 20:5:34:6:1:7:17:11:8:5:10:7 ^a	nd	
AF10H	Fuc, Ara, Xyl, Man, Gal, Glc in the ratios 1:8:47:3:12:29 ª	XXGG XXXG	
AF4OH	Fuc, Ara, Xyl, Man, Gal, Glc in the ratios 2:6:41:7:13:31ª	XXLG XLLG	
P ₁ -H ₂ O	Rha, Ara, Xyl, Gal, Glc in the ratios 5:72:3:15:5 b	nd	Hachem et al. ¹⁸
P ₂ -EDTA	Rha, Ara, Xyl, Gal, Glc in the ratios 6:75.5:1.5:10:7 $^{ m b}$	nd	
H ₁ -KOH 1M	Rha, Fuc, Ara, Xyl, Gal, Glc in the ratios 4:4:18:53:9:14 ^b	nd	
H ₂ -KOH 4M	Rha, Fuc, Ara, Xyl, Gal, Glc in the ratios 4:2:11:47:7:29 ^b	nd	
ALT-WSP	Rha, Fuc, Ara, Xyl, Gal, Glc in the ratios 15.5: 0.5: 65: 2.5 :13.5: 3 ^b	→ [4)- α -D-GalpA-(1→2)- α -L-Rhap-1] →	Hachem et al. ¹⁷
ALT-CSP	Rha, Fuc, Ara, Xyl, Gal, Glc in the ratios 14.5: 0.5 :68: 2.5 :11.5 :3 ^b	→ [4)- α -D-GalpA-(1] → [4)- α -D-GalpA-(1→2)- α -L- Rhap-1]→	

ALS-WSP	Rha, Ara, Xyl, Gal in the ratios 21.7: 64 :2 :12.5 $^{ m b}$		
ALS-CSP	Rha, Ara, Xyl, Gal, Glc in the ratios 25.4 :12.7: 74:	\rightarrow [4)- α -D-GalpA-(1 \rightarrow 2)- α -L-Rhap-1] \rightarrow	Hachem et al. ¹⁶
	1.5:10 :1 ^b		
A10H	Ara, Rha, Xyl, Glc A, Gal A, Gal, Glc in the ratios	\rightarrow 4)- β -(D-Xvlp) ₄₋₆ (1 \rightarrow 2)- <i>O</i> -(4- <i>O</i> -Me- α -D GlcpA	Ray et al. ²⁷
	14:3:64:3:6:6:3 ª	\rightarrow 4)- β -(D-Xylp) ₆₋₇ -(1 \rightarrow 2)-O-(4-O-Me- α -D GlcpA) ₂	5
A40H	Ara, Rha, Xyl, Glc A, Gal A, Gal, Glc in the ratios		
	9:2:80:2:3:2:2 ª		
B10H	Ara, Rha, Fuc, Xyl, Glc A, Gal A, Gal, Glc in the ratios	XXXG	
	14:2:1:32:2:6:11:31 ª	XXFG,	
		XLXG/XXLG	
DIOU	Are Dhe Eve Yel Cle A Cel A Cel Cle in the retice	XLFG	
Б40П	Ara, Kila, Fuc, Ayi, Git A, Gai A, Gai, Git III the ratios $0.1.4.41.1.2.6.10.25$	XUFG	
	9:1:4:41:1:2:0:10:25 "		
PWSF-I	UA, Xyl in the ratios 22.6:76.4 ^b	→4)- β –(D-Xylp)7-(1→2)- <i>O</i> -(4- <i>O</i> -Me-α-D GlcpA	Habibi and
PWSF-II	UA, Xyl in the ratios 22.0:77.5 ^b		Vignon ²⁶
PWSF-III	UA, Xyl in the ratios 22.5:77.3 ^b		_
PWIF-I		\rightarrow 4)- β -D- Xylp -(1 \rightarrow	
PWIF-II	UA, Xyl in the ratios 0:100 ^b		
PWIF-III			
HX	Rha, Xyl, 4-0-Me GlcAin the ratios 0.7:98.6:0.7 a	\rightarrow 4)- β -D- Xylp -(1 \rightarrow	Barbat ²⁵
MGX A	Rha, Xyl, 4-0-Me GlcA in the ratios 0.9:85.8:13.3 ^a	→4)- β -D-Xylp-(1→2)- <i>O</i> -(4- <i>O</i> -Me-α-D GlcpA	
FI KOH	Rha, Ara, Xyl, Man, Gal, Glc, Gal A, Glc A, 4- <i>0</i> -Me Glc	→L-Ara- Xyl ₃₋₆ -4- <i>O</i> -Me-α–D-GlcA	Hachem et al. ²⁴
	A in the ratios	\rightarrow 4)- β –(D-Xylp) ₅ -(1 \rightarrow 2)- <i>O</i> -(4- <i>O</i> -Me- α -D GlcpA) ₂	
	4.3 :17.1 :58.1 :2.2 :1.5 :2.1 :5.4 :0.6 :8.7 ª		
FIII KOH	Rha, Ara, Xyl, Man, Gal, Glc, Gal A, Glc A, 4-0-Me Glc	→L-Ara- Xyl ₃₋₅ -4- <i>O</i> -Me-α–D-GlcA	
	A in the ratios		
	3.3 :20.4 :45.8 :8.1 :14.9 :2.3 :0.3 :1.9 :3.0 a		
FI NaOH	Rha, Ara, Xyl, Man, Gal, Glc, Gal A, Glc A, 4- <i>0</i> -Me Glc	→L-Ara- Xyl ₃₋₄ -4- <i>0</i> -Me-α–D-GlcA	
	A in the ratios		
	4.3:16.1 :24.0 :24.1 :10.2 :6.8 :9.1 :2.6 :2.8 a		
FIII NaOH	Rha, Ara, Xyl, Man, Gal, Glc, Gal A, Glc A, 4- <i>0</i> -Me Glc		
	A in the ratios		
	5.2 :15.8 :31.6 :19.3 :10.0 :10.9 :3.9 :1.2 :2.1 a		
FI KOH	Rha, Gal, Glc, Gal A in the ratios 31.6:1.9:1.9:62.5ª	\rightarrow [4)- α -D-GalpA-(1 \rightarrow 2)- α -L-Rhap-1] ₂ \rightarrow	Hachem et al. ²³
FIII KOH	Rha, Xyl, Man, Gal, Glc, Gal A, Glc A, 4-0-Me Glc A in		
	the ratios 17.1:11.2:0.0:9.2:4.0:48.5:7.3 ^a	→4)- β –(D-Xylp) ₃ -(1→2)- <i>O</i> -(4- <i>O</i> -Me-α-D GlcpA	
FI NaOH	Rha, Xyl, Man, Gal, Glc, Gal A, Glc A, 4-0-Me Glc A in		
	the ratios 22.1:4.6:0.0:2.5:38.7:25.8:6.3 a		
FIII NaOH	Rha, Xyl, Man, Gal, Glc, Gal A, Glc A, 4-0-Me Glc A in		
	the ratios 28.3:4.7:0.0:1.8:32.8:22.8:9.5 a		

^aMol percent; ^bExpressed in relative weight percentages; Rha: rhamnose; Ara: arabinose; Xyl: xylose; Glc: glucose; Gal: galactose; Man: mannose; Fuc: fucose; Gal A:galacturonic; Glc A: glucuronic acid; 4-*O*-Me Glc A: 4-*O*-methyl-glucuronic acid; nd = not determined.

Monosaccharide compositions

The composition of monosaccharides is usually analyzed by methods such as hydrolysis, derivatization and GC detection. A review of the published literature on the polysaccharides of *A. spinosa* indicates the presence of heteropolyoside structures which may have different monosaccharide compositions, which may be due to differences in the raw materials and their origin, the separation methods, the hydrolysis techniques employed and the detection methods used. The polysaccharides of *A. spinosa* are generally composed of arabinose, rhamnose, galactose and galacturonic acid for the pectic fractions. On the other hand, the hemicellulosic fractions are generally composed of xylose, glucose, 4-*O*-Me glucuronic acid, with different molar fractions of the different components according to the pectic fraction isolated. Hachem et al.^{16,17,18} used acid hydrolysis with trifluoroacetic acid (TFA) and GC analysis to separate, identify and characterize the water-soluble pectins (P1-H2O, ALT-WSP and ALS-WSP) and the chelate-soluble pectins (P2-EDTA, ALT-WSP and ALS-WSP) extracted from the polysaccharide fractions of A. spinosa. Their results show that these fractions are essentially composed of arabinose and galactose with a small percentage of rhamnose. The molar ratios are almost similar in the different fractions, which may be due to the same purification conditions. The monosaccharide composition is similar to what has been found in previous studies. Aboughe-Angone *et al.*¹⁹ obtained monosaccharide components of AFRG-I and AFRG-II which consisted of arabinose, galactose and rhamnose, arabinose which are the main components of the pectic polysaccharides of A. spinosa. Moreover, the enzyme treatment did not seem to

influence the monosaccharide compositions of the pectic fractions;–AFRG-I and AFRG-II were hydrolyzed with an endopolygalacturonase¹⁹, and P₁-H2O, ALT-WSP while ALS-WSP, P₂-EDTA, ALT-WSP and ALS-WSP were hydrolyzed with TFA^{16,17,18}.

However, the enzyme treatment appears to affect the monosaccharide composition of the hemicellulosic fractions. The fractions FI KOH, FIII KOH, FI NaOH and FIII NaOH are essentially composed of xylose and arabinose according to the results of an enzymatic hydrolysis by an endoxylanase²⁴, as opposed to the acid hydrolysates of these fractions in which arabinose was completely absent²³; While the fractions have been treated by similar isolation and purification processes, the differences can be attributed to the sensitivity of the few neutral monosaccharides such as arabinose and to the conditions of the acid hydrolysis which led to their degradation³¹.

Chemical structures

The literature contains only few reports devoted to the chemical structures of polysaccharides extracted from *A. spinosa*. These structures are determined by classical methods, namely hydrolysis and methylation. They have been confirmed by MALDI-TOF mass spectrometry and NMR spectrometry.

Using NMR structural analysis, Hachem et al.^{16,17} showed that the pectins of *A. spinosa* extracted with hot water are rhamnogalacturonan type I pectins with $(1\rightarrow 4)$ galactanand $(1\rightarrow 5)$ arabinanchains branched at the *O*-4 position of rhamnose units of the main rhamnosechain. However, chelate-extracted pectins contain homogalacturonan and a type I rhamnoglacturonan. The nature and type of linkages in the side chains are identical to those of all fractions. However, arabinose-rich type II rhamnoglacturonan May exist¹⁹.

The analysis by MALDI TOF spectrometry allowed the determination of the compositions and structures of hemicelluloses of *A. spinosa*. This analysis confirmed the presence of a typical homoxylan (HX) consisting of unsubsituted $\beta(1\rightarrow 4)$ xylopyranose chains ^{25,26} and of $\beta(1\rightarrow 4)$ xylopyranose chains substituted at position 2 of xylose units by uronic acid optionally methylated with 4-*O*-methylglucuronic acid^{25,26,27}or arabinose²⁴. This is generally the case for most xylan-type hemicelluloses isolated from higher plants, some of which, however, may be substituted by 4-*O*-methylglucuronic acids have been found in xylans isolated from *A. spinosa*. These results are similar to those already obtained with xylans from rapeseed stems³² and quince seeds^{33,34}.

Aboughe-Angone et al.¹⁹ and Ray et al.²⁷ demonstrated by MALDI-TOF and HPAE-PAD chromatography the presence of a XXGG xyloglucan-rich hemicellulose fraction generated by hydrolysis with endo- $(1 \rightarrow 4)$ - β -D –glucanase in addition to the XXXG, XXFG, XLXG/XXLG, XLFG fragments, previously characterized in various plants³⁵, a second group of fragments was detected. These latter fragments correspond to oligosaccharides homologous to XLXG, XLLG and XLFG in which a hexose is substituted by a pentose residue²⁷.

BIOACTIVITIES OF ARGANIA SPINOSA POLYSACCHARIDE

Pharmaceutical activity

In addition to the agri-food sector, more fundamental studies have reported biological activities likely to be of interest to the pharmaceutical industry. This is notably the case of antioxidant and anti-tumor properties.

Antioxidant activity

Research work on the antioxidant potential of polysaccharides is very recent. To our knowledge, no study has demonstrated such an activity of native polysaccharides or oligosaccharides, as their structures do not allow us to envisage this type of activity. The research focuses on the study of modified polysaccharides.

Hachem et al.¹⁷ estimated the in vitro quenching activity of the polysaccharides AL-WSP and AL-CSP of *A. spinosa* on 2,2-diphenyl-1-picrylhydrazyl (DPPH) radicals by electron spin resonance (ESR). This study showed that these fractions were able to decrease the production of ROS and that they had a radical scavenging capacity with an antioxidant potential of up to 8%. This low potential can be explained by the extraction method, which can cause structural changes in the polysaccharides by generating new functions or by eliminating acetyl groups, thus affecting their biological properties^{36,37}.

However, this antioxidant activity is generally attributed to the presence of lignin in the polysaccharide fractions. Lignin is a phenol-rich polymer and examples of polysaccharides substituted by phenolic derivatives with good antioxidant activity can be found in the literature^{38,39}.

Anti-tumoral activity

Polysaccharides are molecules capable of fighting tumor lesions, thanks to their immunostimulant activity and have the advantage to be non-toxic^{40,41}.

Barbat²⁵ studied the effects of xylane-type polysaccharides (HX, MGX A) from *A. spinosa* on the multiplication of A431 tumor cells (a human vulvar squamous cell carcinoma line). The HX fractions of *A. spinosa* showed low cytotoxic activity (19%) and only at high concentrations while the MGX A fractions showed no dose-dependent effect and only weakly inhibited cell proliferation (29%). Comparison of the biological responses obtained with neutral HX and acidic MGX revealed an interesting relationship between PD, Xyl/MeGA ratio, MeGA distribution along the xylose skeleton and cytotoxic properties towards A431 cells.

Biosorbent activity

There are many examples in the literature of polysaccharide biosorbents that are capable of retaining metal cations,^{42,43,44,45}.

Hachem et al.46 have characterized the biosorbent properties of the polysaccharides of the bark and the endocarp of Argan tree towards trace amounts of lead and cadmium. The study of the mechanism of interaction between the metal cations and biosorbents used was implemented by the Langmuir method⁴⁷. The adsorption isotherms and their translation by the Langmuir model led to values of maximum adsorption capacity (q max) of 0.162 and 0.116 meq/g and affinity (b) of 1.58 and 2 for raw A. spinosa bark. 19 L/meq, whereas for the crude endocarp of A. spinosa at values of maximum adsorption capacity (q max) of 0.087 and 0.147 meq/g and affinity (b) of 0.27 and 0.35 L/meq for the cations Pb2+ and Cd2+ respectively. Hachem et al.46 also showed that whatever the chemical modification considered (two selective oxidations, alone or in combination, of the following groups: primary alcohols with NaOBr catalyzed by (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl, and vicinal diols with periodate/chlorite.), the adsorption capacities of the trace metal elements were quantitatively improved at q max values of 0.865 and 0.211 meq/g for bark, 0.906 and 0.259 meq/g for the endocarp of A. spinosa, for the cations Pb²⁺ and Cd²⁺, respectively.

CONCLUSIONS AND PERSPECTIVES

In conclusion, the isolation, purification and structural analysis of polysaccharides are very complicated due to the diversity and the complexity of these structures. Consequently, it is difficult to obtain homogeneous and active polysaccharide fractions. This is one of the main factors that hinders the development of polysaccharide research. Since there are many methods and approaches to study polysaccharides, researchers must carefully select the appropriate methods according to the specific properties/characteristics of the polysaccharide to be studied.

With the development and increasing attention paid to A. spinosa, its polysaccharides are more likely to become exploitable and have greater potential for use in different industries. However, due to the existence of multiple structural characteristics, the study of A. spinosa polysaccharides and the correlation between their biological effects and their structures has not been completely elucidated. Further research the structural features and the structure-function relationships is essential and deserves to be pursued to better understand the polysaccharides of this relict.

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