







Review

Polysaccharides and Derivatives from Africa to Address and Advance Sustainable Development and Economic Growth in the Next Decade

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Abstract: Polysaccharides are highly variable and complex biomolecules whose inventory of structures is still very incomplete, as nature still preserves unexplored biotopes. Plants, macroalgae and microalgae are an integral part of the daily life of human being regardless of culture, time, or knowledge development of a country. Natural medicine is an ancestral knowledge widely distributed throughout the world, handed down for centuries from generation to generation by those commonly referred to as “nganga” healers or shamans. It is also called alternative medicine or traditional medicine, and has been associated for millennia to legends. This review gives an emphasis regarding the ethnobotanic approach associated to the structural variability of poly- and oligosaccharides for designing the new polysaccharide-based drugs and hydrocolloids of tomorrow. The guiding thread is to survey the potential of plants (and some macroalgae) from Africa as a source of polysaccharides with original structures and, secondly, to correlate these structures with biological and/or functional properties in particular to address and advance the sustainable development and economic growth of mankind.

Keywords: Africa; polysaccharides; ethnobotany; plants; macroalgae; biological activities

1. Introduction

Polysaccharides are biomolecules that are among the most abundant substances on Earth, which can be found in plants, animals, micro-organisms, and algae [1]. These polymers play mechanical protective and energetic roles but are also involved in many biological processes, including cell-to-cell communication, infection of bacteria and/or viruses, and immunity [2]. These biomolecules have been used for decades in traditional medicine and their usage is increasing in various industries, particularly in food [3]. Bioactive polysaccharides refer to polysaccharides showing biological activities towards “organisms” [4]. They

will be of great importance for the following years due to their physico-chemical and biological properties [5] such as stability, biodegradability, and biocompatibility [6,7]. In the era of “Make our planet green again”, polysaccharides have great potential in many areas such as agriculture, food processing, pharmaceuticals, cosmetics, etc. [4,8,9]. However, biological activities of polysaccharides are strongly influenced by their chemical structures and chain conformations. Macromolecular structures of polysaccharides are extremely complex due to the presence of different monosaccharides such as building blocks, sequence patterns, linkages, branching and distribution of side chains [10]. Polysaccharides from algae, plants and animals are often physically and/or chemically entangled with other biomolecules such as proteins, lipids, and certain inorganic minerals [11]. Plus, structural features of polysaccharides vary according to environment changes.

This review aims to explore, via the ethnobotanic approach, the potential of African plants (including some examples of macroalgae) as a source of polysaccharides with novel/original structures, biological and/or functional properties (Figure 1). It gives an overview of the identification, isolation, characterization, and application of bioactive polysaccharides derived from natural sources. This emphasis could be used for newcomers interesting by working on (African) polysaccharides as a summary and short reference documents for identifying application potentials to design new polysaccharide-based products. The framework is at the core of sustainable development issues and could contribute to a better understanding of Africa’s economic growth in the following decades.

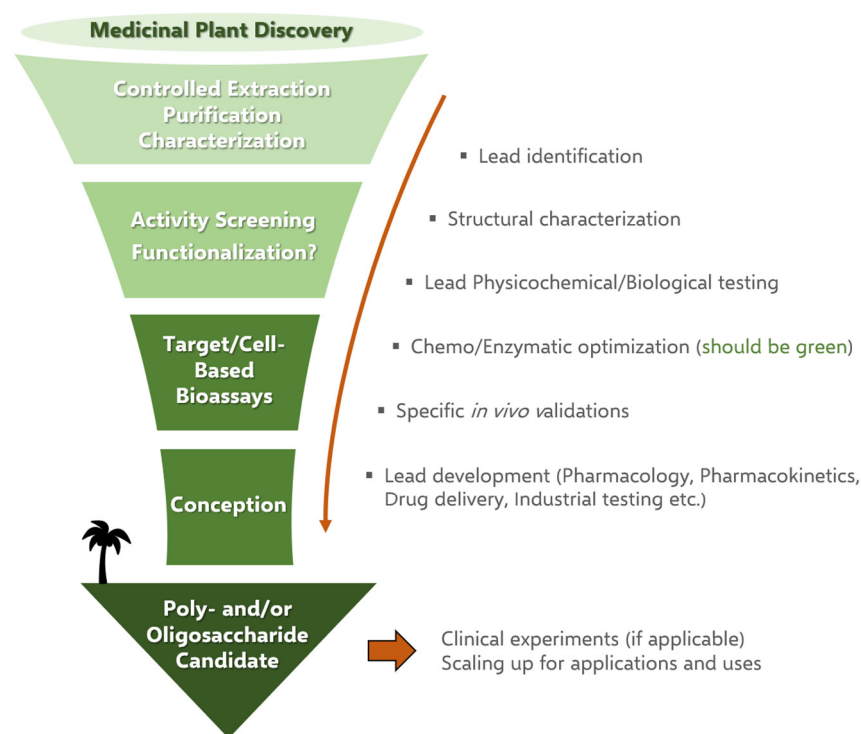


Figure 1. Conceptual approach for exploring the potential of African polysaccharides.

2. A Spoon of (African) Sugar?

2.1. Common Knowledge about Polysaccharides

Polysaccharides are an important class of biopolymers. These polyosides are abundant polymers with physico-chemical and biological properties such as high stability, biocompatibility, biodegradability and non-toxicity [12]. Physicochemical and structural characteristics of polysaccharides mainly depend on the (i) composition of the main backbone (including the nature of the glycosidic units), repetition patterns and branching configurations, (ii) macromolecular chain flexibility, (iii) molar mass distribution, (iv) type and ratio of functional groups (substitution) carried throughout the main chain [13]. Pri-

mary to quaternary structures are used to macromolecularly describe polymers, including polysaccharides. The primary structure corresponds to the chemical sequence of covalently bonded units within a chain, including inter- and intramolecular bonds. The secondary structure refers to the arrangement of locally ordered units. The tertiary one corresponds to the overall spatial organization of the object, which cannot be divided without cleavage of covalent bonds. Finally, the quaternary structure regards the structure of a molecule that cannot be divided. It forms the extended three-dimensional network [14]. Polysaccharides provide a wide diversity of roles from C-storage capacity (starch, glycogen, etc.), structural support in cell walls (cellulose, pectin, chitin.), and adaptation to environmental changes (exopolysaccharides) to cellular regulation and communication (glycosaminoglycans) [15]. Some examples of plants and macroalgae “biotopes” (Table 1) described in the literature are: arabinoxylan, cellulose, glucan hemicellulose (including galactomannan, glucuronoxylan, etc.), inulin, mannan, pectin (including arabinogalactan types I and II, homogalacturonan, rhamnogalacturonan types I and II, etc.), starch, xylan, xyloglucan, agaroid, alginate, carrageenan, fucoidan, laminaran, porphyrin, and ulvan. These polysaccharides can be neutral or acidic, linear, or branched with oligosaccharide chains. They may contain up to 10 different monosaccharides and the main backbone but also side chains that can be substituted with functional groups such as sulfate (in macroalgae polysaccharides only), pyruvate, methyl, and/or acetyl groups. Finally, this structural variability strongly depends on the plant source and/or species, environment conditions and harvest period.

A common error is to not identify the extraction and/or purification procedures as “potential significant bias” for well determining the structural features of polysaccharides. Newcomers but also experienced users should not attribute structural changes of polysaccharides to biotic/abiotic conditions if the methodology is poorly understood or inappropriate. Extraction methods greatly depend on the material availability, the final needs (first approach, industrial developments, etc.) and the will to ensure respect for the famous “12 rules” of Green Chemistry. Addressing sustainable development in Africa enforces the evaluation of both traditional (from traditional healers) and laboratory methods. Ethnic extractions are mostly rudimental procedures using natural products (water, stones, wood stick, etc.). The benefit of this approach is the low cost and speed to “analyze” the final properties. This methodology has often a low efficiency because of unprecise protocols, instrumentation, and a low biochemical understanding of the products (cream, drug, powder, solution, etc.) composition. This kind of extraction *de facto* excludes the so-called biorefinery approach where all the different parts from the plants (or macroalgae) and byproducts should be used. For instance, specific flours (cissus, etc.) were extracted using the traditional methods used by people in rural areas of Nigeria. The seed coats were removed after boiling the seeds in hot water for 45–60 min. The white cotyledons were put in water for 1 h before being washed three times with cold water then soaked in water overnight to remove the remaining residues. The cotyledons were sun-dried for 24 h, grounded into a powder (less than 1 mm diameter) and were air-dried at room temperature for 24 h [16].

Extractions using high temperatures and solvents are most common, hot extractions being ones of the most used maceration approaches. Regarding the use of solvents, ethanol and water are must-haves, since they are user-friendly, inexpensive, and particularly adapted for extracting hydrophilic compounds such as polysaccharides. Other solvents such as chloroform [10] or acetone [17] might be used as upstream steps for the removal of polyphenols, lipids, and proteins before extracting the polysaccharide content. Overall, many recent papers and reviews can be found in the literature, which should be surveyed to adapt the extraction strategy to the experimental bioresources, and above all, to the type and location of the expected polysaccharides [15,18–21]. Those steps are often realized by successive extractions using solvents with growing polarity. The speed and efficiency of this methodology are quite good even if recalcitrant polysaccharides, from insoluble parts of the plant and/or because of their low water-solubility, can be hardly extracted and should need specific procedures. Purification steps are commonly performed to

remove contaminations from other materials (e.g., polyphenols, proteins, lipids, etc.) even if the extraction procedures were previously well-defined. Overall, cold alcoholic precipitation (3/1 *v/v*) or ultrafiltration, including purifying (100, 50 and/or 10 kDa cut-off) and concentrating steps, are described to enhance the global purity of the final enriched-polysaccharide fractions. For instance, *Fleurya aestuans* L. and *Pelargonium capitata* leaves were dried and grounded to a fine powder and resuspended in boiling ethanol (80% *v/v*) for 30 min. The pellets were extracted using successively 90% dimethyl sulfoxide (DMSO), MeOH-CHCl₃, MeOH-acetone and finally acetone-water. The residues were air-dried at 80 °C and resuspended in acetate buffer (pH = 5.4) to recover the cell-wall materials. The starch content was enzymatically (α -amylase/amyloglucosidase) removed at 80 °C. The pectic fraction was then separated from the cell wall materials using boiled ammonium oxaloacetate for 1 h. Xylan and oligoxylan (hemicellulosic fractions) were finally obtained using 4 M KOH solution and enzymatic digestion [17].

Table 1. Some polysaccharide “families” which could be extracted from African plants and macroalgae.

| Type | Name | Composition | Type of Sources (Organism, Part of the Plant, ...) | Ref. for Instance |
|------------|--------------------------|--|--|----------------------|
| Plants | Arabinogalactan | β -(1,4)-D-arabinogalactan (type I) | Cactus (cladodes) | [22] |
| | Arabinoxylan | Branched β -(1,3)-D-arabinoxylan | Plant seeds | [23] |
| | Cellulose | β -(1,4)-D-glucan | Grains, fruits, vegetables, | [21] |
| | Galactomannan | β -(1,4)-D-mannan randomly substituted at O-6 position with α -Galp | Plant seeds | [24] |
| | B-Glucans | β -(1,4)-D-glucan β -(1,3)-D-glucan | Barley grains, Fruits, seeds, Oats | [25] |
| | “Gums” | (Arabino)galactan, xylan, xyloglucan, glucuronic mannan type | Exudates of trees or isolated from seeds | [26] |
| | Hemicellulose | Xylan, mannan, β -glucan and xyloglucan | Vegetative and storage tissues | [27] |
| | Heteroxylan | Highly branched β -(1,3)-D-Xylp and β -(1,4)-D-Xylp backbone | Plant seeds | [28] |
| | Inulin | β -(1,2)-D-fructan | Onion, root, wheat | [29] |
| | Pectin | α -(1,4)-D-GalA and Rha backbone, Ara, Gal, Xyl side chains | Plant primary cell wall, leaves, soft tissues of fruit and vegetable | [30] |
| Macroalgae | Xyloglucan | β -(1,4)-D-glucan backbone with α -(1,6)-D-xylose branches | Tree fruits, seeds | [31] |
| | Alginate | α -L-guluronate (G)/ β -D-mannuronate (M) block structure | Brown algae | [32] |
| | Glucan | Cellulose, laminaran, starch | Brown/Green algae | [33] |
| | Porphyran | Alternating β -(1,3)-linked-D-Gal units and α -(1,4)-linked L-Gal, (1,6)-sulfate, or 3,6-anhydro- α -L-Gal units | Red algae | [34] |
| | Sulfated fucoidan | Branched α -(1,3), α -(1,4)-L-fucan, O-2, O-3, O-4 sulfation | Brown algae | [32] |
| | Sulfated galactan | Backbone of alternating β -(1,3)-linked D-Gal units and α -(1,4)-linked L-Gal, (1,6)-sulfate or 3,6-anhydro- α -L-Gal units. D-Gal units linked on C-3 and C-6, and sulfation mostly on O-4. | Red algae | [35] |
| | Sulfated polysaccharides | (1,3(6))-linked Gal, (1,3(4))-linked Ara, (1,4)-linked Glc and T-Glc, (1,4)-linked Xyl residues | Green algae | [36] |
| | Sulfated rhamnan | (1-2)-L-rhamnan substituted by sulfate groups at C-3, and/or C-4 | Green algae | [37] |
| | Ulvan | Repeating disaccharide ulvanobiouronic acid with Xyl, Glc, Rha, and sulfate groups | Green algae | [38] |
| | Xylan | β -(1,3)-xylan | Green algae | [15] |

Today, tool-assisted extractions (including the use of enzymes) are a classic for obtaining biomolecules (including carbohydrates), such as microwaves, high-pressure systems, or ultrasounds. It results in extracting polysaccharides faster, at lower-water temperatures while conserving the polymer structural features [39]. Ultrasounds disrupt the cell walls of plants and enhance mass transfer of cell content [40]. The method is used to minimize the waste of polysaccharides in plants that might be an interesting resource of molecules [41]. It might also facilitate the drying process of aqueous ethanolic extracts. Tool-assisted extractions are generally dedicated for recovering non-polysaccharidic structures (polyphenols, terpenes, etc.) that easily fulfill the basic criteria for cosolvent extraction at low temperature under heterogeneous (and/or non-conventional) conditions. Numerous decent reviews can be found in the literature regarding the subject and should be firstly analyzed to make practical and viable choices and improvements of polysaccharides extracting/purifying strategies [18,19,21,42]. Figure 2 gives an overview of the main approaches for extracting various (African) polysaccharides regarding their structural location in plants and/or macroalgae. The importance of analytical methods used for determining the structure of (African) polysaccharides is still poorly recognized. Depending on their bad (misunderstood) uses, structural changes of polysaccharides can be falsely observed, and errors attributed to specific species, extraction procedures, etc.

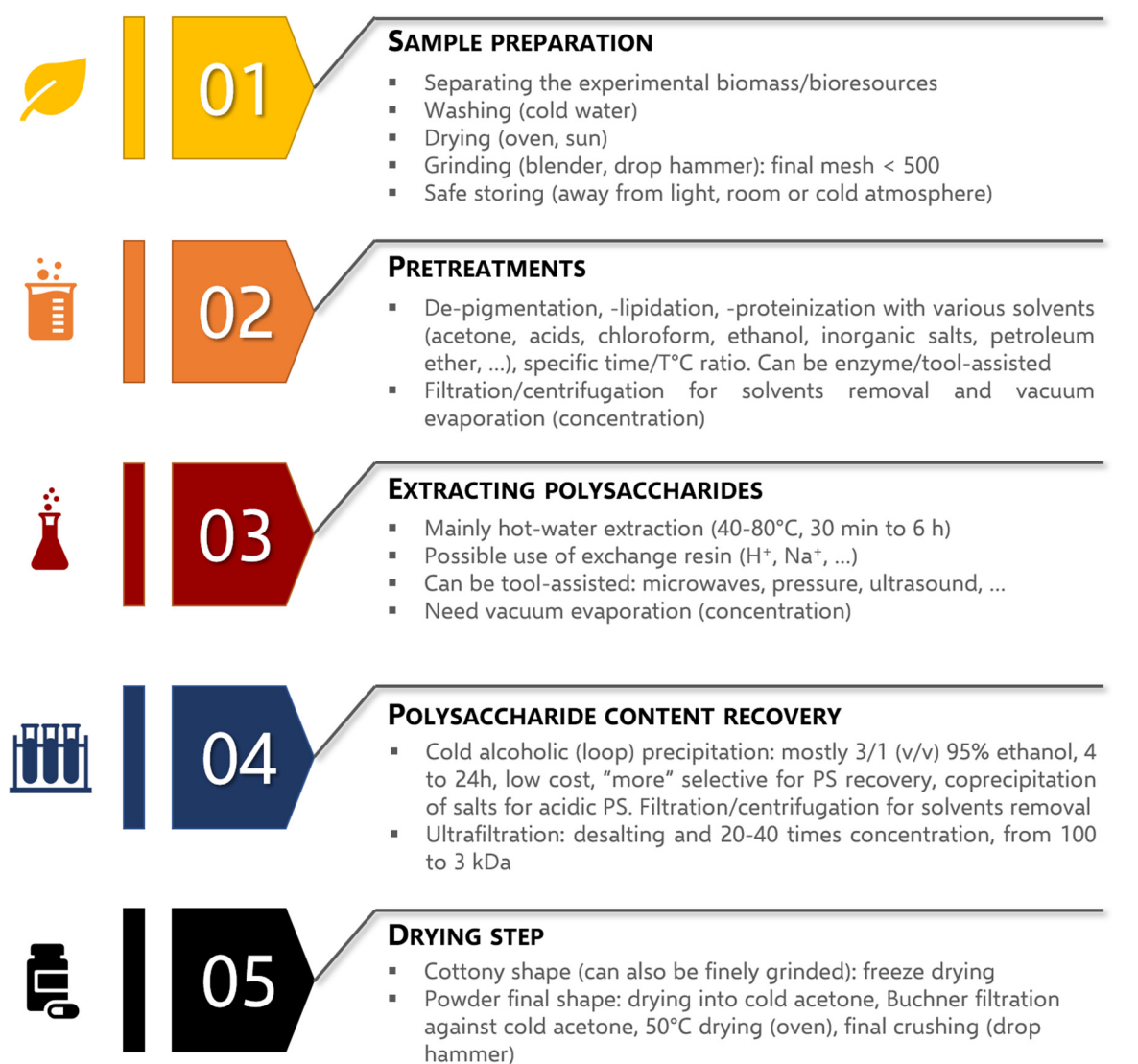


Figure 2. Main strategies for extracting enriched-polysaccharide fractions.

Overall, four main levels can be defined regarding the level of accuracy and details needed for characterizing carbohydrates (Figure 3), i.e., (i) global composition, (ii) primary composition, (iii) first structural analysis and (iv) full structural investigation. Delattre et al. gave an emphasis about the strategies for determining the structure of (exo)polysaccharides and experimenters should strongly read it in its entirety [43].

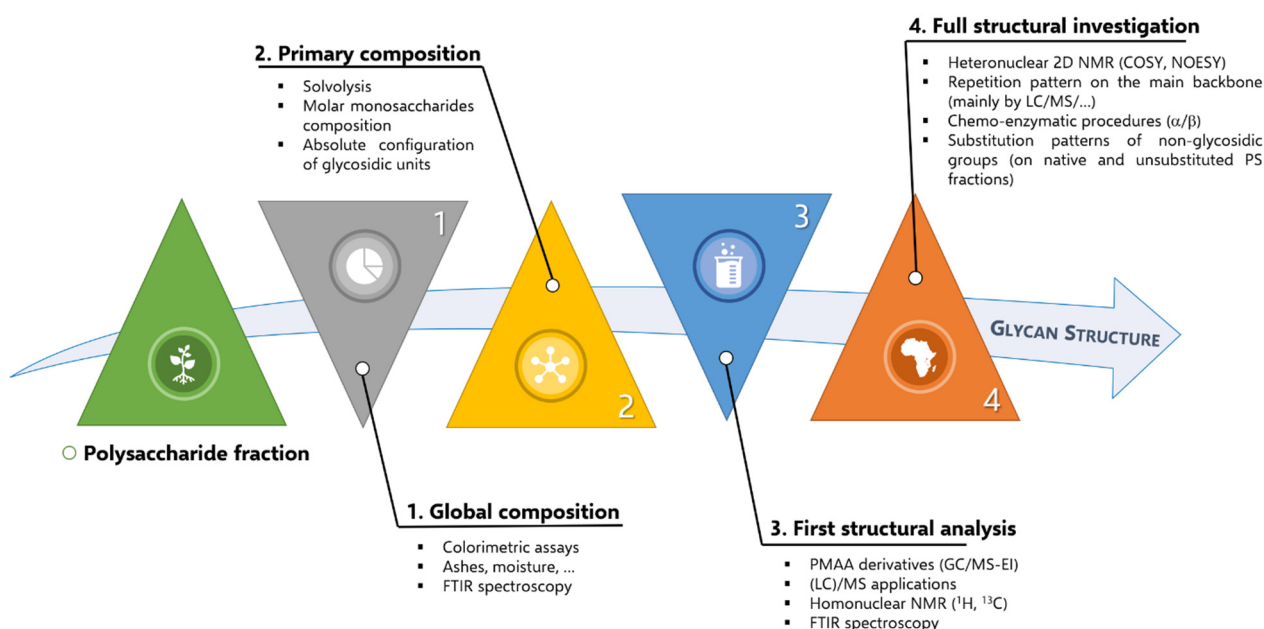


Figure 3. Determining the structural features of polysaccharides.

(i) The total amounts of carbohydrates, neutral sugars and uronic acids, non-carbohydrate substituents and main “contaminants” must be quantified, mainly by colorimetric assays. The phenol and/or orcinol-sulfuric acid are usually used for measuring total carbohydrates content [44]. Uronic acids content is mainly determined by the *m*-HDP (meta-hydroxydiphenyl) assay [45] whereas neutral sugars content is monitored based on the resorcinol–sulfuric acid assay method [46].

A corrective formula should be used for enhancing the results accuracy [47]. Non-carbohydrate substituents such as (a) pyruvate, (b) methyl and acetyl, and (c) sulfate groups can be quantified by performing respectively (a) the method of 2,4-dinitrophenylhydrazine [48], (b) High-Performance Liquid Chromatography (HPLC) methodology prior a saponification step and/or ^1H Nuclear Magnetic Resonance (NMR) (most reliable method for determining methyl and/or acetyl groups) [49], (c) the turbidimetric gelatin/BaCl₂ method [50] and/or the azure A method [51]. Finally, proteins and polyphenols contents can be determined using respectively the “Smith”, “Bradford” or “Lowry” methods [52–54] and the Folin–Ciocalteu assay [55]. Note that the presence of salts, ashes and moisture should be considered. Fourier Transformed InfraRed (FTIR) spectroscopy could also provide useful information concerning vibrationally functional groups of polysaccharides.

(ii) Determination of the primary composition requires the release of monosaccharides by solvolysis, mostly by acidic hydrolysis or methanolysis [56]. This is an important step regarding the literature since the hydrolysis conditions (by mineral acids) greatly change the possibility to quantify different types of monosaccharides (ketoses, aldoses, hexosamines and uronic acids) [43]. The released monosaccharides, but also absolute configuration of glycosides, can then be analyzed by various chromatographic methods such as HPLC, high-performance anion-exchange chromatography or Gas Chromatography (GC). GC is used for analyzing low molecular weight compounds which are not thermolabile and can be vaporized. The method is not suitable for polar and/or high molecular compounds and needs preliminary pretreatments (e.g., solvolysis) and derivatization steps to (a) convert polar or non-volatile compounds to relatively nonpolar or volatile products; (b) improve

thermal stability of target compounds; (c) increase detector response by incorporating functional groups which lead to higher detector signals or improve GC separation performance [57]. Commonly used derivatization reactions include silylation, esterification, acetylation, and alkylation [58]. Note that derivatized monosaccharides are more easily ionized especially if a mass spectrometer is used as a detector with electronic impact (EI). Regarding their abundance, hydroxyl groups give weak volatile properties to polysaccharides. Each released monosaccharide from solvolysis should thus be derivatized. Silylation is probably the most used technique to analyze monosaccharides with GC. The polarity of residues is reduced by switching hydrogens with alkyl-silyl groups. Silyl derivatives are more volatile, less polar, and more thermostable compared to other compounds generated. BSTFA (bis (trimethylsilyl) trifluoroacetamide) and TMCS (trimethylchlorosilane) are the most used reactants for trimethylsilylation [59].

(iii) Investigations by Mass Spectrometry (MS) and NMR spectroscopy are usually performed to determine the main structural features of polysaccharide backbones and associated branched patterns. The PerMethylated Alditol Acetates (PMAA) procedure is often described since it allows the identification of glycosidic linkages, T-units, ring sizes and branching points by GC/MS-EI (mainly EI). Briefly, permethylation of carbohydrates is done followed by an acidic hydrolysis step (e.g., 2M TFA 90 min 120 °C). Solid NaOH pellets in DMSO is one of the safer methodologies for the methylation of free hydroxyl groups. The residues are reduced into alditols then peracetylated into final PMAA, NABD₄ being preferred during the reducing step for facilitating the differentiation between primary OH groups [60]. Specific GC/MS-EI fragmentation patterns of PMAA are widely described in the literature [56]. NMR is a very popular technique used to determine the structure and stereochemistry of polysaccharides. ¹H NMR fingerprints and ¹³C spectra are classically performed for identifying structural features (conformations, monosaccharides, linkages, anomers, substituents, branching patterns, etc.) of polysaccharides [61].

(iv) Enhancing the data should be the last step for giving full and comprehensive details of polysaccharide structures. Thus, uronic acid reduction, partial alkaline reduction, acetolysis, periodate degradation, desubstitution of non-carbohydrate groups and/or partial hydrolysis (solvents and/or enzymes) must be additionally performed. Two-dimensional NMR techniques should be also used (COSY, NOESY, etc.) to improve the structural description. Note that additional depolymerization (chemical, ozonolysis, hydrolysis, etc.) of polysaccharides can help to improve the quality and complexity of NMR spectra [62].

2.2. Screening the Biological Potential of Polysaccharides: Randomly or Not?

Oligo- and polysaccharides have many biological and pharmacological activities such as immunomodulatory, immuno-restorative, immunoregulatory, anti-inflammatory, antibacterial, antioxidant, antiviral, etc. [1,4,6,11,18–22,25,30,34–38,40–43,63]. Thus, numerous reports on the biological activity of polysaccharides extracted from plants and used in traditional medicines have been published. Minor structural differences, e.g., monosaccharide composition and distribution, chain conformation, macromolecular behavior, branching degree and pattern, chemical structures, and presence of non-carbohydrate substituents [13,24], can significantly affect the biological activity of polysaccharides [64]: this is the so-called structure-function relationship. Changes of sulfate content, molecular weight and/or molar ratio greatly affect both biological functions and rheological behavior. Specific neutral sugars (Rha, Fuc, etc.) and uronic acids (GalA, GlcA, GulA, ManA, etc.) are also responsible of specific biological activities. ManA/GulA are well known for their capacity to trap water, especially in presence of divalent cations (eggbox model of alginates extracted from macroalgae) [65]. The main bioactive sites seem to be located both in the most peripheral parts of the molecule and in the inner core, as instance for rhamnogalacturonan (RG) and arabinogalactan (AG) regions which are often extracted from (African) plants and herbs [66]. This statement seems true for both arabinan, arabinogalactan types I (AG-I) and II (AG-II) but also rhamnogalacturonan types I (RG-I) and II (RG-II) [67].

β -D-(1,4) carbohydrate structures as well as β -D-(1 \rightarrow 3,6)-galactan can contribute to the immunomodulation of immunocompetent cells in Peyer patches or macrophages [68]. The main mechanism involves toll receptors [13] including the complement 3 receptor, trapper receptor, dectin-1, mannose receptor, galectin 3 and TLR4. These receptors modulate the activity of leukocytes. Certain polysaccharides are capable of activating macrophages and B cells by interacting with TLR4, activating TNF secretion induced by ZPF1 [69]. Some pectin-like structures can also activate monocytes, leading to modulation of cytokine production [3] in macrophages via TLR4-mediated signaling pathways [3,69]. For example, a potent immunomodulatory pectic arabinogalactan, Vk2a, showed high complement fixation activity (human complement) and independent induction of B-cell proliferation by T cells, in addition to the promotion of chemotaxis by human macrophages, T cells and NK cells [66,70]. Several studies have also shown that the biological activity of pectin-like structure on the immune system is mainly linked to the RG-I side chains [17]. It has also been reported that RG-II consisting of homogalacturonan (9–10 GalA units) and substituted by four highly conserved side chains can present significant immunomodulatory properties [68]. In addition, β -D-4-O-methyl-GlcpA or β -D-GlcpA-1,6- β -D-Galp- β -D-1,6- β -D-Galp inside RG-I structures could be the most active groups responsible of this kind of biological activity [68]. Galactosyl chains substituted by T-GlcA, 4-O-Me-GlcA can induce B-cell proliferation. Galactan oligomers composed of β -D-(1,3) and (1,6)-Galp units in the main backbone and some branches (1 \rightarrow 3,6) have been reported for their complement activities [17]. Finally, the reported effects range from complement fixation, antiulcer function [71] to the activation of macrophages and dendritic cells [70]. Overall, many polysaccharides (including AG and RG) isolated from botanical sources have excellent immunomodulatory activities. The wide range of efficiency may be probably due to the structural heterogeneity as stated above [63]. Note that immunomodulatory polysaccharides do not cause damage and additional stress to the body, because they only act as modifiers of the biological response [24].

Polysaccharides (not only from plants, herbs or macroalgae) are also a promising source of antioxidants [13]. They have nutraceutical effects and act as scavengers of DPPH, hydroxyl, and lipid peroxidation radicals. It can be attributed to specific groups such as $-\text{OH}$, $-\text{O}-$, $-\text{SH}$, $-\text{PO}_3\text{H}_2$, $-\text{C}=\text{O}$, $-\text{COOH}$, $-\text{NR}_2$ or $-\text{S}-$ [65]. Specific side chains, such as 1 \rightarrow 2, 1 \rightarrow 4 or 1 \rightarrow 6, can also modify these activities as well as Rha, Fuc or Man residues. In addition, cationic and anionic functional groups, such as uronic acids, are also considered to affect the antioxidant activity of polysaccharides. Low molecular weight polysaccharides and/or oligosaccharides have the best antioxidant activities due to the higher ratio of terminal reducing units [65]. Thus, polysaccharides may be useful as free radical scavengers against oxidative damage. Many natural polysaccharides are now being used as sources of new potential dietary antioxidants for pharmaceutical and food applications [63]. The antioxidant activity is explained by the chelating activity of polysaccharides. It is achieved by inhibiting the production of superoxide anions ($\text{O}_2^{\cdot-}$). In other words, it limits the activation of NADPH oxidase by inhibiting the phosphorylation of p47 phox and its translocation to the plasma membrane. Antioxidant sugars may also inhibit DFO degranulation. Polysaccharides therefore have a strong antioxidant action on neutrophils. Anti-inflammatory and hepato-protective activities are also reported as biological properties of natural polysaccharides [72]. Polysaccharides may help to dampen or regulate the strength of inflammatory processes [70]. This activity is exerted by inhibiting neutrophil functions, limiting the spread of reactive oxygen species to neighboring tissues and preventing the degranulation of primary human phagocytes. Certain carbohydrates are effective in inhibiting the superoxide anion of neutrophils induced by PMA or fMLF. Thus, stimulation of leukocytes by polysaccharides could improve resistance to infection [3]. Hemostatic, antiseptic and antiparasitic activities on wounds and skin infections are also reported for polysaccharides extracted from plants. These carbohydrates can also be used as tonic, stomach, abortifacient, antipyretic and for rheumatism [73] and some plants also have a piscicidal property. Polysaccharides can provide lubrication and thus facilitate the

propulsion of colon contents by acting as a short-chain fatty acid production [13]. Finally, there are anti-diuretic, anti-fatigue and anti-nocturnal enuresis and obesity activities [1]. As an ingredient in medicine and food, these polysaccharides can then be used in functional and health products because of their abundant pharmacological effects.

Obviously, this short enumeration could not be exhaustive and hundreds of decent reviews described tens of biological activities for polysaccharides, including natural ones extracted from plants, macroalgae or herbs. Thus, the first questions before screening the biological potential of a “new” polysaccharide (e.g., from Africa) should come down to the final needs or purposes of the investigations (Figure 4). It is easy to find a positive “biological activity” regarding the quantities of friendly-users in vitro tests, for which no real understanding of the intrinsic understanding is needed. From today, the real challenge for the following decades should address a strong scientific lock: “apprehending the relationship between structural features and biological activities” by precisely targeting oligo- and/or polysaccharides/cells interactions, in vivo. Without this, no real outbreak will happen for the discovery of “the new enriched-polysaccharide drugs” for tomorrow (in particular for emerging countries like Africa). Note that this approach is clearly not compatible with the actual fast-publishing contest in 2021.

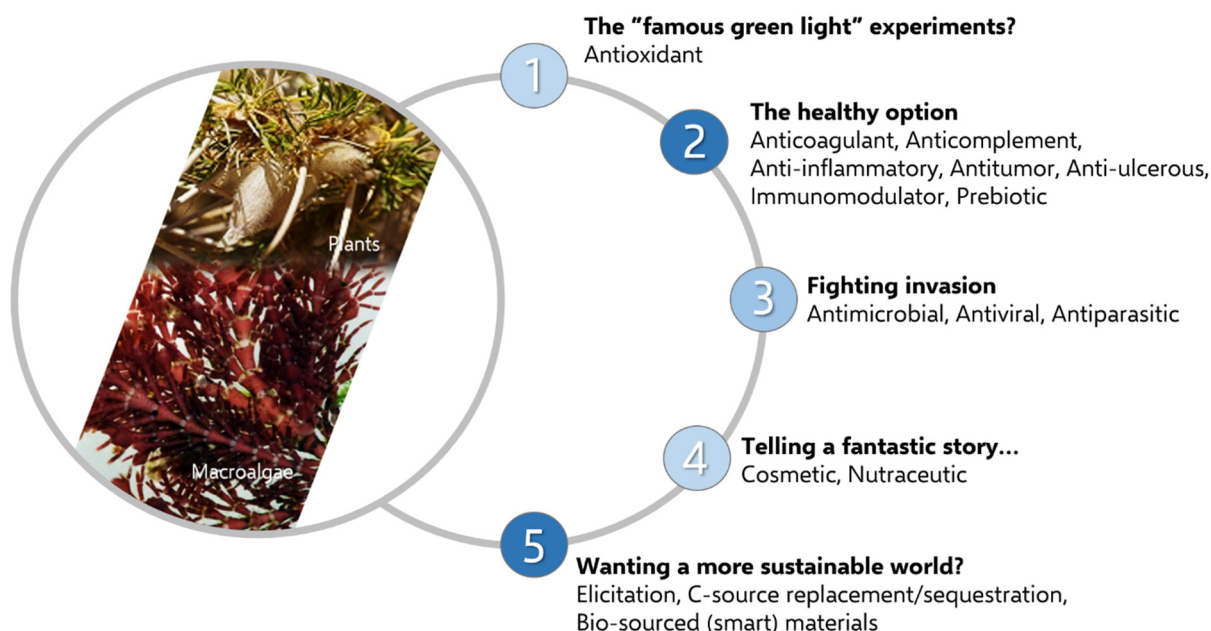


Figure 4. The first questions before screening the biological potential of (African) polysaccharides.

3. Discovering Polysaccharides in Africa

The diversity of Africa flora can be explained by the various climates of the continent, i.e., equatorial, tropical wet and dry, tropical monsoon, semi-arid, hyper-arid and arid, subtropical of the highlands, etc. Some of those climates might be hard for the development of a plant because of the lack of water or drastic changes of temperatures. Many plants learned to adapt and changed their biochemical and cellular mechanisms, leading to structural changes that appeared over time. African flora is composed of about 62,000 species of flowering plants and more than 200 new species are found every year [74]. A strong biodiversity can be observed especially in the East African region with more than 21,000 higher plant species counted in 2009 [75]. Geophytic flora is particularly based in the winter-rainfall region of South Africa, which is considered as one of the biggest natural stock of geophytes in the world. The main specificity of geophytic plants is their adaptation to hostile environment. The growth period is during winter and spring under more favorable conditions. Note that 40% of the total flora in Africa is represented by the geophytic plants [76,77].

3.1. Research Methodology

In Section 3, the three last decades have been reviewed with a strong focus on papers and reviews published during the last one (and if possible, the last 5 years). Polysaccharides from plants have been mainly reviewed using the keywords “polysaccharide” AND/OR “oligosaccharide” AND/OR AND/OR “natural polymer” AND/OR “exudate” AND/OR “gum” AND/OR “exopolysaccharide” “African plant” AND/OR “ethnobotany” AND/OR “biological activity” AND/OR “structure” AND/OR “phytochemistry” AND/OR “Africa” AND/OR “Ethnopharmacology” AND/OR “properties” AND/OR “uses” AND/OR “active molecules” AND/OR “Acacia” AND/OR “Argania” AND/OR “Opuntia” AND/OR “Plantago” AND/OR “Astragalus” AND/OR “Pheonix” AND/OR “Retama” AND/OR “Zyzyphus” AND/OR “economic interests” AND/OR “market” AND/OR “valorization” AND/OR “bioprocess” AND/OR “biotechnology” AND/OR “elicitation” AND/OR “anti-inflammatory” AND/OR “anticomplement” AND/OR “diabete” AND/OR “antioxidant” AND/OR “prebiotic” AND/OR “disorders” in Scopus, NCBI (National Center for Biotechnology Information), ScienceDirect and PubMed data bases.

3.2. The Concept of Ethnobotany for Giving Birth to Ethnopharmacology and Phytochemistry

Ethnobotany is defined as how people of a particular culture and region make use of indigenous plants, such as food, medicine, shelter, dyes, fibers, oils, resins, gums, soaps, waxes, etc. [78]. This concept gathers many other sciences such as history, botanic and bio-ethnology. Most of the time, the first part of the study is an investigation of the population [79]. Questioning people about how they use living plants found in their environment is of primary importance. Then, ethnobotanists focus on the methodology people use for making their formulations. These data combined to folklore knowledge can help for identifying structure, functions, and biological activities of these plants [78]. This simple but fundamental way of investigation can be summarized by the following items: (i) basic documentation of traditional botanical knowledge; (ii) quantitative evaluation of the use and management of botanical resources; (iii) experimental assessment of the benefits derived from plants, both for subsistence and for commercial ends; and (iv) applied projects that seek to maximize the value that local people attain from their ecological knowledge and resources [80]. Ethnopharmacology and phytochemistry directly derive from ethnobotany and are based on social information from medical ethnography and physiologic action of medicines. Both deal with the study of chemicals produced by plants, particularly secondary metabolites. It considers synthesis of secondary metabolites, plant metabolisms, elicitation, and cell communication mechanisms. It also obviously encompasses medicinal, industrial, and commercial applications of plant natural products [81]. Overall, a general understanding and use of these concepts allow:

- (i) Discovering new natural drugs or reusing existing ones for treating disorders,
- (ii) Developing new chemicals mimicking active structural features,
- (iii) Rising knowledge on:
 - Characteristics and functions of medicinal plants;
 - Toxicity level of plants,
 - Biosynthetic pathways and metabolomics;
 - Classification, chemical variability (inter and intraspecific);
 - Biotechnology and genetic engineering for optimizing the synthesis of specific compounds;
 - Phytoremediation, plant growing and elicitation.

These concepts are not really applied today to macroalgae which is probably a strong misunderstanding, probably due to harvesting conditions and a certain variability of their compositions and metabolites.

3.3. A Focus on Bioactive and/or Functional Polysaccharides from Arid and Semi-Arid Lands

Herbs, plants and trees growing up in particular climates, e.g., arid or semi-arid, exhibit specific adaptations and changes for accumulating storage substances and water. Obviously, polysaccharides play a major role as hydrocolloids but the inventory of their other biological functions, in close relation with new structural (original) features, is clearly incomplete [82]. Table 2 gives some examples of African plants described for their bioactive polysaccharides regardless the climate conditions. Most of them were founded by ethnobotanical and/or ethnopharmaceutical studies.

Table 2. Some African plants which were investigated regarding ethnobotanical and/or ethnopharmaceutical approaches.

| Name | Region | Type | Part(s) | Properties and Uses | Active Molecules | Ref. |
|--|----------------------------------|---------------------|-------------------|--|--|---------|
| <i>Aloe vera</i> Barbadensis Miller | Northern Algeria | Plant | Leaves | Anti-inflammatory, antioxidant | Pectin-like structure | [30] |
| <i>Angelica acutiloba</i> | Sahara | Perennial herb | Roots | Anti-complement activity | Arabinogalactan | [83] |
| <i>Annona senegalensis</i> Pers. | Western Mali | Plant | Bark, roots | Anti-complement, antiparasitic, insecticide, antiulcer, antispasmodic, wound healing | Glucan, pectin-like structure | [84] |
| <i>Astragalus armatus</i> | Septentrional Algerian Sahara | Perennial plant | Seeds | Anti-complement activity, antioxidant | Galactomannan | [63] |
| <i>Astragalus gombo</i> | Septentrional Algerian Sahara | Perennial plant | Seeds | Antioxidant, prebiotic, texturing agent | Galactomannan | [24] |
| <i>Bauhinia thonningii</i> Schumacher. | Western Mali | Savanna tree | Leaves | Anti-complement, antitussive, hemostatic activity, wound healing | Arabinan | [84] |
| <i>Biophytum petersianum</i> Klotzsch | Western Mali | Flowering plant | Aerial parts | Anti-complement, wound healing | Pectic arabinogalactan | [84] |
| <i>Burkea africana</i> Hook. | Western Mali | Savanna tree | Bark | Anti-complement, immunomodulator, hemostatic activities, wound healing | Arabinan, glucan, pectic-like structure | [84] |
| <i>Carica papaya</i> L. | Western Africa | Flowering plants | Leaves | Buruli ulcer, liver damage, dysentery, diabetes, constipation, and chronic indigestion | Extracts | [85] |
| <i>Cassia sieberiana</i> | Western Africa | Leguminous plant | Bark, roots, stem | Diabetes, malaria | - | [86] |
| <i>Catharanthus roseus</i> | Madagascar | Flowering plant | Areal parts | Anti-leukemic agents | Glycosides | [87] |
| <i>Ceratonia siliqua</i> | Middle East | Tree | Seeds | Diarrhea, eye infection, visual disturbances, intestinal parasite infestation | Glycosides | [88] |
| <i>Cereus triangularis</i> | Madagascar | Cactus | Cladodes | Anti-inflammatory, anti-complementary, gastro-protectors, immuno-modulators, prebiotic | Arabinogalactan (Type I) (poly- and oligosaccharides) | [22,89] |
| <i>Chamaecrista nigriscans</i> (Vahl) Green | Western Mali | Woody plant | Leaves | Anti-complement, antiulcerogenic property, wound healing | Arabinan, pectin-like structure | [84] |
| <i>Citrullus colocynthis</i> | Sahara | Desert viny plant | Fruits | Diabetes, asthma, gastrointestinal disorders, different microbial infections | Glycosides, oils | [90] |
| <i>Cochlospermum tinctorium</i> | Western Africa | Flowering plants | Bark, roots | Anti-complement, anti-Malaria, anti-viral, hepatoprotective | (Rhamno)galactan, glucan | [84] |
| <i>Codonopsis pilosula</i> | Sahara | Flowering plant | Roots | Anti-complement activity | RG-I containing AG-I and AG-II sidechains | [91] |

Table 2. Cont.

| Name | Region | Type | Part(s) | Properties and Uses | Active Molecules | Ref. |
|---|---------------------------------|-----------------------------|------------------------|---|--|-------|
| <i>Cola cordifolia</i> (Cav.) R. Br. | Western Africa | Tree | Bark, leaves, stems | Abdominal pain, anti-complement, fever, anti-ulcer, headache, wound healing | Pectic arabinogalactan, glucan | [84] |
| <i>Commiphora myrrha</i> Engl. | Septentrional Algerian Sahara | Small tree or large shrub | Gum-resin | Antihyperglycemic and phagocytic activities | Arabinogalactan-like structure | [92] |
| <i>Crossopteryx febrifuga</i> (Afzel. ex G. Don) Benth. | Western Mali | Tree | Bark, fruits | Anti-complement, antimicrobial property, respiratory disorder, wound healing | Glucan, pectic-like structure | [84] |
| <i>Cymbopogon citratus</i> | Madagascar | Tropical plant | Leaves | Fever | Extracts | [93] |
| <i>Cyperus esculentus</i> | Cameroon | Edible plant | Tubers | Prebiotic, texturing agent | Starch | [94] |
| <i>Entada africana</i> | Tropical and subtropical Africa | Tree | Bark, leaves, roots | Hepatic diseases | Pectin-like structure, RG-I, AG-II | [95] |
| <i>Fenugreek</i> | Northern Africa | Leguminous plant | Leaves, seeds | Promoting digestion and reducing blood sugar levels in diabetics | Galactomannan, glycosides | [96] |
| <i>Gomphrena celosioides</i> | Western Africa | Herbaceous perennial | Areal parts and roots | Viral hepatitis A and C, liver damage, urinary tract, kidney stones | Extracts | [97] |
| <i>Harrisonia abyssinica</i> | Tropical Africa | Shrub | Bark, roots | Infectious diseases | Extracts | [98] |
| <i>Lannea velutina</i> A. Rich. | Western Africa | Tree | Bark (stem) | Anticomplement, anti-inflammatory effect, wound healing | Arabinogalactan | [94] |
| <i>Morinda lucida</i> | Central Africa | Flowering plant | Leaves, roots | anti-allergic, anti-carcinogenic, anti-inflammatory, antioxidant, anti-proliferative, anti-viral | Crude extract including polysaccharides | [99] |
| <i>Nitraria retusa</i> | Northern Africa | Shrub plant | Aerial parts | Antioxidant, anti- α -amylase, anti-inflammatory, antinociceptive activities, anti-edematous effects | Pectin-like structure | [100] |
| | Northern Africa | Shrub plant | Fruits | Antioxidant, hypolipidemic activity | β -(1 \rightarrow 3)-glucan, traces of pectin | [25] |
| <i>Ocimum canum</i> | Sahara | Perennial herbs | Mucilage, roots, seeds | Antiparasitic, antioxidant, antiulcer | Acidic “bacterial-like” polysaccharide, acidic xylan, (galacto-) glucomannan | [101] |
| Olive tree | Northern Africa | Tree | Wastewater | Antioxidant, biobased polymer films, prebiotic | Glucan, xyloglucans, pectin fractions | [102] |
| <i>Opilia celtidifolia</i> Endl. Ex Walp. | Western Africa | Tree | Leaves | Complement fixing, immunomodulator, macrophage stimulator, regulating inflammatory | Type II arabinogalactan, Rhamnogalacturonan I regions | [3] |
| <i>Opuntia ficus indica</i> | Northern Africa | Cactus | Cladodes | Antioxidant, bioassay applications, texturing agent | Pectin fractions | [103] |
| <i>Phyllanthus amarus</i> | Western Africa | Flowering plant | Roots | Anti-hyperglycemic, antiviral, anti-ulcer | Crude extract including polysaccharides | [104] |
| <i>Parkia biglobosa</i> | Western Africa | Perennial tree | Bark, seeds | Antiviral, complement fixation, immunomodulator, | Type II arabinogalactan | [105] |
| <i>Podaxon aegyptiacus</i> Mont. | Western Mali | Mushroom | Spores | Anticomplement, burn/wound healing | (Galacto)mannan | [84] |
| <i>Plantago ciliata</i> Desf. | Septentrional Algerian Sahara | Spontaneous flowering plant | Seeds | Anti-inflammatory, medicinal cream, prebiotic, wound healing | Arabinoxylan | [23] |

Table 2. Cont.

| Name | Region | Type | Part(s) | Properties and Uses | Active Molecules | Ref. |
|--|-------------------------------|-----------------------------|-------------------------------------|--|---|-------|
| <i>Plantago major</i> | Sahara | Flowering plant | Leaves | Anti-complement activity, prebiotic | Pectin-like structure (poly- and oligosaccharides) | [106] |
| <i>Plantago notata</i> | Septentrional Algerian Sahara | Semi-annual flowering plant | Seeds | Antioxidant, prebiotic | Heteroxylan | [28] |
| <i>Pterocarpus erinaceus</i> Poir. | Western Mali | Tree | Bark | Anticomplement, wound healing | Glucan, pectin-like structure | [84] |
| <i>Sansevieria liberica</i> | Western Africa | Flowering plants | Leaves, roots | Anti-inflammatory, antioxidant | Crude extract including glycosides | [107] |
| <i>Senna Alata</i> L. (<i>Cassia alata</i>) | Western Africa | Flowering plant/herb | Bark, flowers, leaves, roots, seeds | antibacterial, antidiabetic, antifungal, anti-inflammatory, antihelminthic, antimicrobial, antioxidant, antitumor, wound healing activities | Crude extract including reducing sugars | [108] |
| <i>Stereospermum kunthianum</i> Cham. | Western Mali | Tree | Bark, leaves | Anticomplement, burn/wound healing | (Rhamno)glucan, pectic-like structure | [84] |
| <i>Strophanthus hispidus</i> | Africa | Liana | Roots, seeds | Antidiabetic, antihyperlipidemic, cardiac insufficiency | Crude extract including polysaccharides | [109] |
| <i>Tamarindus indica</i> | Eastern Africa | Leguminous tree | Fruits, seeds | Antidiabetic, anti-inflammatory, anti-hepatotoxic, Antioxidant, antimutagen, antimitotic, blood tonic, digestive, carminative, expectorant, immunomodulator, laxative, texturing agent | Heteropolysaccharide (Gal, Man, Glc), xyloglucan | [110] |
| <i>Trichilia emetica</i> Vahl. | Western Mali | Tree | Leaves | Anticomplement, anti-inflammatory, immunomodulatory, phagocytic activities, wound healing | Arabinogalactan, traces of pectin | [84] |
| <i>Thymus vulgaris</i> | Sahara | Flowering plant | Leaves | Anti-complement, antioxidant, complement activator | Type II arabinogalactan, type I rhamno-galacturonan | [111] |
| <i>Vernonia kotschyana</i> (<i>Baccharoides adoensis</i> var. <i>kotschyana</i>) | Sahara | Annual plant | Roots | Anti-ulcer properties arthritis, complement fixing activity, immunomodulator, | Glucan, inulin, pectic arabinogalactan, type II arabinogalactan | [67] |
| <i>Xeroderris stuhlmannii</i> (Taub.) Mendoza and E.C. Sousa | Tropical Africa | Tree | Leaves | Anticomplement, wound healing | Pectic arabinogalactan | [84] |
| <i>Ximenia americana</i> L. | Western Africa | Tree | Bark, roots, leaves | Anticomplement, carcinostatic, antibacterial activity, wound healing | Arabinogalactan | [84] |
| <i>Xylopia aethiopica</i> | Western Africa | Aromatic tree | Bark, fruits, seeds | Antioxidant, Buruli ulcer, excipient, post-partum care | Mainly phenols and flavonoids | [112] |
| <i>Ziziphus mauritiana</i> | Eastern and Western Africa | Tree | Bark, leaves, mucilage, roots | Anti-diabetic, epithelium wounds and mucous membrane irritation, skin treatment, | Galactan, glucan, rhamnan, pectic-like structure | [113] |
| <i>Zygophyllum album</i> | Mediterranean Africa | Halophytic plant | Areal parts | Asthma, diabetes, diuretic agent, dermatosis, indigestion, local anesthetic, rheumatism | Essential oil | [114] |

The following sections give some details concerning the structural variability of well-known African plant polysaccharides from arid and semi-arid lands, i.e., *Acacia*, *Argania*, *Opuntia*, *Plantago*, *Astragalus*, *Phoenix*, *Retama* and *Zizyphus*.

3.3.1. Acacia

More than 1000 of *Acacia* species were described around the world, but the gummy exudates are produced from specific acacia trees growing in a large belt of semi-arid land across sub-Saharan Africa. It extends through northern central Africa, from east Africa to southern Africa. The world largest producer is Sudan with production achieving forty thousand tons in 1996 followed by Nigeria then Chad, Mali and Senegal [115]. Polysaccharides extracted from *Acacia* species are often described as β -(1,3)-galactan, and the presence of other monosaccharides such as Ara, Rha and GlcA are often also reported (Table 3).

Table 3. Monosaccharide compositions of polysaccharides extracted from some *Acacia* species in arid lands.

| Acacia Species | Main Monosaccharides (% Molar Ratio) | | | | Reference |
|---|--------------------------------------|-------|-------|-------|-----------|
| | Gal | Ara | Rha | GlcA | |
| <i>A. glomerosa</i> | 46 | 27 | 15 | - | [116] |
| <i>A. macracantha</i> | 43 | 30 | 5 | 22 | [117] |
| <i>A. senegal</i> | 39–42 | 24–27 | 12–16 | 15–16 | [118] |
| <i>A. seyal</i> | 38 | 45 | 4 | 7 | [119] |
| <i>A. tortilis</i> var. <i>raddiana</i> | 19 | 78 | 2 | 4.4 | [120] |

The polysaccharide isolated from *A. glomerosa* gum was very close to those reported from *A. senegal*. It was mainly consisting of a β -(1,3)-D-Galp backbone, and Ara residues can be branched up to four units along to the galactan backbone in O-6 position. Terminal residues were often described as Rha unit, and GlcA and its 4-O-Me derivative seemed to represent the two kinds of uronic acids for this gum [116]. Water-soluble light brown gum was produced by *Acacia macracantha* gum, found close to Madagascar [121]. This gum species was characterized for its atypical features, such as negative specific rotations and a Gal/Ara ratio > 1 [122]; in comparison to few reports for other *Gummiferae* spp. gums [121]. Regarding the literature, it was reported as a complex arabinogalactan-protein [123]. Gal, Ara and GlcA, with a molar ratio around 3:2:1, were the major monosaccharides described for *A. macracantha* gum polysaccharide. The main backbone was essentially a β -(1,3)-galactan, with GlcA, Ara as well as Rha residues [117,123]. Arabic gum (GA), also known as Acacia gum, is obtained from exudates of *A. senegal* and *A. seyal* trees, which can be found across the Sahelian area of Africa [124]. GA was described as a naturally complex polysaccharide, used especially in food industry as emulsifier and stabilizer agent [125]. The main backbone was described as a β -(1,3)-galactan with uronic acids and Rha in terminal positions all along the structure and some side chains composed of uronic acids, galactan or both [126]. Regarding the species, some differences can be found in the composition of these β -(1,3)-galactan from *A. senegal* and *A. seyal* (Table 4).

Table 4. Main characteristics of *A. senegal* and *A. seyal* gums.

| Characteristics | General Information | <i>A. senegal</i> Gum | <i>A. seyal</i> Gum |
|----------------------------|---|--|--|
| Specific rotations | Differences were described is due to the variation of monosaccharide. <i>A. seyal</i> gum contained more Ara than Rha residues [127] | Negative specific rotations: −26 to −34° [128] −30° [127] | Positive specific rotations: +60° [129] +54° [127] |
| Rheological behavior | Gums are more described for their emulsifying properties | Viscous [130] | Low viscosity [130] |
| Molecular weight | Molecular weights are often higher than 1M Da | 0.485×10^6 g.mol ^{−1} [131] | 1.14×10^6 g.mol ^{−1} for <i>A. seyal</i> [131] 2.1×10^6 for <i>A. seyal</i> var. <i>fistula</i> [132] 1.7×10^6 for <i>A. seyal</i> var. <i>seyal</i> [132] |
| Monosaccharide composition | Both are rich in D-Gal and L-Ara in addition to some minor carbohydrates, including L-Rha, D-GlcA and 4-O-Me-GlcA [18] | Ara/Gal ratio < 1 [126,130] Higher proportion of rhamnose [130] | Ara/Gal > 1 [126,130] Low rhamnose content [130] |
| Structural features | Main chain structures of β -(1,3)-D-Gal with numerous branching points in O-6 positions of D-Gal residues. Lateral chains have units of α -L-Araf, α -L-Rhap, β -D-Glcp and 4-O-Me- β -D-Glcp, the last two mainly as end-units [8,17,21,26]. | Hyperbranched structure with degree of branching up to 78% with more branched Galp, shorter Araf ramifications, and more Rhap in terminal positions [125,133]. | Less degree of branching (around 59%) [125,133] |

A. tortilis is also called Israeli Babool or umbrella thorn. This species can tolerate drought and stretches extensively over arid and semi-arid regions of Africa, Algeria, Egypt, Israel, Asia and India. The seeds were composed of 14.3% fiber and 45.3% carbohydrates [134]. Kumar Lakhera indicated that the gum exudates of *A. tortilis* ssp. *raddiana* (Savi) Brenan consisted of L-Ara, D-Gal, D-Glc, L-Rha and D-Man, with some molar ratios around 78%, 18%, 0.6%, 1.7% and 0.7% respectively [120]. Gas chromatographic analyses also showed the presence of 4% and 4.4% of D-GalA and D-GlcA respectively.

3.3.2. Argania

Sapotaceae is a family included eight genera, i.e., *Syderoxylon*, *Tsebona*, *Bumelia*, *Argania*, *Chrysophyllum*, *Pouteria*, *Calocapum* and *Pycnandra*. *Argania* genus consists of unique endemic species named *A. spinosa*. As example, *A. spinosa* L. skeels is an endemic species of Algerian [135], Moroccan drylands where it plays a vital role against desertification [136]. Sequential alkaline extractions from *A. spinosa* leaf cell walls, pericarp of seeds and fruit pulp, respectively allowed to obtain different hemicellulose-type polysaccharides with variable yields [137]. Polysaccharides extracted from *A. spinosa* L. skeels leaves from Morocco were reported as xylan, made up of a β -(1,4)-D-Xylp main chain, substituted with 4-O-Me-D-GlcpA [138]. Hachem et al. described the same xylan structure in polysaccharides extracted from Algerian *A. spinosa* L. Skeels leaves, but the main chain was also substituted with L-Araf residues, in addition to 4-O-Me-D-GlcpA [139]. Other specific patterns and distributions all along the main backbone were described in the literature, with specific xyloglucan oligosaccharides such as XXXG, XXFG, XLXG/XXLG, XLFG fragments. A novel XUFG motif was also distinguished for *A. spinosa* species, characterized by a lateral chain consisting of two Xyl residues linked in β -(1,2). This disaccharide was attached on the sixth carbon to the second Glc unit from the nonreducing extremity of the cellotetraose sequence, as described by Ray et al. [138]. Water-soluble and water-insoluble fractions were also obtained from pericarp of seeds, respectively [140]. The first one was composed of a 4-O-Me-D-glucurono)-D-xylan, with 4-O-Me-D-GlcpA groups attached to the second carbon of the xylan backbone. The second one, recovered after alcohol precipitation, consisted exclusively of a neutral linear xylan. Note that Aboughe-Angone et al. obtained a xyloglucan from argan fruits. This hemicellulosic polysaccharide had no novel XUFG fragment and was mostly composed of XXGG, XXXG, XXLG and XLLG oligosaccharides (0.6:1:1.2:1.6 in molar ratio) [137]. The same study indicated that pectin from *Argania* fruits were a combination of non-equal homogalacturonan, rhamnogalacturonan-I (RG-I) and rhamnogalacturonan-II (RG-II) fractions, where RGI was the predominant polysaccharide in contrast to RG-II. Further, water-soluble pectic fractions (ALS-WSP) and soluble-chelating pectic fractions (ALS-CSP) were isolated from argan tree leaves. The results showed the presence of high rates of Ara and uronic acid residues in both fractions. AL-WSP was composed of a RG-I structure, with arabinan and galactan side ramifications on the main chain in O-4 position. Additionally, AL-CSP was described as a homogalacturonan fraction [141].

3.3.3. Opuntia

Opuntia genus has over 181 species (Cactaceae family). This intriguing genus are widespread in dry, arid, and rocky pastoral zones across the Mediterranean area but also North and South Africa [142]. *Opuntia ficus-indica* (OFI) is probably one of the most species studied and described in the literature for its content in polysaccharides, associated to functional properties [143]. Hemicellulosic polysaccharides were isolated from the seeds of OFI prickly pear fruits by alkaline extraction [144]. Six fractions of water non-soluble and water-soluble polysaccharides were thus obtained and were mainly composed of Xyl with minor quantities of Glc and Ara. Uronic acid amounts were variable depending on the fractions. Both water-soluble and water non-soluble xylans had unique non-reducing end of 4-O-Me-GlcA, for every 11 to 14 and 18 to 65 Xyl units, respectively [145]. Secondly, two major xylans CASF1 and HASF1 were extracted by sequentially cold and hot alkali treatments, respectively, from depectinated cell walls material of seed endosperm.

Interestingly, a fucosylglucuronoxylan was characterized in CASF1 and consisted of a β -(1,4)-D-Xylp main chain, with 4-O-Me-GlcA and Fucp residues attached to the second and third carbon of Xylp. HASF1 was fully composed of Xyl units with a backbone made of β -(1,4)-D-Xylp [144]. Besides, polysaccharides extracted from skin, peeled or total OFI fruits were also studied in many reports. On one hand, Habibi et al. highlighted the presence of arabinogalactan type I. It was mainly composed of Gal and Ara with a molar ratio of 6.3:3.3, with some traces of Glc, Rha and Xyl, but no uronic acids [146]. The backbone was described as a β -(1,4)-linked D-Galp, with sidechains of mono-L-Araf residues or di-L-Araf linked in α -(1,5). Besides, another acid soluble pectin (ASP) was obtained after sequential hot water and hot EDTA extraction from skin of OFI. Acid extraction yielded 8.7% of ASP, including a considerable amount of GalA (50.7%), in addition to variable rates of neutral sugars, including Rha, Gal, Glc, Ara and Xyl (12.5%, 10.8%, 2.9%, 1.2% and 0.8%, respectively) [147]. Three main fractions called ASP1, ASP2 and ASP3 were studied. The results revealed that the first one was a linear β -(1,4)-galactan. The main chain of the second fraction was made of an alternation of homogalacturonan blocks and disaccharide units $[-\rightarrow 2)-\alpha$ -L-Rhap-(1 \rightarrow 4)- α -D-GalpA-(1 \rightarrow]. Lateral chains of β -(1,4)-galactan have been connected to Rha residues in position O-4. The third fraction ASP3 was composed of homogalacturonan blocks, i.e., α -(1,4)-D-GalA, and rhamnogalacturonan units, i.e., $[-\rightarrow 2)-\alpha$ -L-Rhap-(1 \rightarrow 4)- α -D-GalpA-(1 \rightarrow] [147]. On the other hand, extraction of peeled fruits allowed to obtain 3.8% of mucilage which was described as some heterogeneous polysaccharides with 23.4% of GalA and no trace of proteins. Neutral sugars included Ara, Rha, Xyl and Gal residues with molar ratios around 1.0:1.7:2.5:4.1 [148]. Additionally, Ishurd et al. [149] obtained 0.65% of a water-soluble polysaccharide through hot soaking of peeled OFI (L.) Miller. This homogeneous polysaccharide presented a positive optical rotation value and an approximate average molecular weight of 360 kDa. It was highly rich in neutral sugar (more than 80% w/w) and exclusively composed of Glc. The backbone was made up of α -(1,4)-D-Glcp, while side chains were attached through (1,6)-linkages [149]. Lastly, Lefsih et al. obtained three pectic fractions from whole cladodes of OFI [103]. The results showed that all pectin fractions were mainly composed of GalA with ratios close to 66.6%, 44.3% and 81.1% for water-soluble, chelating-soluble, and acid-soluble pectin, respectively.

3.3.4. Plantago

Plantago spp. are valuable officinal plants belonging to the family Plantaginaceae. They are distributed in temperate regions, tropical zones [150] but also in drier environments such as deserts and oases [151]. The most dominant polysaccharides in psyllium are described as a complex of heteroxylans [152]. *P. major*, *P. ovata* and *P. notata* are largely described in the literature. *Plantago notata* Lagasca is a spontaneous plant from Septentrional Algerian Sahara used by the Ghardaïa population for its medicinal effects. Water-soluble polysaccharides extracted from its leaves and seeds were mainly composed of neutral sugars (around 80% w/w for both). Note that the polysaccharides from leaves were richer in uronic acid than for the ones extracted from seeds, with values reaching 20.3% against 4.9%, respectively [28]. Boual et al. studied the monosaccharides composition of a water-soluble polysaccharide from *P. notata* leaves [153]. The polymer consisted of Gal (44%), Rha (20%), Glc (11%), Ara (10%) and GalA (13%). In the same way, Benaoun et al. determined the monosaccharide composition of water-soluble polysaccharide from *P. notata* seeds [28]. The polysaccharide was an heteroxylan with a high molecular weight (2.3×10^6 Da), composed of Xyl (77%) in addition to Rha (9%), Ara (8%), Gal (3%), Glc (1%) and GalA (2%). The structural analysis revealed that the backbone was a β -(1,3) and β -(1,4)-linked D-Xylp. Several lateral chains and terminal residues linked in O-2 and O-3 positions were identified, such as α -L-Araf-(1,3)- β -D-Xylp, β -D-Xylp-(1,2)- β -D-Xylp, terminal Xylp or terminal Araf. As another example, *P. ovata* Forsk. called Isabgol is growing in drought prone areas. Producing mucilage from this species has an economical importance, especially in India [154]. The analysis of *P. ovata* Forsk. seeds mucilage revealed the presence of two polysaccharide fractions, one soluble in cold water and the other one in hot water. The

first fraction was composed of 46% of D-Xyl, 40% of an aldobiouronic acid, 7% of L-Ara, and 2% of insoluble residue, whereas the second fraction contained 80% of D-Xyl, 14% of L-Ara, 0.3% of aldobiouronic acid and traces of D-Gal [155]. Pawar et Varkhade found that an arabinoxylan (73% *w/w*) structure could be extracted from *Psyllium* husk, composed of a Xyl main chain branched with Ara, Rha and GalA [156]. More recently, Addoun et al. described an arabinoxylan structure from *Plantago ciliata* seeds [23].

3.3.5. Astragalus

Astragalus genus belongs to Fabaceae family considered as the vulgar genera of flowering flora with roughly 3000 species, widespread in desert continental areas [63]. Ten endemic *Astragalus* species are scattered in North Africa, such as *A. armatus* Willd. [157], *A. gombo* Bunge in Algeria [158] or *A. corrugatus* in Tunisia [159]. Other species are founded in Iraq drylands, such as *A. hamosus*, *A. tribuloides*, *A. adscendens*, *A. susianus* or *A. verus* [160]. The hot soaking of *A. armatus* Lam. seeds yielded 4.21% of a water-soluble polysaccharide (WSPF) [63]. This fraction consisted of $83.4 \pm 1.29\%$ neutral carbohydrate with an average molecular weight close to 1.59×10^6 Da. WSPF was identified as a galactomannan, with a Man:Gal ratio around 1.13:1. WSPF was made up of a linear backbone of β -(1,4)-D-Manp with α -(1,6)-D-Galp side chains. Besides, Chouana et al. extracted a water-soluble polysaccharide (WSP) from *A. gombo* seeds [24]. The fraction had an average molecular weight of 1.1×10^6 g/mol and was composed of Gal (37% \pm 0.9) and Man (63% \pm 0.7), with a Man:Gal ratio close to 1.7:1. WSP had a β -(1,4)-linked D-Manp main chain, substituted by single α -Galp residues in O-6 positions.

3.3.6. Phoenix

Areaceae or Palmae family included *Phoenix* genus can be detailed in 14 species. *Phoenix dactylifera* or also date palm is the most known species and can be found in oases and hot arid deserts [161]. Salem and Hegazi showed, after ethanolic extractions for *P. dactylifera*, that flesh was richer in total carbohydrates than seeds (72.5%) but contained less fiber (17.9%) [162]. The analysis of these samples showed the presence of Glc, Fru and sucrose in both parts with ratio around 19.5%, 1.1%; 15.4%, 1.8 % and 37.5%, 2.8% (*w/w*), for flesh and seeds, respectively. Water-soluble polysaccharides extracted from *P. dactylifera* L. cv aple variety seeds contained 71.8% Man and 26.6% Gal with a molar ratio close to 2.69:1. The identified galactomannan backbone constituted in β -(1,4)-D-Manp residues with side chains of α -(1,6)-linked D-Galp residues [163]. Alkaline treatment (NaOH 4%) produced 20.4% of a cellulose-rich material [164]. The results showed a composition rich in Xyl and 4-O-Me-GlcA with a molar ratio of 5:1, but also minor quantities of Gal, Glc and Man. The backbone of this polysaccharide consisted of (1,4)-linked D-Xylp residues. In the core chain, for each five units of D-Xylp, a single residue of 4-O-Me-GlcA was identified [164]. Additionally, Bendahou et al. [165] characterized an arabinoglucuronoxylan from leaflets, which were substituted in C-3 by Araf residues and a 4-O-methyl-glucuronoxylan structure from rachis.

3.3.7. Retama

This genus is endemic to semi-arid and arid Mediterranean environments since these shrubs can survive in periods of severe dryness. Two species are well described in the literature, i.e., *R. sphaerocarpa* growing in semi-arid lands of central Spain and *R. raetam* growing in arid regions of Tunisia. *R. raetam*, is a Saharan Fabaceae that prevalent desert environments and which is used in Tunisia to reduce desertification process [166]. In general, extraction of water-soluble polysaccharides from *R. raetam* seeds allowed to obtain galactomannans. A specific structure was obtained in comparison to other studies about galactomannans from *R. raetam* seeds [167]. This one contained occasional β -(1,4)-D-Manp groups, with a main backbone of β -(1,3)-D-Manp. Some lateral chains of mono-D-Galp residues were also reported and seemed to be attached in O-6 positions of D-Manp [167]. Wu et al. extracted, thanks to hot alkaline procedure, a polysaccharide from *R. raetam* Webb

and Berthel. ssp. *gussonei* seeds (yield close to 16.9% *w/w*) [168]. This polymer was made up of β -(1,4)-linked D-Xylp as the main backbone. For each seven or fifteen D-Xylp residues, 4-O-Me-GlcA or unique di- α -(1,2)-D-Glcp were identified.

3.3.8. Zizyphus

Zizyphus trees and shrubs can be found in arid environments and are thus naturally tolerant drought stress. The major species of *Zizyphus* genus in dry lands are probably *Z. spina-christi* in the hyper-arid deserts of Abu Dhabi, *Z. lotus* (L.) Lam. locally called “Sedra or Sidr” in Laghouat and Djelfa-Algeria or *Z. mauritiana* L. in semi-arid region of Punjab-India [113]. *Z. jujuba* has also been studied for its polysaccharide content. Elaloui et al. studied the monosaccharide compositions in the pulps of four *Z. jujuba* Tunisian ecotypes (Choutrana, Mahdia, Mahres and Sfax), and highlighted that the polysaccharides from Mahdia ecotype was the richest in Glc, Gal and sucrose with 0.45, 136.51 and 113.28 mg/L, respectively [169]. *Z. lotus* L., particularly found in the Mediterranean areas, including southern European countries, but also in the northern Algerian Sahara [170], has also been described for the polysaccharides extracted from its pulp (fruit). Chouaibi et al. obtained a water-soluble polysaccharide containing 11% of uronic acids and many neutral sugars, such as Glc (23%), Ara (9.6%), Man (8.3%), Rha (7.3%) and traces of Xyl and Gal residues [171]. Pectin structures were also determined in *Z. lotus* fruits (3.78% *w/w*) [170]. In general, these polysaccharides possessed high average molecular weight, higher than 2000 kDa [172]. Finally, Boual et al. determined the monosaccharides composition of a water-soluble polysaccharide extracted from the leaves of *Z. lotus* and found significant amount of Gal and GlcA (24% and 23% respectively), but also Glc (21.3%), Rha (20.3%) and Ara (9.6%) [173].

4. Economic Interests

As natural biopolymers, polysaccharides have excellent bioavailability, biocompatibility, and biodegradability, which have versatile applications in food, medicine, cosmetics, and nanomaterials [174]. In recent years, polysaccharides have led to strong development in global industries such as food, pharmaceuticals, nutraceuticals, cosmeceuticals, and functional products but also in many other sectors still under-exploited such as bioremediation, pollution control and energy (Figure 5). This growth can be explained regarding the will for industries to make more natural and organic products. 72% of consumers estimate that organic products are better in quality [175]. Areas that can provide health benefits beyond basic nutrition have therefore been the focus of increasing interest [174]. Global polysaccharide industry operates in a highly regulated environment and exploiting plant material for polysaccharides extraction often requires respecting the famous Nagoya rules [1]. This protocol is based on access to genetic resources and associated traditional knowledge and the sharing of benefits arising from their use [1]. In other words, it aims to (i) share in a fair and equitable manner the benefits; (ii) establish a climate of mutual trust between users and providers; (iii) ensure legal security of transactions and (iv) encourage users and providers to allocate in-kind and financial benefits for the conservation and sustainable use of biodiversity.

Polysaccharides from plants could be an important potential for their use in the medical and biomedical field as they are natural products. The global biopharmaceuticals market accounted for USD 186,470 million in 2017, and is projected to reach USD 526,008 million by 2025, registering a CAGR (Compound Annual Growth Rate) of 13.8% from 2018 to 2025 [176]. As seen previously, the absence of polysaccharide toxicity (or very low) is an important aspect for their medical use [177]. Toxicity testing is an important step in the drug development process evaluating the potential of a medicinal plant before it can be considered for clinical trials [73].

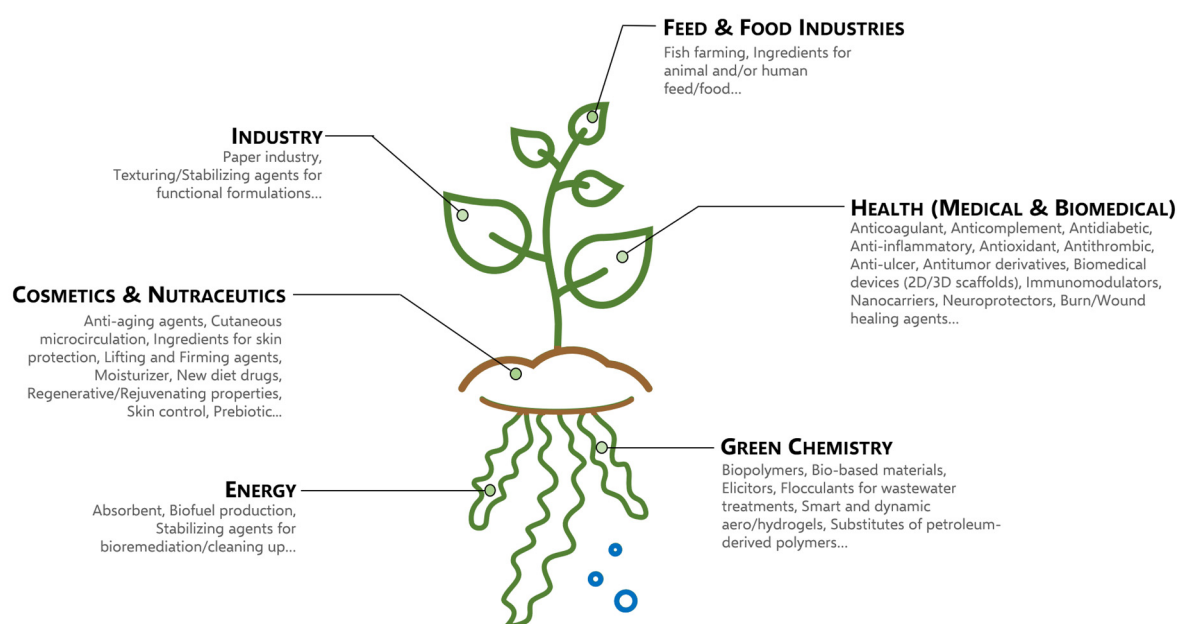


Figure 5. Main probable uses of African poly- and oligosaccharides from plants and macroalgae for the following decades.

Numerous patents have been filed on the use of natural polysaccharides as active drug ingredients [178]. Polysaccharide products are applied almost exclusively by oral administration as immunostimulants and less frequently by injection or immersion for protection against pathogens. They could also reduce fatigue, enhance human immunity, or disturb sleep, regulate the endocrine system, or delay aging [179]. Polysaccharides can be used for tissue engineering, dressing (wound healing), and for administering controlled-release drugs. They can also be used as biosensors, but also implantable devices or for bio-imaging [180]. Polysaccharides have also enabled the development of biomedicine and biomaterials technologies. Galactoglycogen nanoparticles could be used as a functional material for multivalent binding with lectins [174]. Phytoglycogen nanoparticles possess properties of high-water retention, low viscosity, and exceptional aqueous dispersion stability, all of which will enable promising new technologies and therapies based on this natural nanomaterial [179,180]. The other role of polysaccharides in nanomaterials functions as a nano-factory for certain reactions. The specific characteristics of polysaccharides might also be used for aerogels. Developing aerogels to mimic extracellular matrices (ECM) in the body has led to various biomedical applications. Dynamic hydrogels are made from different polymers, but among them polysaccharides seem to be the most suitable mainly due to their abundance, low cost, adaptability, and biocompatibility. In addition, the large functional groups in their backbone make polysaccharides ideal for making dynamic hydrogels. Such unique versatility allows these intelligent and durable hydrogels to be used in a wide range of applications, such as tissue engineering, biomedical devices, soft electronics, sensors, and actuators, among others; biomedical, controlled release and bioelectrode devices, minimally invasive deployment, gastric mucosal seals and perforations, electronic skin and electrochemical display devices, agricultural systems [1,179]. An increasing number of studies have focused on polysaccharide-based nanoparticle synthesis due to their unique structural properties [73]. One of the roles of these spherical biopolymers is to act as stabilizers as nano-carriers. The most hit countries are in North America, Europe, Asia-Pacific, and Latin America Middle East and Africa (LAMEA). Target companies are mostly AbbVie Inc, Amgen Inc., Bristol-Myers Squibb Company, Eli Lilly & Co., Johnson & Johnson, Novartis AG, Novo Nordisk Inc., Pfizer Inc., GlaxoSmithKline PLC, F. Hoffmann-La Roche AG [181].

The organic cosmetic market represented 4% of global market in 2007. The market growth is estimated today between 30% and 40% every year. Polysaccharides also have a powerful ability to protect the skin through a wide range of bioactivities. Sulphated

polysaccharides have powerful antioxidant activity, tyrosinase, inhibit elastase and can absorb and retain moisture *in vitro*. Therefore, these sugars can be used as an active ingredient for skin protection [182]. Asia (China and South Korea) represents 30% of the market and Europe represents 20%. USA and Brazil also represent an important part of the market. The demand comes from traditionalist and neo-traditionalist companies. Many major brands are willing to make green product: Nuxe, Sanoflore (bought by L'Oréal), Yves Rocher. In 2013, they were more than 500 brands around the world interested in organic cosmetic and the leading ones are mainly in Germany and France [183]. Telling a fantastic and green story about new miraculous anti-aging polysaccharides from exotic countries in Africa (e.g., Madagascar, etc.) is the trademark and guidelines for these (commercial) approaches.

The safety and biodegradability of polysaccharides have also attracted the attention of food industry. The organic food market is estimated more than 100 billion dollars in 2018 and is facing an important growth for the last decade [181]. Polysaccharides have versatile rheological properties, which affect their applications in food products [184]. Highly branched structures give to polysaccharides some good solubility, low viscosity, and gelation properties. Therefore, they are a convincing source of emulsifier and stabilizer in the food industry. Numerous studies have evaluated the effects of marine polysaccharides on fish, shrimp, and other aquatic animals on growth index parameters such as weight gain, length gain (LG), specific growth rate (SGR), or survival (SUR). Several marine polysaccharides have been shown to be growth promoters in many aquatic species. Thus, diets supplemented with polysaccharides are digested and absorbed more efficiently due to the ability of polysaccharides to stimulate the secretion of digestive enzymes (amylases, proteases, and lipases etc.) which leads to improve nutrient utilization and digestion, then health and growth of aquatic animals [1,185]. Organic agriculture is now going mainstream, demand remains concentrated in Europe and North America in 2019. 93 countries had regulation laws concerning the organic agriculture. Major brand such as Nestlé and Danone develop more and more natural product based on organic agriculture. However, the cost of research and development on polysaccharide make the food industry a less attractive target for the organic polysaccharides [186], which is particularly true for countries like Africa for which niche markets are still the best chances of success for bringing out a new active cost-effective polysaccharide.

Polysaccharides may also play a role in pollution clean-up. Global environmental remediation market was valued at around 79.57 billion dollars in 2016 and is expected to reach approximately 122.80 billion dollars in 2022. The CAGR is estimated between 7.5% between 2017 and 2022 [187]. Polysaccharides can be used as adsorbents for various pollutants such as heavy metals from different environmental and food samples [188]. Their functionalities such as hydroxyl, carboxyl and amine groups along their chains give them a high affinity for heavy metals [177,188]. The advantages of sugars (biodegradability, non-toxicity, environmental friendliness) make them promising, ecological, and economical. However, their application as adsorbents is generally hampered by their low mechanical resistance [188]. These limitations can be reduced by chemical modifications due to their various functional groups [156]. The adsorption capacities of these polysaccharides for heavy metals can be improved for instance by carboxymethylation [188]. Polysaccharides also have enormous potential as flocculants for use in wastewater treatment due to their hyper-branched structures, numerous spatial cavities, and many terminal functional groups [185]. Target companies are AMEC Earth & Environmental, Arcadis, Bechtel, CH2M, Environmental Resources Management, Golder Associates Hill, Tetra Tech, URS and Veolia Environmental Services North America [189]. The market is mostly located in North America, Europe, Asia, Latin America, Middle East and Africa.

In 2019, the global biofuels market amounted to over 136 billion U.S. dollars. By 2024, the market is expected to grow to almost 154 billion U.S. dollars [190]. Finally, research on the cationization of polysaccharides could replace petroleum-derived polymers. This is a particularly promising area for the replacement of synthetic materials that is still little

researched [191]. As biofuel is viewed as an energy of the future, many companies are developing biofuel from different sources (organic and inorganic): Acciona Energy, Anchor Ethanol Ltd., Biodiesel International Ag (Bdi), China Clean Energy Inc., Cosan Group, Inbicon, Ineos Enterprises Ltd., Novozymes, Shaval Biodiesel, Synthetic Genomics, etc. The market is mostly located in North America, Europe, Asia Pacific, Latin America, Middle East and Africa [192].

5. Conclusions

Today, many African plants but also macroalgae are used by people in traditional medicine for their therapeutic properties. The change of lifestyle of these populations and the use of modern therapeutic practices is resulting in the gradual disappearance of ethnobotanical knowledge accumulated over the last centuries. Inventorying this biodiversity is also partly motivated by the search for new active ingredients which may, in the long term, become one of the levers allowing the preservation of species facing the climatic and energy challenges of the Mediterranean and African areas. Today, the very perceptible greenhouse gas emissions constitute a real threat to natural resources, landscapes, biodiversity, and the future of potentially new natural resources not yet discovered. The inventory of existing structures is still very incomplete while its exploration, through research running programs, is often associated with the (i) identification of new polysaccharides carrying biological activities, (ii) increase in structure-function relationships understanding and (iii) scientific rationalization of traditional uses. For example, the EXPLORE 2019–2021 (PHC Maghreb, Campus France) international project between 4 countries (Algeria, France, Morocco, and Tunisia) aims to (i) explore the potential of Saharan plants and macroalgae from the Mediterranean coast of North Africa as a source of polysaccharides of original structures and (ii) correlate these structures with technofunctional properties but also biological activities (health and agronomy fields) potentially valuable.

Despite this favorable context where medicinal plants hold an important place in the socio-economic development of Africa, the potential of many plants is not studied because of geographic, geopolitics, economic and legal problems that are obstacles to the development of new “revolutionary” products. Another challenge for the following decades is also to address *in vivo* the relationship between structural features and biological activities. Without this, no real outbreak will happen for the discovery of new enriched-polysaccharide drugs for an emerging country like Africa. Obviously, questions should also be raised about financial returns, types of targeted markets (niche markets in cosmetics and/or nutraceuticals, etc.) or regarding the 2021 current international context which clearly shows the importance of having a large phytochemical library of molecules available for quickly resolving major events such as an epidemic. Note that research on polysaccharides will probably strongly evolve thanks to the use of “-omics” technologies which are changing scientific work approaches.

Finally, we invite the readers and scientific community working on ethnobotany to ask the following questions: Does the interest still only lie in the “finding and harvesting of other new plants/carbohydrates” or is it in identifying active chemical structures to mimic them in laboratories (using green biochemistry/bioprocess engineering)? In other words, ultimately, taking inspiration from nature to create the new polysaccharide-drugs of tomorrow.

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