

Bark extractives as sources of carbon-efficient functional precursors and materials

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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- Concise overviews of bark extractives are outlined, highlighting their chemical variety and possible applications.
- Self-assembly of bark extractives into complex suprastructures is key to developing materials with specific functions.
- Perspectives for converting bark extractives into eco-friendly, value-added materials for circular bioeconomy.



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Biomass residues generated in forest operations represent an abundant and renewable resource in need for valorization. Bark is becoming increasingly relevant, not only in the bioproducts sector, but also in the context of the circular bioeconomy, which is placing emphasis on underutilized residues and waste. Among these, tree bark is one of the largest forestry by-products, accessible at a megaton scale but so far mostly utilized for its solid fuel value. Bark valorization should include the isolation of valuable natural compounds that add functionalities to a variety of bioproducts. This is the subject of this review, which considers bark extractives prospects, under the biorefinery concept, placing attention on extractives' chemical profiles and properties. We introduce the most recent pathways reported for bark fractionation and the opportunities to achieve new materials by using the concepts of supramolecular chemistry, leading to special assemblies. We show that value-added chemicals and materials are possible and expected to become most relevant in efforts aimed at maximizing bark utilization.

INTRODUCTION

The shift of our dependence on fossil carbon to biogenic sources is moving society closer to the goals of the sustainable development and the circular bioeconomy.¹⁻⁷ This requires recognizing the importance of biogenic materials that are widely accessible but otherwise considered low-value. Addressing resource efficiency and environmental impact, for example, requires utilization of biomass that can be readily reintegrated into the biosphere.^{8,9} Bark is a ubiquitous forest residue, with an estimated annual availability of over 360 million cubic meters (m³) calculated assuming a 10% by weight of the global roundwood production.¹⁰ Indeed, residual coniferous bark in the European Union has been estimated to amount to 14 million tons, with Sweden, Finland, and Germany as the largest contributors. In Canada, an estimated 17 million m³ of bark per year was reported to be available.¹¹ Such mass of bark is mainly used as an inexpensive solid biofuel, burned by direct combustion, or as compost in horticulture.¹² The former use still poses operational challenges associated with the failure of the combustor and air pollution from minor amounts of sulfur. For this and other reasons, more than half of the bark is just removed from mill sites and landfilled as waste.¹³ Considering other uses, it has been noted that bark is not a favorable feedstock for the production of fermentable sugars due to its high content of lipophilic and aromatic compounds (e.g., suberin, tannins, and lignin).¹⁴ Direct processing and conversion of bark into panels or boards has been reported in the building sector. Nonetheless, the substantial waste generated in board production and the emission of toxic volatiles during usage present constraints on the sustainable utilization of bark. This justifies the need for innovative strategies to promote alternative applications, offering both positive environmental and economic outlooks. Besides, a drawback of untreated or chemically-treated bark is its hygroscopicity, due to its porous nature, as well as the lower density and poorer mechanical quality compared with wood. To this end, one can take advantage of the structural characteristics of barks at the cell scale, with lignocellulose (bark fiber) built as a skeleton that also contains valuable

fine chemicals, produced in the biosynthesis process to fulfill a number of functions.

Bark's structural components, as in wood, include lignocellulose that provides benefits in the areas of materials science, food, and agricultural engineering, drug delivery chemistry, energy and fuels, water treatment, catalysts, polymer science, nanofibers, etc.¹⁵⁻¹⁷ Wood has long been used in the construction, pulp, and paper industries. Some uses can be determined by the presence of lignin and its removal is not an uncommon step, mainly in wood pulp production. Beyond the multiple methods developed for the utilization of lignocellulose, especially, cellulose, lignin, or hemicellulose, effective fractionation of extractives is expected to contribute to their processing into biochemicals and materials. Also, compared with wood, bark is inexpensive and can be used or integrated in value-added products. Since debarking is one of the first operations in typical wood pulp production or sawmilling, collecting and extracting bark, on site, can save transportation costs. Also, some of the infrastructure used for lignin dissolution and processing can be adapted for the processing of extractives. Moreover, extractive-related production can be integrated in a pulp mill to generate value-added bioproducts that can open new markets. Valorization of bark can complement strategies to engineer wood for timber and wood pulp and achieve better material integration and utilization and carbon efficiency.

The so-called "extractives" are elementary components of bark, featuring attractive chemical and biological activity. Indeed, in its natural form, bark's lipophilic and hydrophilic extractives bring properties such as color, odor, and protection (resistance against water, insects, microbes, pathogens, and fires).¹⁸ These functions inspire interest in transferring such roles to man-made materials.^{19,20} For instance, in ancient times, (fossilized) tree resins (amber or rosin) were widely used in medicine, lighting, and as natural adhesives for sealing in the naval industry.²¹

Overall, bark extractives have been considered for the production of essential chemicals and materials under the framework of the "bark biorefinery" (Figures 1A-B). Several obstacles have delayed the industrial implementation of the latter, including supply chain and market factors. These are issues that need attention along with the development of technologies to advance the transition from laboratory to industry. At present, bark extractive valorization is in the early stages but has gained momentum over the past decade (Figure 1C). Understanding bark ultrastructure along with advanced fractionation to make the functional features of extractives available will inspire the development of a new bioproduct generation.

Scope of the review

This review addresses the topic of natural building blocks available in bark and their assemblies as source of value-added materials. We emphasize the utilization of bark extractives to enhance the accessibility and utilization of forestry waste. Furthermore, we underscore their suprastructural assembly, which outperforms other biomass-derived alternatives in functionality. We first discuss the origin of bark, main extractives, and interactions affecting their assembly. We further introduce prospective extractives uses considering the biorefinery concepts. Bearing in mind the recent efforts to transfer

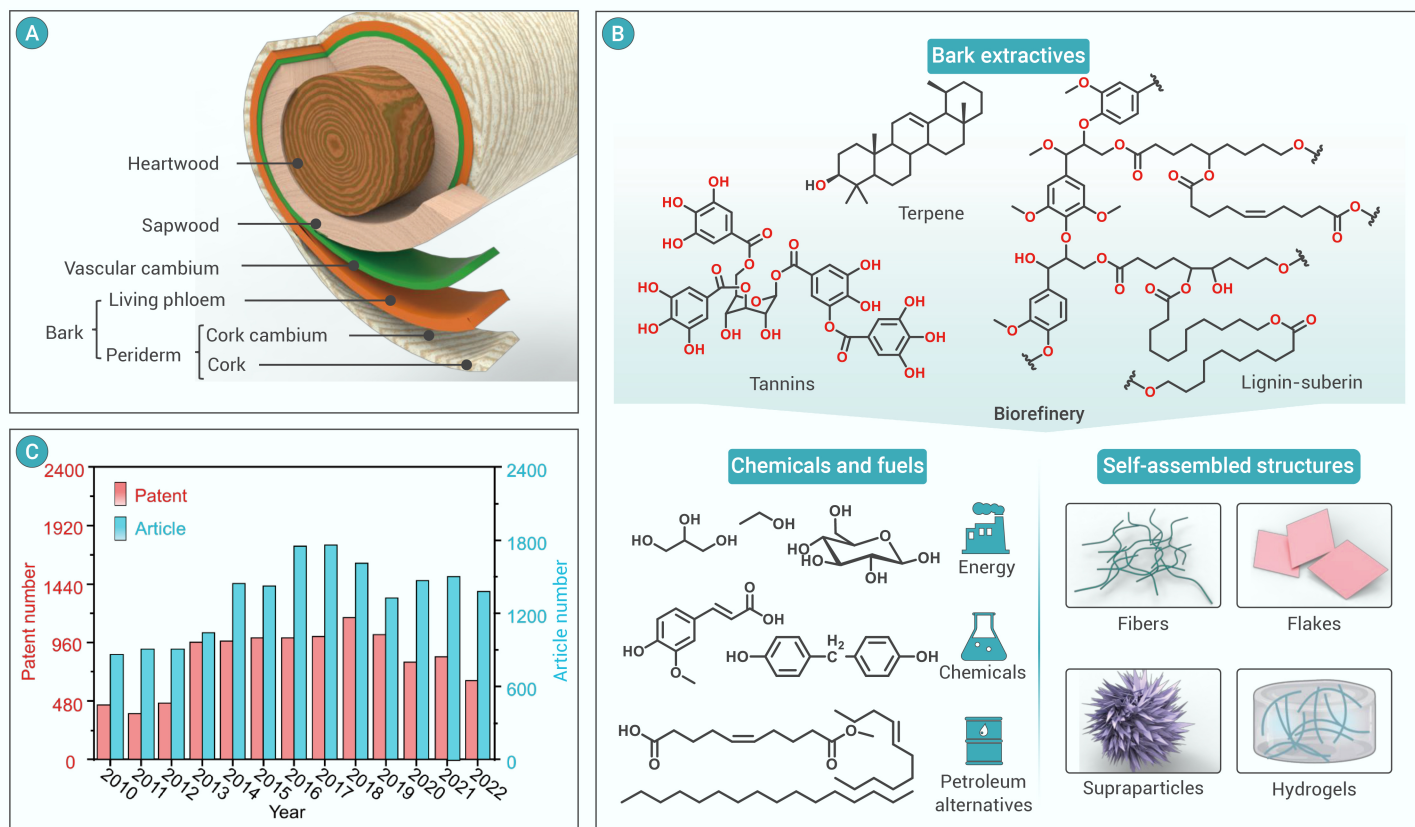


Figure 1. Bark and extracts in current research (2010-present) (A) Schematic illustration of bark anatomy. (B) Main bark components within a biorefinery. (C) Publication and patent figures according to the available literature since 2010 obtained in bibliographic search under the keyword "bark extract" (Source: Web of Science).

structure-property correlations to bulk materials, we introduce the potential of bark building blocks by considering their chemistry, processing, and supramolecular structuring.

BARK ANATOMY

The term "bark" generally refers to plant tissues outside the vascular cambium layer, the non-wood part of a tree stem. However, bark consists of two distinct tissue layers of different meristematic origins and functions: (1) the inner bark, or phloem, which is the living, nutrient-conducting tissue that derives from vascular cambium cells. It consists of conducting sieve elements, various parenchyma cells (e.g., resin ducts in some conifer species), and sclereids or bast fibers. (2) The outer bark, or periderm, which covers the phloem and replaces the epidermis as an outer barrier of the stem as the tree grows thicker over time. It derives from a secondary cambium (i.e., phellogen) and acts as a protective layer for the plant. Periderm formation also plays an important role in the reaction of trees to injuries and damage, resulting in extractive-rich traumatic tissue. The structure and composition of the outer bark and its surface are determined by the structuring of single or multiple periderm layer(s). The texture and thickness of the bark surface differ widely between tree species, from smooth and papery (e.g., *Betula* spp., *Populus* spp., and *Fagus* spp.) to flaky, patchy, furrowed, or fissured (e.g., *Quercus* spp., *Pinus* spp., *Abies* spp., and *Picea* spp.) and often change with the maturity of the bark periderm.

Consequently, phloem and periderm differ significantly in their cell structure and chemical composition according to their biological functions.²² Phloem is rich in cellulose (e.g., in bast fibers, sclereids), starch, sugars, lipids, proteins, and many secondary metabolites (e.g., polyphenols) due to the presence of specialized parenchyma cells. In contrast, the periderm, especially the outermost cell layers (i.e., the cork or phellem), exhibits high lignin and suberin content, as cell wall components, and a considerable amount of extractives.^{23–28} The exact chemical composition of bark is directly linked to the tree species, individual tree location, past injuries, and longitudinal position on the tree (i.e., tissue maturity).^{28,29} These differences in composition

must be considered in the use of bark as a material since they affect many physical properties (e.g., density, mechanical strength, elasticity, hydrophobicity, and thermal conductivity). Table 1 summarizes the differences between the two layers of bark. Moreover, knowledge of the bark composition is paramount for the efficient extraction of compounds, affecting the yield, selectivity, purity, and quality of the extracts. Important for the industrial use of bark are the storage time and the technology applied for debarking (or bark sorting), since they affect the proportion of inner-to-outer bark and the content of extractives.^{30–33}

BARK COMPONENTS BEYOND CELLULOSE AND LIGNIN

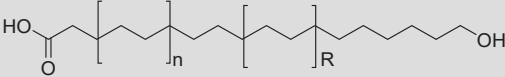
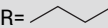
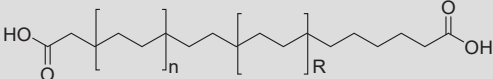
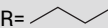
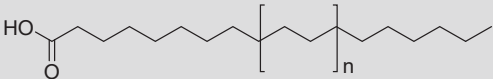
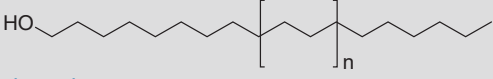
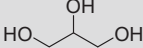
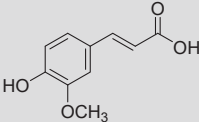
Bark extractives have garnered interest in many industries, including those related to paints, fertilizers, surfactants, rubbers, adhesives, pharmaceuticals, among others. For instance, some lipophilic extractives are inert to various chemicals and bring enhanced stability.^{34–36} As such, suberin can improve the mechanical strength of epoxy resins from linseed oil via crosslinking, bringing a tunable glass transition temperature to the resulting materials.³⁷ Many hydrophilic extractives show antioxidant, anti-inflammatory, and antimicrobial properties.^{38–40} In addition, hydrophilic extractives have been employed as an alternative to fossil-based plastics in particles and bio-based films.^{41,42}

From the technical perspective, extractives are compounds that are separated from a solid (bio)resource, such as bark, by means of solvent extraction. Hence, the term *extractives* comprises a wide range of compounds that differ significantly in their chemical structure. Typically, extractives are classified based on their polarity, lipophilic or hydrophilic compounds, which is tantamount to their solubility in certain solvents. Lipophilic extractives from bark include fatty acids, fatty alcohols, waxes, terpenes, resin acids, sterols, sterol esters, and glycerides. Meanwhile, hydrophilic extractives include water-soluble carbohydrates and polyphenols (i.e., stilbenes, flavonoids, and tannins).^{39,43,44} Information on the inherent chemistry and biological origin of bark extractives is required in defining their applications. In this section, we give a short account on representative compounds that have shown potential in given chemical applications.

Table 1. Main features of the inner and outer bark

	Inner bark (phloem)	Outer bark (periderm)
Origin	Vascular cambium	Secondary cambium
Type of tissue	Living tissue	Mostly dead tissue
Functions	Conducting layer	Protective layer
Physical structures	Sieve elements, parenchyma cells, and bast fibers	Cork skin, cork cambium, and cork
Main components	Cellulose, starch, sugars, lipids, proteins, and secondary metabolites	Higher lignin and suberin content, and a considerable amount of extractives

Table 2. Structure of common suberin monomers and their range in relative abundance

Monomer type	Chain length	Composition (%)
ω- Hydroxyacids 	R=  or  or  n=1-8 for 	11-43%
α, ω- Dicarboxylic acids 	R=  or  or  n=1-8 for 	24-45%
Fatty acids 	n=1-8	1-10%
Fatty alcohols 	n=1-8	1-6%
Glycerol 	-	14-26%
Phenolics 	-	0-10%

Suberin

Suberin is a widely known lipophilic component found in the outer bark of trees, especially in birch and cork oak (*Quercus suber*), playing a crucial role in regulating water, gases, solutes, and microbial movement in plant cells.⁴⁵ Chemically, suberin is a bio-polyester of glycerol with α,ω -dicarboxylic acids, and ω -hydroxyacids, with chain lengths ranging from C16 to C30 (Table 2).⁴⁶ In suberin, glycerol acts as a multifunctional crosslinker, resulting in an extended three-dimensional network whose structural details remain far from being fully understood. The current knowledge on the chemical composition of suberin is primarily based on analyses through depolymerization *via* cleavage of ester bonds by hydrolysis, alcoholysis, or hydrogenolysis, followed by the identification of fragmented monomers or oligomers by gas chromatography coupled with mass spectrometry (GC-MS).⁴⁷

Suberin aliphatic polyester, a widely recognized structural template, forms a transparent lamellar structure similar to that of suberized cell walls. Long-chain monomers are aligned at right angles to the lamellar plane within the chains extended, leading to the lamellar growth in all three dimensions. The macromolecular structure of suberin may be based on long-chain di-acid monomers anchored on both sides by glycerol. Both suberin and suberin fatty acids have been identified as potential sources for value-added biobased materials, such as plasticizers, moisture barriers, additives for surface treatments, and others. The hydrophobicity of suberin makes it suitable for creating hydrophobic surfaces, coating, and compatibilizers in reinforced polymer composites.⁴⁸

Terpenes

Terpenes are an important class of natural metabolites that share isoprene as a common building block. They are classified based on the number of

carbons into mono- (C10), sesqui- (C15), di- (C20), tri- (C25), tetra- (C30), and poly-terpenes (*i.e.*, natural rubber). Oxygenated derivatives are referred to as terpenoids. Terpenes and terpenoids fulfill multiple biological functions and are decisive for many properties in plants, wood, or bark.

Rosin is the non-volatile, solid fraction of conifer (pine) resin that is left after evaporation of the more volatile mono- and sesquiterpenes. It consists of a mixture of different diterpenes and terpenoids, mainly abietic acid and its isomers neoabietic acid, palustric acid, and levopimaric acid. Abietic acid derivatives possess one to four conjugated double bonds of different configurations and functional groups, such as carboxylic acids, hydroxyls, or endoperoxides, rendering rosin an interesting polymer precursor.^{49,50} Rosin terpenes can undergo many different chemical reactions, including esterification, isomerization, Diels-Alder addition, and amidation under mild conditions.⁵¹ Rosin and its derivatives have been considered as polymer feed-stocks in paper sizing and emulsions by imparting hydrophobicity to the given material (*e.g.*, paper surfaces).^{49,52} Recent reports have summarized the results of the synthesis of compounds from rosin, with an emphasis on upgrading tall oil.^{53,54}

Triterpenes and triterpenoids comprise important compounds, including (phyto)sterols, steroids, and saponins, with important physiological functions. They are a very diverse class of chemicals with predominantly tetra- or pentacyclic structures. Most famously, the bark of the white birch tree is rich in a pentacyclic triterpenoid, betulin (up to 30 wt%). Betulin (BE) and the betulinic acid (BA) derivative are based on the lupane skeleton, a five-membered E-ring, and an isopropylidene group. BE-derived compounds show therapeutic potential for anticancer treatments and are currently undergoing clinical trials.^{55,56} BE and most of its derivatives are poorly water-soluble, which challenges some pharmacological uses. The bioactivity and phar-

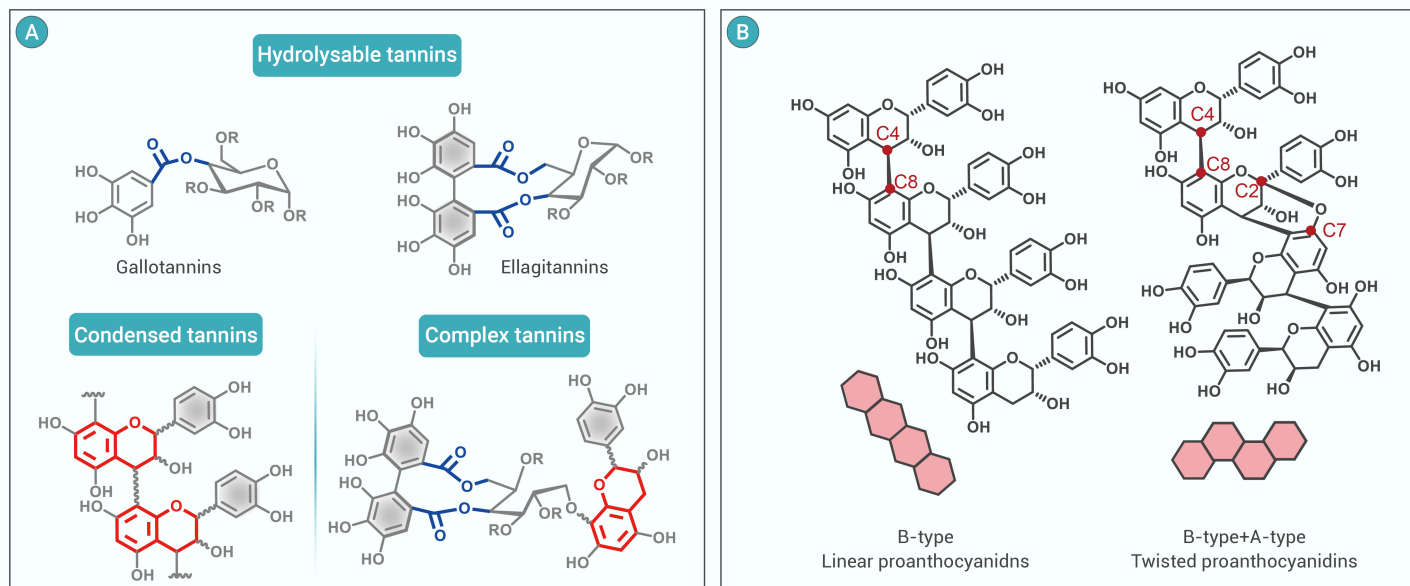


Figure 2. Structures of polyphenols extracted from bark (A) Typical structural characteristics of hydrolysable, condensed, and complex tannins. Reproduced with permissions.⁶¹ Copyright 2001, Royal Society of Chemistry. (B) Configurations of proanthocyanidins based on interflavan linkages. Reproduced with permissions.⁶⁵ Copyright 2019, John Wiley & Sons.

macological properties of betulin and its derivatives have been reviewed to advance or improve their pharmacokinetic properties.^{57–59}

Polyphenols

Bark polyphenols, which include tannins, are one of the most abundant hydrophilic extractives found in bark. The early use of polyphenols included tanning industry, to convert animal hide into leather to impart thermal stability and antibacterial properties.⁶⁰ Two basic categories of tannins can be listed: (1) hydrolysable (i.e., gallotannins and ellagitannins) and the more common (2) condensed tannins (Figure 2A).⁶¹ Hydrolysable tannins are derivatives of gallic acid, usually esterified to a core polyol (such as glucose), and the gallic acid groups may be further esterified or oxidatively crosslinked to obtain more complex hydrolysable tannins.⁶² Gallotannins produce gallic acid moieties upon hydrolysis, whereas ellagitannins produce ellagic acid. Ester bonds between crosslinked gallic acid groups are classified as either *meta*- or *para*-depside, or if units are oxidatively coupled, a C-C bond is formed between the aromatic rings. Condensed tannins are oligomers or polymers consisting of flavanol units (i.e., combination of a catechol/pyrogallol with a resorcinol/phloroglucinol ring) exhibiting great diversity of structural features based on their number and position of the hydroxyl groups, the presence of esterification by gallic acid, the degree of polymerization (DP), and the position of the interflavan linkages in a very wide range of molecular sizes.^{63,64} Two linking modes can be observed within condensed tannins: flavanol units either linked by C2-O-C7 or C2-O-C5 interflavan bonding (A-type), or C4-C8 or C4-C6 (B-type), which directly affects the final molecular configurations into linear, or twisted structures (Figure 2B).⁶⁵ Proanthocyanidins (PA) are a class of condensed tannins comprising catechin/epicatechin units that are commonly found in many plants. PA oligomers (DP<5) exhibit powerful antioxidant capabilities and have been reported to protect or prevent aging, cancer, and cardiovascular diseases.⁶⁶ A high PA DP can result in a lower reactivity due to the steric hindrance within the polymeric structures.⁶⁷ Depolymerization of condensed tannins could produce functional monomers with more promising properties.

In terms of the physicochemical features of polyphenols, the catechol/pyrogallol moieties are the basis for the reaction or binding via different molecular interactions (i.e., metal coordination, hydrogen bonding, and π - π interactions). Metal-phenolic coordination can form a class of amorphous metal-organic network systems, which enable a broad spectrum of structures with varied morphologies, and metal-centered functionalities.^{68–74} Polyphenols often show characteristic reactions with other biomacromolecules (i.e., proteins, deoxyribonucleic acids (DNAs), and phos-

pholipids) and cells, exhibiting potential as delivery vectors.^{75–80} Dynamic covalent bonds (e.g., imines and boron-diols) can also be introduced to impart stimulation with small organic molecules, typically within the case of boronate-catechol interactions.^{81–83} Materials such as foams at the macroscopic level can be achieved by the modification of cellulose fibers with metal-phenolic networks. The physical and mechanical properties are governed by the composition, content, and types of polyphenols.⁸⁴ Hence, natural polyphenols have been widely implemented in biomaterials, nanoparticles, nanocapsules, and hydrogels, for applications in biomedicine, energy, and environmental sciences.^{85–89}

Non-cellulosic saccharides and their conjugates

Sugar occurs in the bark in several forms: (1) monosaccharides (only present in small amounts); (2) polysaccharides for energy storage (i.e., starches) and structural elements (e.g., cellulose, hemicelluloses, and pectins), and (3) glycosides (i.e., mono- or oligosaccharides linked to organic molecules).⁹⁰ Polysaccharides are typically classified based on their monosaccharide composition (e.g., glucose, xylose, arabinose, galactose, etc.) and bonding pattern. For instance, cellulose and starch are both composed of glucose units but differ in the interunit bonding type. In contrast, hemicelluloses show a distinct diversity as far as their monosaccharide composition, linkages and branching (Figure 3A).⁹¹ The presence and proportion of certain hemicelluloses in the cell wall are strongly related to the tree species, with distinct differences between softwoods and hardwoods. In contrast to cellulose, hemicelluloses, pectins, and starches are water-soluble and can be readily extracted from bark. Such extract usually comprises a mixture of (xylo)glucans, β -1,4-xylans (i.e., glucuronoxylan, arabinoxylan, and unsubstituted xylans),⁹² mannans (i.e., glucomannan, galactomannan, galactoglucomannan),⁹³ or arabinogalactans.⁹⁴ Some xylans are reported to be feruloylated and are antioxidative due to the polyphenolic side chains.⁹⁵ Additionally, these ferulate side chains are also points for crosslinking with lignin, making these types of hemicelluloses recalcitrant to digestion and fermentation to biofuels.^{96–98}

Pectin represents the most structurally intricate polysaccharide in nature, with D-galacturonan as its main structural component (Figure 3B).⁹⁹ Furthermore, pectins are classified in four subclasses: homogalacturonan (65%), rhamnogalacturonan I (20–35%), rhamnogalacturonan II (10%), and xylogalacturonan. According to the stage of development, the degree of acetylation of pectins ranges from 40 to 85%. A functional property of pectins is their ability to form gels through crosslinking by Ca^{2+} ions along with hydrophobic interactions. Such interactions dependent on the charge distribution in the

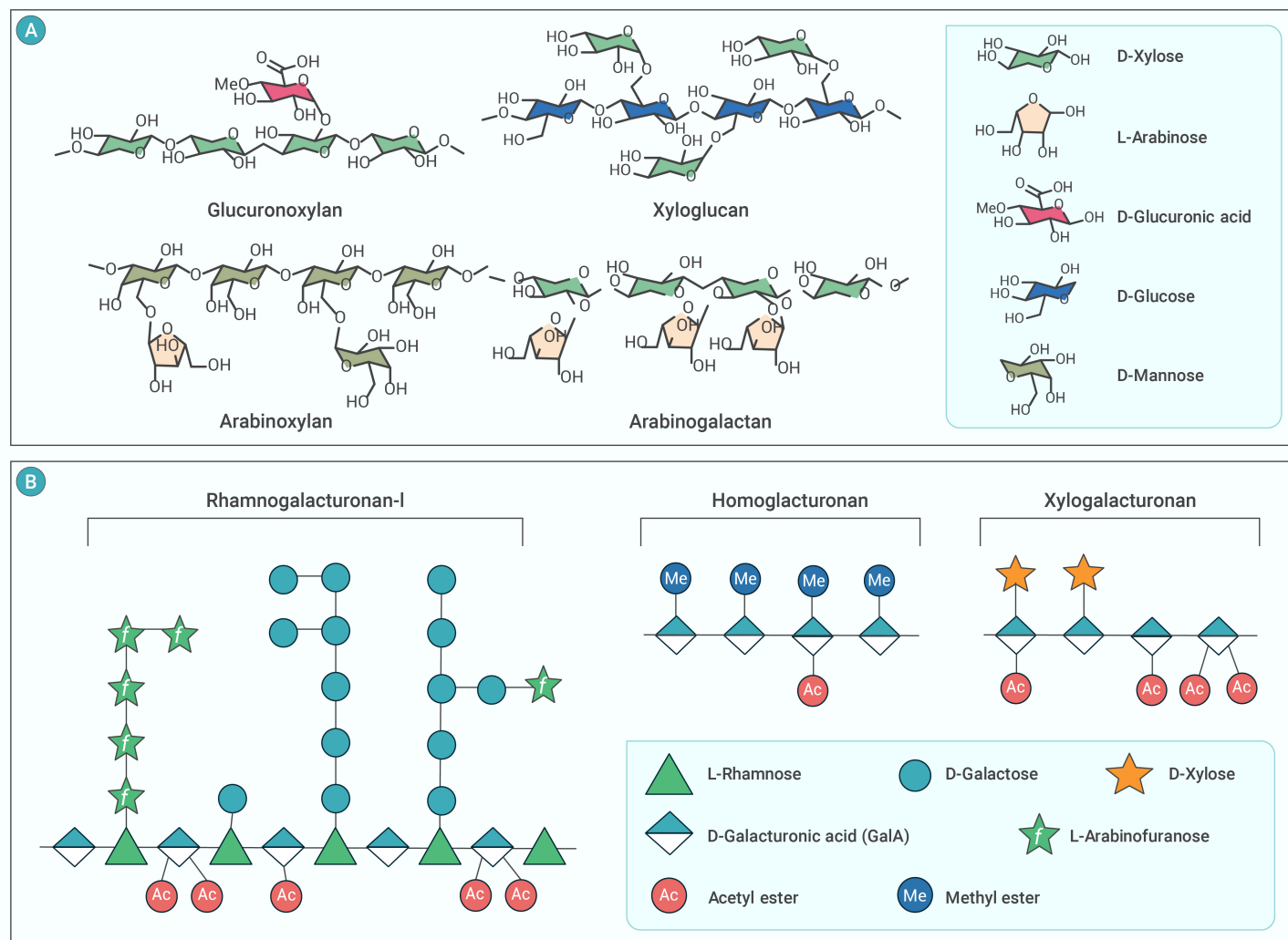


Figure 3. Typical structures of saccharide-based bark extracts (A) Typical hemicellulose structures (reproduced with permission.⁹¹ Copyright 2023, Elsevier). (B) Representative structure of pectin (reproduced with permission.⁹⁹ Copyright 2023, Elsevier).

backbone of the pectin, the molecular weight, and degree of acetylation, and methylation.¹⁰⁰ Low molecular weight pectins with a high degree of methylation are good emulsifiers while pectin acetylation and methylation contribute to an increased viscosity in solution and influence the entire dynamics of the polysaccharide.^{101,102}

Many phytochemicals are present in living cells as glycosides to control their biological availability and function. Glycosides consist of a sugar moiety (glycone) that is covalently bonded to a biologically active compound (i.e., non-sugar moiety or aglycone).¹⁰³ This bond needs to be broken to activate the aglycone's physiological function in the plant. Variability in the structure of glycosides occurs due to (1) variations in the sugar moiety (e.g., monosaccharides such as β -D-glucose or even oligosaccharides), (2) position and type of the covalent bond, and (3) variation in the type and structure of the aglycone moiety. A large variety of compounds qualify as aglycone moiety in glycosides, including flavones, flavanones, stilbenes, steroids, terpenoids, gallic acid derivatives, and condensed tannins, among others. Above all, phenolic glycosides, flavonoid glycosides, saponin glycosides, and cardiac glycosides comprise the most important bark glycosides and are of great interest because of their bioactivities and functional properties (e.g., amphiphilicity).¹⁰⁴

BARK EXTRACTION

Extraction process

From the technical point of view, extracts are compounds that are separated from a solid (bio)resource such as bark employing solvent extraction. However, the term *extractives* is used as an umbrella term for a wide range of

different compounds that differ significantly in their chemical structure. As discussed above, extracts can be classified based on their polarity into lipophilic or hydrophilic, e.g., solubility. Consequently, the choice of solvent (polarity) has a crucial impact on the yield and selectivity of the extraction. For lipophilic compounds, organic solvents such as n-hexane, n-heptane, cyclohexane, acetone, dichloromethane (DCM), ethyl acetate (EtOAc), or toluene are typically used for their good selectivity. However, organic solvents are expensive and pose potential risks to safety and health (i.e., fire hazard, toxicity, etc.). Hence, the use of sub- and supercritical CO₂ has gained acceptance as a safer alternative with similar selectivity towards lipophilic compounds.¹⁰⁵ For hydrophilic compounds, water and/or polar solvents such as ethanol (EtOH), methanol (MeOH), or acetone are frequently used for extraction. Although water is cost-effective and available, the high energy demand for evaporation and the limited selectivity prevents, at least to some extent, its economic viability. Polar solvents offer tailorable selectivity but are more expensive and pose safety risks. Important parameters in extraction include solid-to-liquid ratio, temperature, time, and particle size of the biomass feedstock.

The extraction efficiency is usually judged by extraction yield and purity (i.e., selectivity in chemical composition), which depend largely on the selection of an appropriate solvent and optimization of extraction conditions. However, the extractives content and composition of biomass (i.e., bark) vary significantly between species, individual trees, and tissues, which impacts the extraction efficiency. Hence, the availability and supply of extractive-rich biomass is crucial for economic viability of the extraction processes. In the forest industry, extractive-rich by-products are frequently produced by

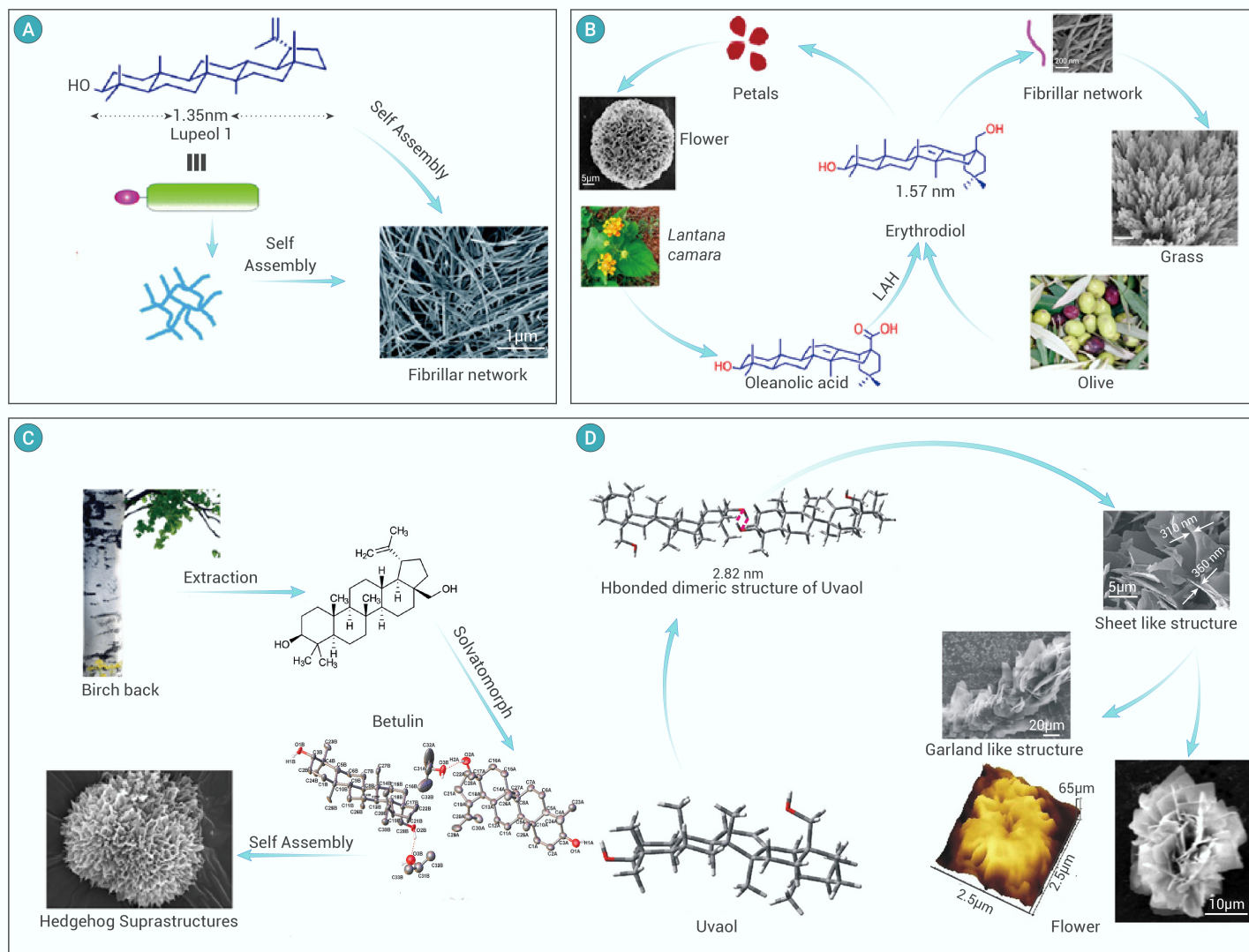


Figure 4. Superstructures formed from terpenoids (A) Schematic illustration of the isolation of lupeol from *Bombax ceiba* and its self-assembly in liquids yielding gels via formation of the fibrillar network for various applications.¹⁴⁸ Copyright 2019, American Chemical Society. (B) Isolation and synthesis of erythrodiol and its self-assembly yielding flowers, fibers, and grass-like architectures.¹⁴⁹ Copyright 2020, American Chemical Society. (C) Betulin self-assembly: from birch bark to hedgehog suprastructures.¹⁵⁴ Copyright 2022, John Wiley & Sons. (D) Proposed model of self-assemblies of uvaol yielding flower and garland-like architectures.¹⁵² Copyright 2021, American Chemical Society.

mechanical or chemical separations (e.g., debarking, sawing, chipping, steaming, pulping, etc.) and the valorization of extractives has attracted great economic interest. In the following, we review the current industrial practice of extractive recovery from biomass as well as future developments.

Nowadays, chemical pulping is the major source of extractives from woody biomass. Lipophilic extractives show high resistance to degradation during pulping (digestion). In kraft pulping, turpentine (i.e., a mixture of volatile monoterpenes) is readily recovered from the digester relief condensate. At the same time, so-called tall oil is skimmed from the black liquor and subjected to further refining by acidification and distillation to recover fatty acids, sterols, resin acids, and di-/triterpenes (i.e., rosin).¹⁰⁶ The economic and technical importance of these by-products is enormous, with an annual production of more than 1.6 million ton.¹⁰⁷ However, the recovery potential is not fully exploited yet.^{108,109} Again, differences in turpentine and tall oil yield and composition are related to the pulping feedstock (i.e., softwoods vs. hardwoods). Although any of these lipophilic compounds could be extracted from the bark as well, industrial implementation has often been restrained by the hurdles of economic feasibility. Currently, sequential extraction with polar organic solvents and supercritical CO₂ is considered as most promising for future implementation.^{105,110–115}

Extractives purification

Efficient separation of inner from outer bark remains one of the key chal-

lenges because of their differences in extractive composition and content.^{30,116} For instance, the outer bark is the only tissue that contains suberin as part of the cell wall. Tree species relevant to the forest industry include those related to cork (e.g., *Quercus suber*, *Betula pendula*, *Pseudotsuga menziesii*, and *Abies concolor*), industrially important sources of suberin.²² Its complex macromolecular structure renders suberin virtually resistant to dissolution in common solvents. Thus, alkaline hydrolysis followed by extraction with polar organic solvents (e.g., MeOH, EtOH, DCM) are usually applied to recover suberin monomers and oligomers.^{116,117}

Betulin is another important compound found in the outer bark of trees. In the *Betulaceae* tree family, betulin content in bark can reach up to 45% dry weight.¹¹⁸ Trees of this family (e.g., *Betula pendula*, *pubescens*, *papyrifera*, and *platyphylla, alba*.) are important sources of lumber and pulp wood, and their bark.¹¹⁶ Demets et al. reviewed the most common methods for betulin isolation from bark, including extraction by organic solvents, supercritical CO₂, vacuum sublimation, and vacuum pyrolysis. Betulin extract can be further purified by re-crystallization with organic solvents and/or alkaline treatments.¹¹⁹

In contrast to suberin and betulin, polyphenolic compounds are located mainly in the inner bark of trees. Commercially relevant tree species include *Acacia mearnsii* (i.e., mimosa, black wattle tree), *Schinopsis balansae* or *lorentzii* (i.e., quebracho), *Pinus spp.*, *Quercus spp.*, *Castanea sativa*, and many more.¹²⁰ The composition and structure of tannin extracts can vary

greatly between species and suppliers. A number of agricultural residues are important sources as well (e.g., tea, coffee grounds, persimmon hulls, grape skins, walnut shells, etc.).^{121,122} The annual global production is around 200–300 kt, with condensed polyphenols heavily dominating the market (>90%).^{120,123–125} However, the potential production capacity is estimated to be in the 1 to 1.5 Mt range.¹²³ The hydrophilic character of polyphenols affords extraction with polar solvents, i.e., water, EtOH, MeOH, acetone, or their mixtures. For detailed reviews on advanced extraction techniques, the reader is referred to the recent literature.^{122,125–127}

Finally, saponins are a family of glycosides that naturally occur in a range of plants such as soapwort (*Saponaria officinalis*), soap bark tree (*Quillaja Saponaria*), horse-chestnut (*Aesculus spp.*), maple trees (*Acer spp.*), or in soybeans (*Glycine max*).¹²⁸ An extensive review of saponin natural occurrence and extraction can be found in the literature.¹²⁹

SUPRAMOLECULAR ASSEMBLY OF BARK EXTRACTIVES

Nature uses self-assembly to create structures and functions.¹³⁰ Supramolecular structures display critical biological roles following a complex yet efficient bottom-up process. Manipulation of the self-assembly of naturally occurring compounds, such as extractives from bark, can advance their sustainable development. Attempts have been made to mimic the self-assembly processes using extractives as building blocks and creating multifunctional suprastructures.¹³¹ However, a high level of control over the process is mandatory to promote further development. In this section, we examine the self-assembly of common extractives, following three perspectives, namely, (i) molecular building blocks, (ii) interfacial behavior, and (iii) biological assembly. We also correlate the respective driving forces with the resulting structures and performance.

Assembly at the molecular scale

Supramolecular gels resulting from hierarchical self-assembly have had a significant influence on the development of cutting-edge functional materials.¹³² Low molecular weight compounds self-assemble into supramolecular physical gels by non-covalent interactions such as hydrogen bonding, van der Waals, dipole-dipole, charge-transfer, aromatic-aromatic, and coordination.¹³³ The self-assembly of various types of amphiphiles and hydrophilic compounds (e.g., proteins and peptides, sugars, sphorolipids, and steroids), have been reported elsewhere and are therefore not part of this review.^{134–136} Instead, we focus on the formation of structured gels from lipophilic bark extractives.

Organic compounds with low molecular weight (< 3000 Da) can self-assemble in solvents, leading to the creation of three-dimensional entangled networks with elongated fibrillar structures (suprastructures). Once the solvent molecules are trapped inside the network, a flexible solid is obtained. The molecular structure, fiber shape, and junction zones are influenced by molecule-solvent interactions. Moreover, the gelled network is significantly influenced by the sizes of the building blocks, solvation, and the competitive bonding relative to the solvent.¹³⁷

As discussed earlier, terpenes and terpenoids are a significant family of secondary plant metabolites that have a variety of uses. They show tremendous chemical diversity and facilitate the design of structurally diverse building components for constructing supramolecular structures. A report of a terpenoid-based suprastructure, dating back to 2005 (Bag et al.) reported the first isolation of a derivative of arjunolic acid-formed gel in an organic solvent. Since then, the studies on terpenoid self-assembly in organic solvents have been expanded to more than sixty molecules, including asiatic acid,¹³⁸ betulinic acid,¹³⁹ β -glycyrrhetic acid,¹⁴⁰ oleanolic acid,¹⁴¹ glycyrrhetic acid,¹⁴² betulin,¹⁴³ ursolic acid,¹⁴⁴ crotoembraneic acid,¹⁴⁵ α -onocerin,¹⁴⁶ corosolic acid,¹⁴⁷ maslinic acid,¹⁴⁸ erythrodil,¹⁴⁹ andrographolide,¹⁵⁰ lupeol,¹⁵¹ uvaol,¹⁵² and maslinic acid.¹⁵³ Tubules, strands, tapes, chiral ribbons, flowers, vesicles, and other aggregates with high aspect ratio are possible forms of the resulting suprastructures (Figure 4). The stiffness of the microstructure within the gel matrices is related to the junction zones and branching between these supraparticle strands. The junction zones act as a “glue” that joins 1D fibers to form 3D networks that permeate the whole system. On a macroscopic scale, they capture the liquid component through capillary forces and surface tension.

The ability of small molecules to self-assemble into supraparticles largely depends on both the chemical structure of the compound and the involved solvent(s).¹⁵⁵ The self-assembly motif of the suprastructure can be adjusted by employing solvents that modulate the dissolution characteristics. Although the solvent-dependent formation of suprastructures has been reported, the detailed mechanisms involved remain subjects for elucidation. The ability to form supraparticles appears to be related to thermodynamic dissolution parameters.¹⁵⁶ Terpenoids and other extractive molecules with similar skeletons, including alkaloids and steroids, have been explored as building blocks for self-assembly under specific solvent conditions.¹⁵⁷ Identifying the single crystal configuration of these natural small molecule-derived structures is very challenging due to the differences in the type and strength of the involved interactions, i.e., the molecule-molecule relationships and the solvent-molecule specific (e.g., H-bonding) and non-specific intermolecular interactions.¹⁵⁸ Amphiphiles (possessing both hydrophilic and lipophilic moieties) provide a model for understanding how to control solvophobic and solvophilic effects in a system.¹⁵⁸ For instance, steric repulsion between molecules can be decreased by promoting π - π stacking of aromatic rings. A series of triterpenoid-based compounds have been synthesized by attaching a chromophore unit to a triterpenoid, including pyridinium-tailored oleanolate amphiphile (1-[2-(methyl oleanolate)-2-oxoethyl] pyridinium bromide),¹⁵⁹ π -chromophore-contained glycyrrhetic acid amphiphile (1-[2-(methyl glycyrrhetate)-2-oxoethyl]pyridinium bromide),¹⁶⁰ N-azobenzeneimide-pimaric carboxylates,¹⁶¹ and dehydroabietylamine-tailored symmetric benzamides (Figure 5A).¹⁶²

A way to tune the amphiphilicity of terpenes and terpenoids and reduce their inherent hydrophobicity is to chemically modify their cyclic terpene skeleton. For instance, rosins have been chemically modified to produce a wide variety of derivatives, particularly amphiphilic molecules. The latter are easily generated from rosin by introducing hydrophilic groups onto the lipophilic diterpene skeleton. This can be done by amination (primary, secondary, tertiary, and quaternary amine),^{163,164} sulfonation,¹⁶⁵ or phosphorylation. Another way is ether- or esterification with a conventional surfactant or lignosulfonate.^{166,167} By selectively adjusting their amphiphilicity, the assembled morphology of triterpenoid derivatives could be varied from regular rod-like fibers¹⁶⁸ or fiber networks to hexagonal, mainly rectangular, vesicles (Figure 5B),¹⁶⁹ filamentous clusters (Figure 5C),¹⁶² nano/micro twists,¹⁶⁰ and other micellar structures.¹⁶¹ These developments are useful in fabricating supramolecular macroscopic structures and in introducing new possibilities in high-performance materials from simple, low-cost bark extractives.

Assembly at interfaces

In the assembly of bark extractives, the resulting structure and performance of the material greatly depend on the nature of the interface (i.e., air and liquid, liquid and liquid, or liquid and solid). In general, liquid-liquid interfaces are suitable scaffolds for the organization of nanometer-sized objects from molecules comprising hydrophilic and lipophilic moieties (i.e., amphiphiles).¹⁷⁰ For amphiphiles, interface-driven self-assembly at the oil-water interface provides structuring opportunities. Surface localization drives the free interfacial energy, which causes the amphiphiles to adsorb and reorganize at the liquid-liquid interface.¹⁷¹ In this situation, the fluid interface serves as an ideal substrate that facilitates close packing and orienting of the amphiphilic molecules.¹⁷² The latter has the ability to stabilize multiphase systems (e.g., emulsions and foams) by adsorbing at aqueous surfaces due to their surface activity.

Saponin glycosides are amphiphilic and show excellent surface activity; thus, they can be used to stabilize multiphase systems by adsorption at interfaces (e.g., emulsion and foams).¹²⁸ In such applications, micelle formation is influenced by the chemical structure of the amphiphile, the pH, ionic strength, and temperature of the medium.¹⁷³ *Quillaja* saponins (QS) and glycyrrhizic acid (GA) are two well-studied saponins that serve as models to understand the structure and its influence in the ability to self-assemble and interact with surfaces. GA molecules form lengthy nanofibrils and supramolecular hydrogels in water at high concentrations; their chirality leads to a distinct hierarchy (Figure 6A).¹⁷⁴ The assembled GA nanofibrils can serve as a sole building block for the development of stable emulsions, foams, and complex emulsion foams (Figures 6B–D).¹⁷⁵ Saponin nanofibrils are excellent

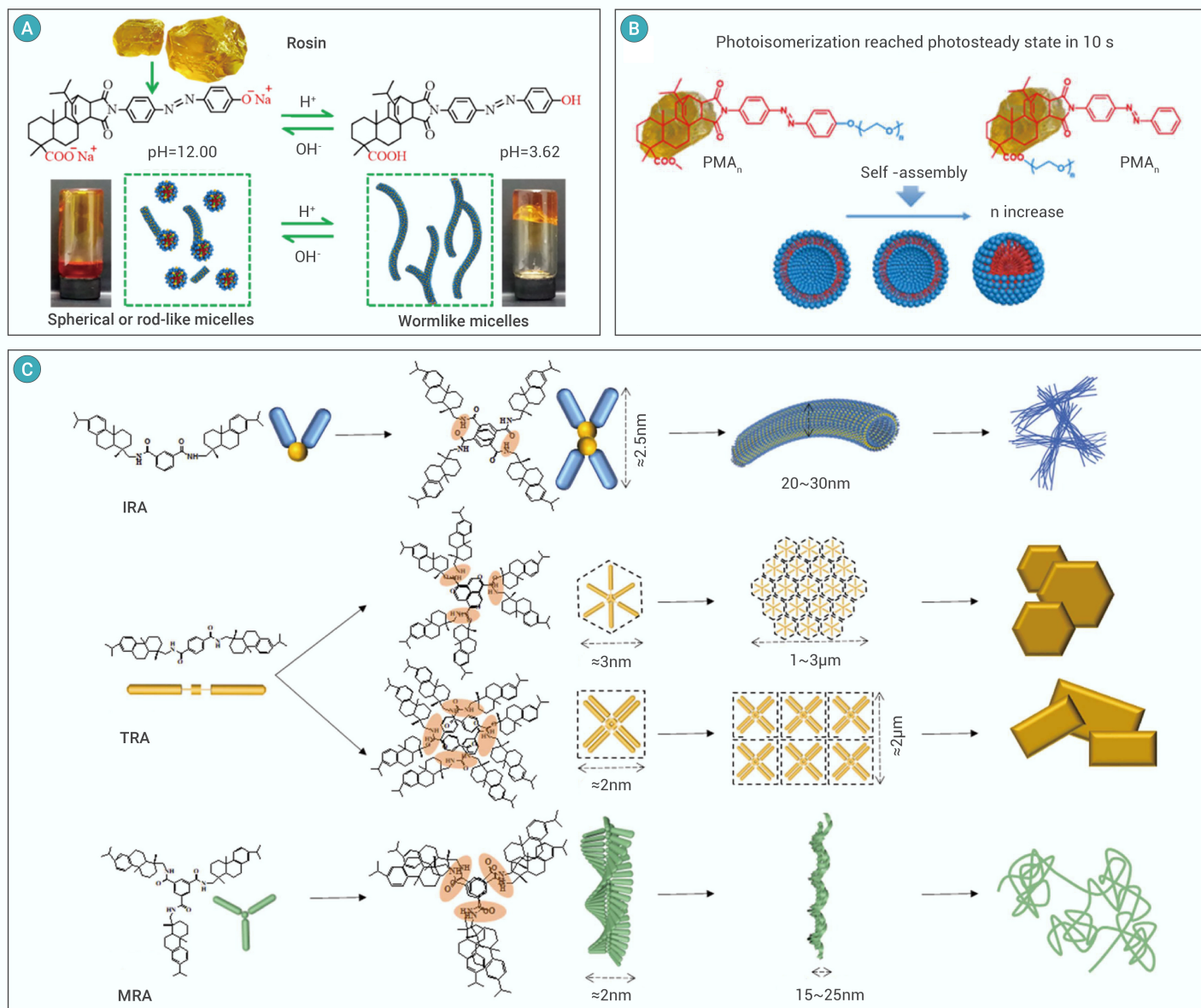


Figure 5. Self-assembled structures formed by amphiphilic terpenoids (A) pH-responsive wormlike micelles formed by an anionic surfactant derived from rosin.¹⁶¹ Copyright 2020, American Chemical Society. (B) Fast and reversible photo responsive self-assembly behavior of rosin-based amphiphilic polymers.¹⁶⁹ Copyright 2022, American Chemical Society. (C) Assembly mechanism of dehydroabietylamine-tailored symmetric benzamide organogels by amide bonds and rigid rings coordinated self-assembly in organic solvents.¹⁶² Copyright 2023, Elsevier.

building blocks for constructing stable emulsion gels due to the combination of gelation and emulsifying capabilities (Figure 6E). In the outer water phase of water–oil–water emulsions, GA fibrils have great potential as a bifunctional agent (e.g., texture modifiers and emulsifiers). For instance, they can be utilized to develop a gelled multiple emulsion system characterized by exceptional stability.¹⁷⁶ Inspired by the structure of GA, we designed an all-biobased type of nanoparticle surfactant from BE (hydrophobic unit) and nanochitin (hydrophilic unit) interfacial assemblies. BE and nanochitin spontaneously stabilized an organic phase in a continuous hydrogel phase and eventually formed an emulsion gel.¹⁷⁷

In terms of their interfacial properties, *Quillaja* saponin (QS) molecules form highly viscoelastic adsorbed layers, particularly at the air–water interface, via multiple hydrogen bonds between the neighboring saponin sugar groups. In contrast, GA molecules do not form such a viscoelastic layer, likely due to their extremely low solubility in water (Figure 7A). QS assembly at liquid interfaces (air–water and oil–water, Figure 7B)¹¹⁴ follows given adsorption kinetics,^{182,183} transitions at the three phases,¹⁸⁴ and rheology (Figure 7C).^{185,186} The implications of molecular structure, pH,¹⁸⁷ and the nature of the hydrophobic oil phase on QS interfacial characteristics have been studied. Interactions

with other components, such as food proteins,^{188–190} polysaccharides,^{191,192} and membrane lipids,¹⁹³ in bulk solutions, and at the air–water/oil–water interfaces have been explored as well. Relevant QS applications, including emulsions (e.g., nanoemulsions,^{194,195} multiple emulsions,^{196,197} emulsion gels,¹⁹⁸ foams,¹⁸⁹ and carriers) have been investigated (Figures 7D–E).^{199–201}

Assembly in biological environments

Polyphenols, particularly, tannins, represent an important class of hydrophilic bark extractives that undergo self-assembly to form a wide range of materials, including nanoparticles, gels, hollow structures, and nanofilms.²⁰⁴ The presence of multiple amphiphilic catechols or pyrogallol groups in polyphenols enables synergistic noncovalent interactions (i.e., metal–phenolic coordination, hydrogen bonding, hydrophobic, and electrostatic interactions). They drive the formation of a wide range of assemblies and suprastructures.⁶⁹ The advanced biological functions of polyphenols, such as biocompatibility, antioxidant, free radical scavenging, UV absorption, and protein-binding interactions, render the assembled structures formed by polyphenols as promising high-valued nanomaterials for application in biomedicine, energy, and environmental technologies.^{60,205,206}

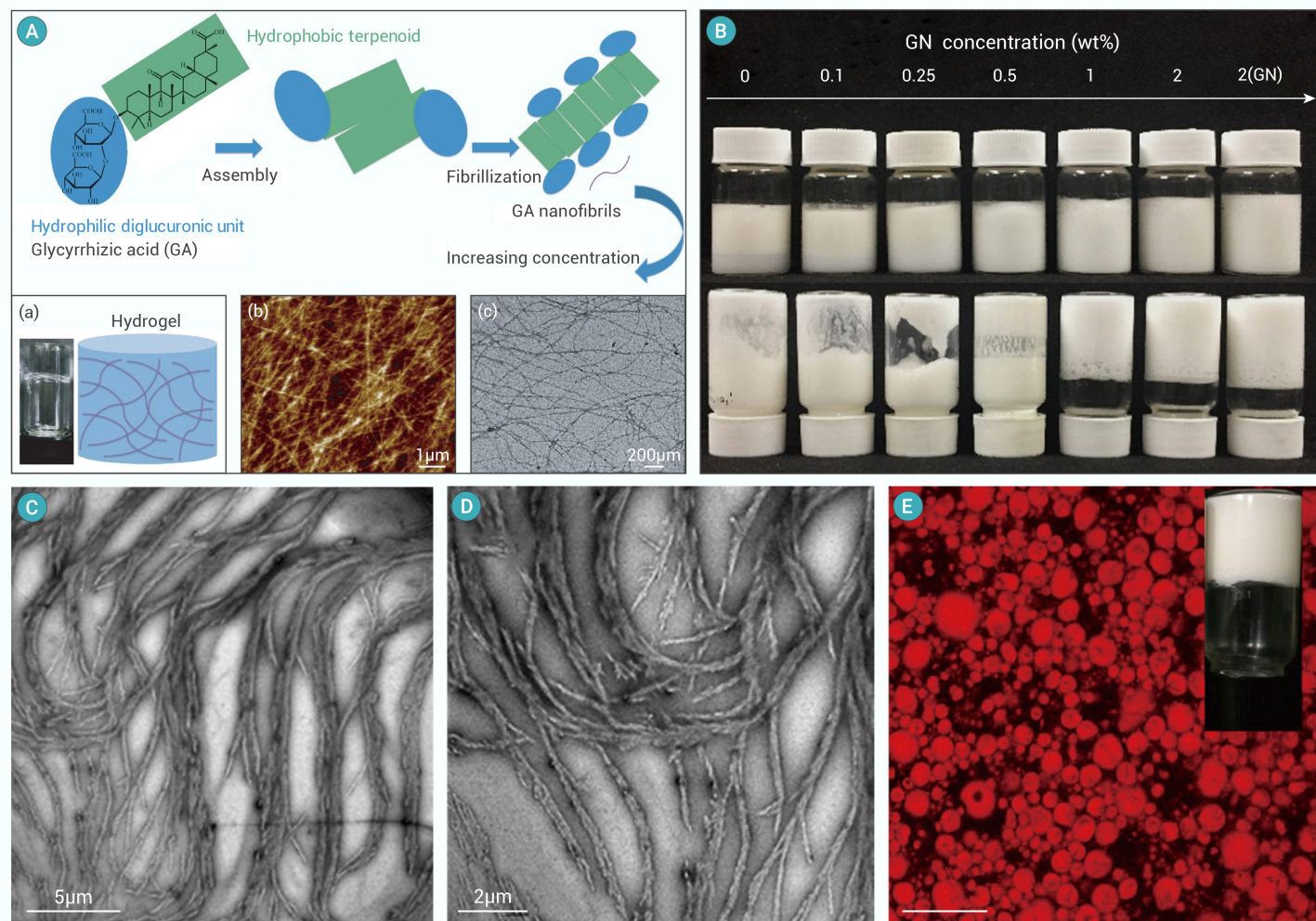


Figure 6. Self-assembly of glycyrrhizic acid (A) Schematic illustration of the self-assembly behavior of glycyrrhizic acid (GA) molecules in water. Reproduced with permissions.¹⁷⁸ Copyright 2022, Elsevier. (B) Photographs of emulsion gels (30 wt% sunflower oil) prepared by mixed systems, namely, 0.3 wt% SPNPs with different GA concentrations (0–2 wt%).¹⁷⁹ Copyright 2020, American Chemical Society. (C) TEM images of a GA aqueous solution (0.25 wt%) (D). SEM image of a GA hydrogel (3 wt%).¹⁸⁰ Copyright 2022, Elsevier. (E) Confocal laser scanning microscopy images of emulsion gels containing 50 wt% sunflower oil prepared at a constant GA nanofibril concentration (4 wt%) and different concentrations of sterols in 30 wt% oil. Oil droplets are shown in red in the images. Scale bar = 20 μm.¹⁸¹ Copyright 2021, Elsevier.

Polyphenols form nanocoatings on most surfaces to allow universal adherence and functionalization of living cell surfaces, which leads to enhanced cell performance facing external stimulation. For instance, a series of mammal cells (i.e., cancer cells and red blood cells) were wrapped with tannic acid-Fe(III) complexes to improve cellular viability under UV-C irradiation and toxicant treatment.^{207,208} The coordination between tannic acid and Fe³⁺ ions generated multiple layers of nanocoatings, which performed as superior cytoprotective agent on the cell surfaces given their adhesive properties. The disassembly under mild conditions of the nanocoatings allowed fast recovery of cell proliferation (for cancer cells) and no scarification on the original functions (for red blood cells). This approach of single cell-based modification has been expanded to protect bacterial cells under extreme antibiotic conditions.⁷⁶ The tannic acid-Fe(III) layer can trap antibiotic molecules, prevent internalization, and maintain bacteria alive (Figure 8A). This strategy provides an efficient, feasible, and non-covalent approach for inflammatory bowel diseases.

Recent developments enabled polyphenol-based assemblies as effective carriers for diverse payloads on cell surfaces to achieve functions in delivery and therapy, termed “Cellnex” (Figure 8B).⁷⁹ Nanocarriers were formed by the complexation of polyphenols and different counterparts, including metal ions, proteins, DNA, polysaccharides, and polymers. Following simple mixing with living cells, a hybrid structure was constructed by the assembled nanoparticles on the cell surfaces. Yeast cells were assembled with inorganic nanoparticles to realize the efficient production of fine chemicals under light irradiation.²⁰⁹ The polyphenols acted as a “glue” to stick the inorganic photo-

sensitizer to the cell surfaces, further allowing the photoelectron transfer in yeast for shikimic acid production. The strategy was further applied to a wide range of immune cells (e.g., T-cells, monocytes, macrophages, dendritic cells, and natural killer cells) to produce a modified surface with therapeutic agents to achieve synergistic effects for cell-based treatments. Finally, a responsive polymeric nanosponge containing drug molecules was loaded to the surface of macrophages to achieve automated homing by polyphenol-based surface modification (Figure 8C).⁷⁸

Polyphenols can be modified to produce amphiphiles, which assemble into fluorescent nanoparticles for fast labeling on cell surfaces (Figure 8D).⁸⁰ The multiple molecular interactions, especially H-bonding and hydrophobic interactions of catechol or galloyl groups, promote adherence to biological surfaces under physiological conditions. This demonstrates the great potential of bark extracts for advanced biological applications. The building blocks capable of forming supramolecular assemblies from bark extracts are summarized in Table 3.

SUMMARY AND PERSPECTIVES

The forests are main resources containing the largest mass of living organisms on Earth. Trees provide raw materials for various applications, including wood and their products for construction, pulp & paper, and biofuels. The perceived low-value components of trees, such as bark, branches, tree tops, and reaction wood, are generally considered as wastes due to the variability in shape, properties, and composition. Bark alone is produced in a massive quantity, with half of burned, landfilled, or left to decay. Although the

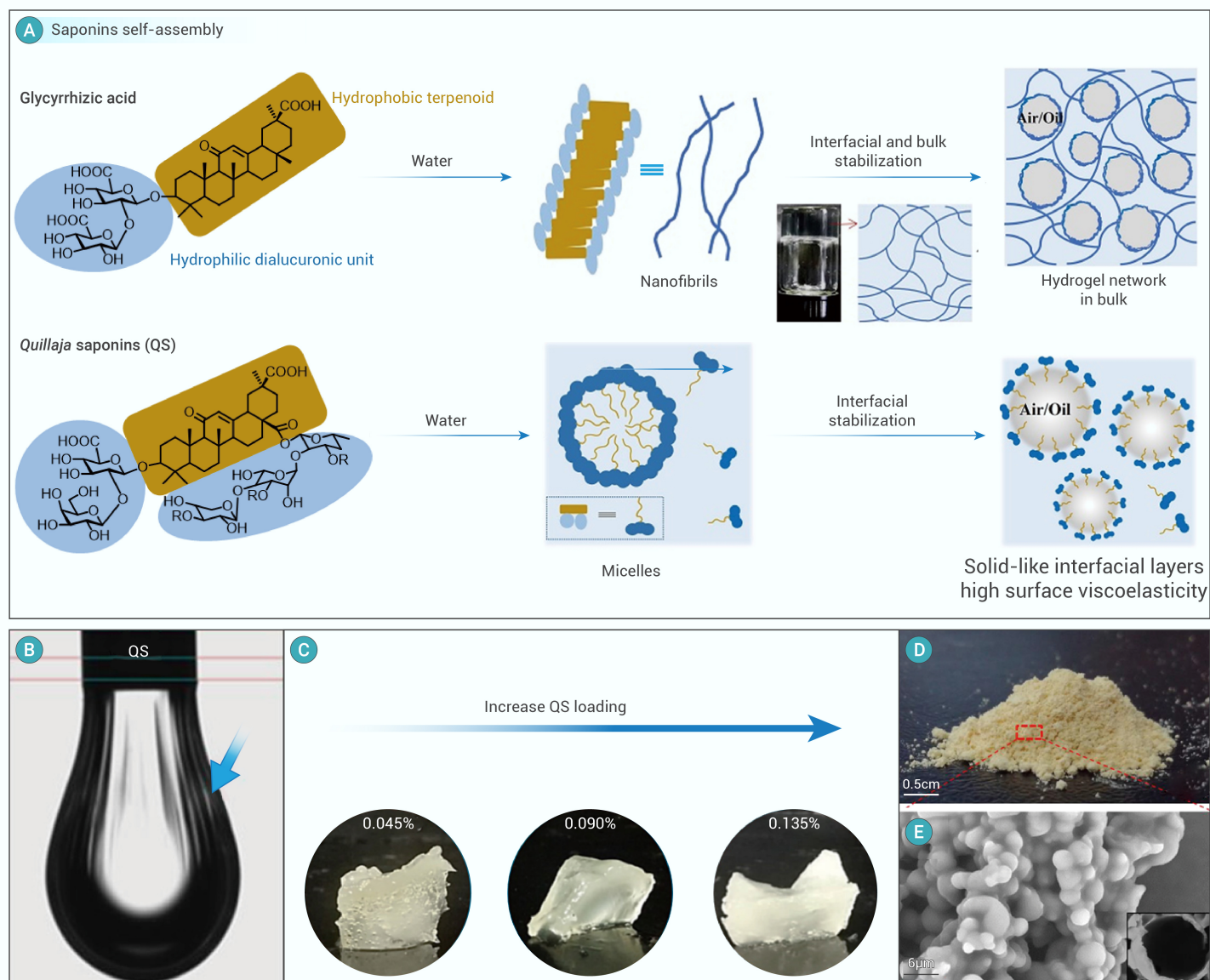


Figure 7. Assembly of small molecular amphiphiles (A) Illustration of quillaja saponin (QS) and glycyrrhizic acid (GA) structural features and their subsequent self-assembly and interfacial properties.²⁰² Copyright 2021, MDPI. (B) Dynamic interfacial tension and droplet surface gelling behavior of a water droplet containing 0.15 mg/g of QS. (C) The influence of the concentration of QS on the appearance of oleogels.²⁰³ Copyright 2023, Elsevier. (D) Appearance of QS-stabilized emulsions after spray drying at 10 wt%, orange oil in original emulsion templates, and (E) SEM images of powder produced by spray drying.¹⁹⁷ Copyright 2019, American Chemical Society.

combustion of bark for energy purposes is common, they have a low calorific value and is high in ash content. Yet, bark is one of the most promising resources for renewable chemicals and biobased materials, with a huge potential for economic expansion. In this review, we highlighted the rich diversity of chemicals within bark and highlighted their potential application in new functional materials.

Today's "extract-produce-use-dump" mentality is inefficient from the standpoint of material usage. In contrast, the concept of circular economy pursues a sustainable economy without sacrificing the environment and its resources. This model prioritizes waste management by reinforcing reuse, reduction, recycling, and ethical manufacturing. In this way, natural resources are used more efficiently, and emissions are reduced. Waste from industry, therefore, can be useful in another to create wealth (Figure 9). Lignocellulosic biorefineries have been expanded, along with the advancement of industrial biotechnology. However, it is crucial to consider the capital and operational costs necessary for economic viability. Moreover, important considerations include the volatility in biomass prices, availability, and quality; costs in storage and transportation; and loss in material or quality during the typical seasonal storage. Industrial sites, particularly pulp and paper mills, along with first-generation biorefineries, have been increasingly adopting lignocellulosic

materials. Nevertheless, many wood industries generally prefer feedstocks with low extractive contents due to the related problems of mass loss, processing difficulties, and lower (mechanical) performances of their products. Establishing extraction facilities could address these concerns while opening up new markets and revenue streams for these industries. The integration of biobased chemicals and materials into the existing technosphere remains one of the biggest challenges of the 21st century.

Compared to lignocellulosic components, the chemistry and material science of bark extracts are largely underexplored and underutilized. One of the main missions for bark biomass and other renewable materials is to replace synthetic, petroleum-based materials. However, we face great challenges for the scale-up of bark extraction and the production of the corresponding materials and chemicals. Our inadequate understanding of bark chemistry and the challenges imposed by its inherent structural variability limit efforts in developing chemicals and associated bioproducts. This review offers a perspective to draw interest toward bark extracts for future applications. Attention should be placed on aspects such as:

- The heterogeneous nature of bark biomass requires extraction pathways that should focus on debarking technologies and fractionation of extractive-rich components. Holistic concepts are needed to open new appli-

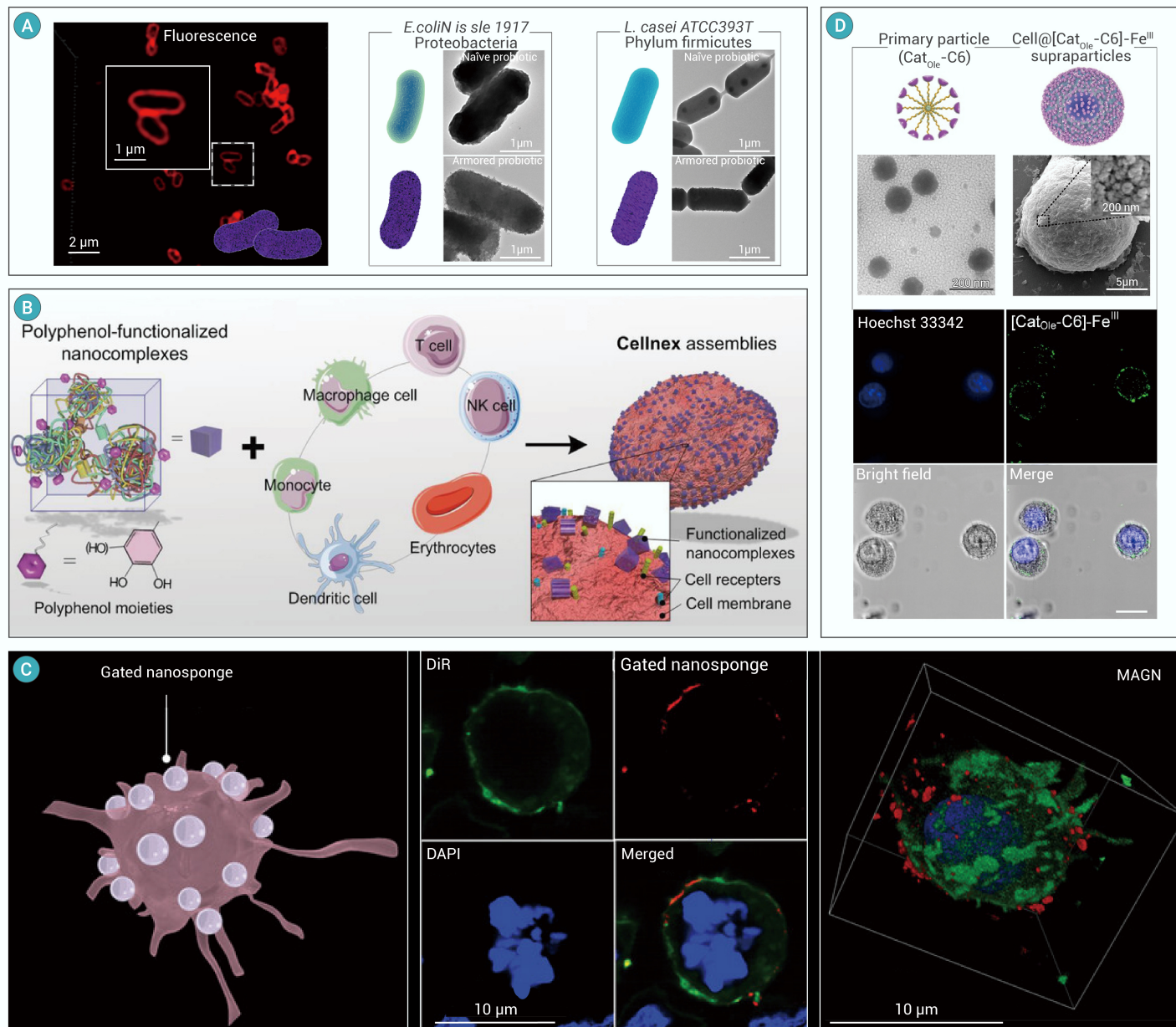


Figure 8. Polyphenol-based assemblies at cellular surfaces (A) Confocal and TEM images showing polyphenol-based nanocoatings.⁷⁶ Copyright 2022, Springer Nature. (B) Schematic illustration of polyphenol-based single-cell surface functionalization on diverse cells.⁷⁹ Copyright 2020, John Wiley & Sons. (C) Polyphenol-mediated polymeric nanosponge assembled on the surface of a cell.⁷⁸ Copyright 2023, John Wiley & Sons. (D) Fast cell labeling of chemically-modified polyphenol-derived assemblies.⁸⁰ Copyright 2023, John Wiley & Sons.

cations for product streams and to ensure economic viability. Steam explosion, solvent extraction, and mechanical processing should be refined to maximize the recovery of valuable extractives while minimizing waste and energy consumption.

- Innovative technologies that adapt to the variability of bark composition. In turn, this will open the way to broader applications, such as discovering new compounds for drugs, nanoparticles, and functional additives, where the involvement of novel catalytic and bio-catalytic conversions could be particularly transformative.

- Industrial adoption needs to be realized. The main challenge lies in finding an efficient way to separate the vast mixture of constituents from bark at a competitive cost and with the required level of purity. Advanced separation technologies, such as membrane filtration, chromatography, and crystallization, are suggested to promote yield and purity of the bark-derived extraction. Alternatively, the incorporation of bark extractives into existing industrial operations, notably within the pulp and paper as well as biorefinery sectors, has the potential to create fresh revenue channels. This,

in turn, could stimulate the formulation of protocols aimed at replacing traditional raw materials with alternatives derived from bark.

- Our current knowledge is lacking, and many questions need to be addressed concerning the chemical structure of bark extractives and their physical properties, self-assembly, and behavior as far as material synthesis. Research is needed to establish reliable structure-property relationships and to optimize fractionation schemes. This is especially important considering the inherent structural diversity in chemical composition of bark extractives.

- Bark valorization will ultimately use a sustainable approach that simultaneously fulfills market demands, encompassing the entire value chain from raw material sourcing to product and market development. Policy incentives and comprehensive economic analyses are needed to promote the adoption of bark biomass for functional materials and foster partnerships between academia and industry. As the scientific community advances its understanding of bark chemistry and develops methods to harness its full potential, bark can transition from a low-value byproduct to a high-value resource in the quest for sustainability.

Table 3. Summary of natural building blocks found in bark extractives that lead to supramolecular assemblies

Building blocks	Extractive type	Assembly scale	Isolation	Suprastructure	Applications (reference)
Arjunolic acid, asiatic acid, betulinic acid	Terpenes	Molecule	Solvent	1D-helical structure, fibrillar networks	¹³⁸⁻¹⁴⁰
β -glycyrrhetic acid	Terpenes	Molecule	Solvent	fibrillar networks	Template for nanoparticle growth ¹⁴¹
Glycyrrhetic acid, crotocembranic acid, α -onocerin, corosolic acid, maslinic acid, andrographolide, uvaol,	Terpenes	Molecule	Solvent /binary solvents	Vesicles, fibrillar network, vesicles, flower-like, garland, and petal-like architectures	Drug delivery ^{141,145-147,149,152}
Betulin, erythrodiol	Terpenes	Molecule	Solvent	Flowers, hedgehog, and grass-like architectures	Water treatment ^{143,149} Superhydrophobic coating ¹⁵⁴
Lupeol	Terpenes	Molecule	Solvent /binary solvents	Nano-fiber and sheets	Water treatment and drug delivery ¹⁵¹
Maslinic acid	Terpenes	Molecule	Binary solvents	Vesicles	Anti-inflammatory ¹⁵³
1-[2-(methyl oleanolate)-2-oxoethyl]pyridinium bromide	Terpenes derivatives	Molecule	Binary solvents	Rigid microrods and flexible nanofibers	¹⁵⁹
1-[2-(methyl glycyrrhetate)-2-oxoethyl]pyridinium bromide	Terpenes derivatives	Molecule	Binary solvents	Fibrils, helical fibers	Scaffolds for supramolecular helical structures ¹⁶⁰
Sodium N-azobenzenemaleimidepimaric carboxylate	Terpenes derivatives	Molecule	pH-response	Wormlike, spherical micelles	Surfactant ¹⁶¹
Isophthaloyl dehydroabietamide, Terephthaloyl dehydroabietamide and M-benzoyl dehydroabietylamine	Terpenes derivatives	Molecule	Solvents	Fibers, rods, hexagonal sheet, helical filaments, lamellar structure.	¹⁶²
N-[5,5'-acrylpimaryl-[1,3,4]thiadiazol-2-yl]-diamide, N-[5-dehydroabietyl-[1,3,4]thiadiazol-2-yl]-amide	Terpenes derivatives	Molecule	-	-	Insecticides ¹⁶³
Maleic rosin-based ester tertiary amine	Terpenes derivatives	Molecule	pH-response	Worm-like, spherical micelles	Emulsifiers ¹⁶⁴
Lignosulfonates	Lignin derivatives	Molecule	-	-	¹⁶⁵
Anionic rosin-based phosphate diester sodium	Terpenes derivatives	Molecule	Binary solvents	Spherical micelles, vesicles	Emulsifier ¹⁶⁶
Rosin-modified lignosulfonates	Terpenes and lignin derivatives	Molecule	Binary solvents	-	Emulsifier ¹⁶⁷
2,3-dihydroxyimino-oleanic acid	Terpenes derivatives	Molecule	Solvents	Helical or twisted fibers	Biomedical engineering ¹⁶⁸
Rosin-based azobenzene amphiphiles	Terpenes derivatives	Molecule	UV irradiation	Vesicles and spherical micelles, sheets	Nanocarriers ¹⁶⁹
Glycyrrhizic acid	Saponin glycosides	Interface	Chemical structure, the pH, ionic strength, and temperature	Nanofibrils	Emulsions, foams, complex emulsion foams, ^{174,175,179-181} and texture modifiers ¹⁷⁸
Quillaja saponins	Saponin glycosides	Interface	Molecular structure, pH, and hydrophobic oil phase.	Micelles, interactions with other components, proteins, ^{133,188,190} polysaccharides, ¹⁹² and membrane lipids, ¹⁹³	Emulsions, ¹⁹⁴⁻¹⁹⁷ emulsion gels, ¹⁹⁸ foams, ¹⁸⁹ and carriers ¹⁹⁹⁻²⁰¹
Tannic acid	Polyphenol	Cell	Fe ³⁺ , metal organic framework, complexation.	Nanocoatings	Cytoprotective agent ^{207,208}
Tannic acid functionalized <i>S. cerevisiae</i> -indium phosphide	Polyphenol derivatives	Cell	Metal ions, proteins, DNA, polysaccharides, and polymers.	Nanocarriers	Cell-based treatments ^{76,78,209}
N-(3,4-dihydroxyphenethyl)isonicotinamide, (E)-N-(3,4-dihydroxyphenethyl)-4-(phenyldiazenyl)benzamide, (Z)-N-[2-(3,4-dihydroxyphenyl)ethyl]-9-octadecenamide	Polyphenol derivatives	Cell	Coordination, host-guest, and hydrophobic interaction.	Hollow supraparticles	Fast labeling ⁷⁴

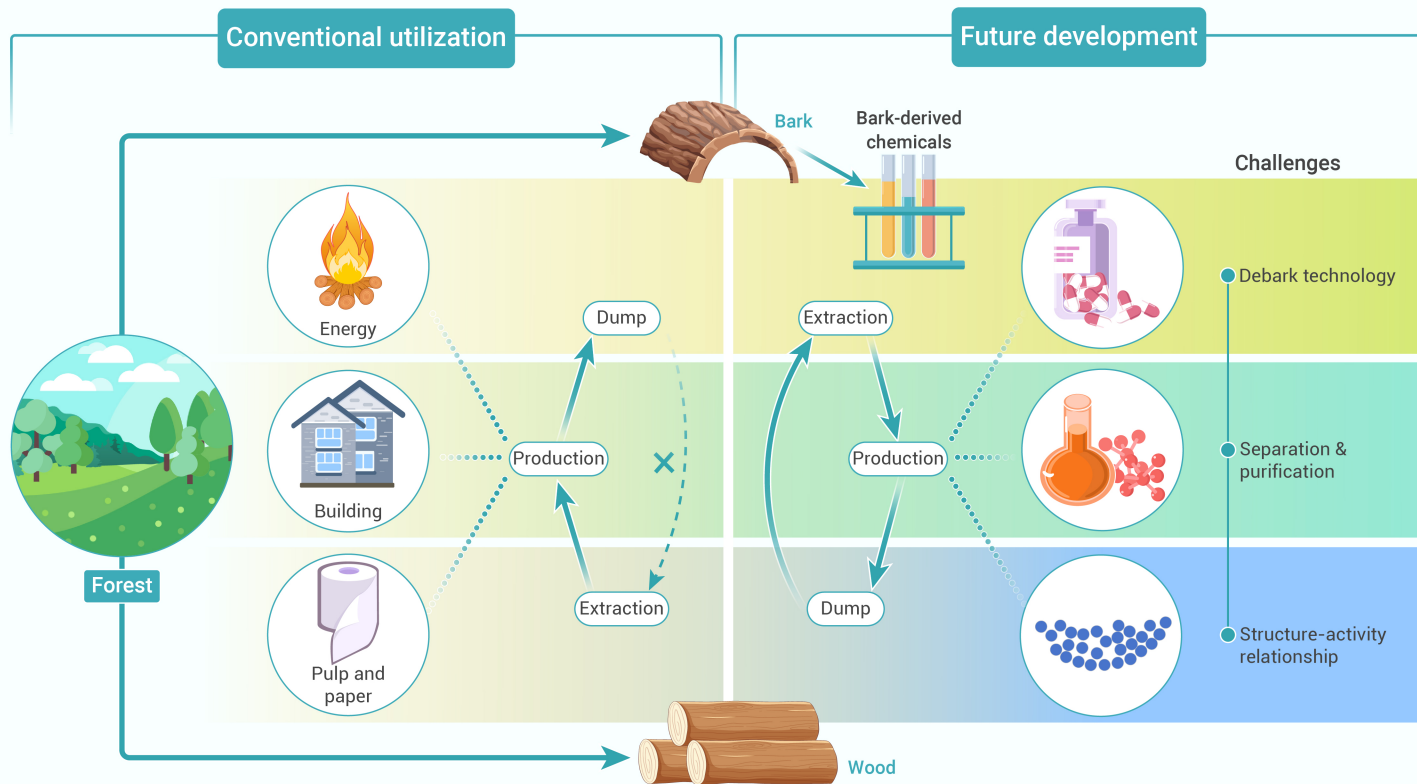


Figure 9. The valorization of bark-derived materials Conventional utilization of the forest resource should consider full use of the resource and avoid “extract-produce-use-dump”. Bark-derived chemicals provide new opportunities for functional materials in areas such as biomedicine, nanoparticles, and catalysis. Challenges exist for technology upgrading as far as extraction, purification, and production. Fundamental studies on molecular structures and properties will assist the understanding of biomass as a source of functional materials.

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AUTHOR CONTRIBUTIONS

X.N., Y.H., O.M., G.F.M.B., J.G., and O.J.R., conceived, organized, and revised the manuscript, and wrote the abstract, introduction, scope of this review, summary, and perspectives. O.M., and X.N., wrote the section about the bark anatomy. X.N., G.F.M.B., and Y.H. wrote the section about classes of bark extractives. X.N. and O.M. wrote a section about bark extraction. X.N., Y.H., J.G., and O.J.R. wrote the section about the supramolecular assembly of bark extractives. Y.H., Q.X., and Y.W. organized and revised references. All authors discussed and approved the final manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.