

Suberin: A promising renewable resource for novel macromolecular materials

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Abstract

Suberin, an aliphatic-aromatic cross-linked natural polymer present in the outer tissues of numerous vegetable species, is discussed in terms of (i) its occurrence, particularly where it dominates the bark composition of some trees, (ii) its macromolecular structure and positioning within the cell wall, (iii) its controlled chemical splicing (depolymerization through ester cleavage), (iv) the qualitative and quantitative composition of the ensuing monomeric fragments, and (v) the exploitation of this mixture of monomers in macromolecular science, both as a possible functional additive and as a source of novel materials. The presence of terminal carboxylic and hydroxy groups and of side hydroxy and epoxy moieties on the long chains of suberin “monomers” makes them particularly suited as building blocks for polymers with original architectures and interesting properties.

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1. Introduction

Suberin is a natural aliphatic–aromatic cross-linked polyester, almost ubiquitous in the vegetable realm, albeit in very variable proportions. It is mostly found in the cell walls of normal and wounded external tissues of aerial and/or subterranean parts of plants where it plays the fundamental role of a protective barrier between the organism and its environment [1–4]. In higher plants, suberin, organized in a characteristic lamellar structure, is one of the main components of the outer bark cell walls.

As in the case of lignin, there is no unique chemical “structure” of suberin (as opposed, e.g. to cellulose or natural rubber), since its constitutive moieties can vary appreciably both in their specific nature and relative abundance within the macromolecular network.

The main components of the aliphatic domains of suberin are ω -hydroxyfatty acids, α -, ω -dicarboxylic acids and homologous mid-chain di-hydroxy or epoxy derivatives, whereas the aromatic domains are dominated by variously substituted phenolic moieties [1–11]. Although the suberin “monomer unit” composition is relatively well known for many species, its detailed macromolecular structure (i.e. the precise assembly of the units in the network) and its association to other cell wall biopolymers are still not completely understood.

The availability of hydroxyfatty acids in nature is concentrated in specific plant seed oils such as *Ricinus communis* (castor oil) or *Lesquerella spp.*, cutin (an extracellular aliphatic polyester covering most of the aerial surfaces of plants) [12] and, particularly, in suberin [13]. On the other hand, epoxy derivatives of fatty acids are present in significant amounts almost exclusively in the suberized cell walls of plant periderms and tree bark tissues [1–3].

The foreseeable depletion of fossil resources and the need for sustainable development are driving both the scientific community and industry to look for alternative (renewable) resources for the production of energy and chemical commodities. Thus, for example, the implementation of the biorefinery concept in agroforest-based activities and the concomitant need to upgrade the by-products generated in the processing of agricultural and forest products, represent a clear response to this situation [14]. These growing concerns have also been the object of thorough appraisals by govern-

ments and international institutions, with the very important result that the funding for basic and applied research in the various relevant areas has been increasing dramatically in the last few years.

Forest-related industries produce huge amounts of barks that represent a potential source of green chemicals [15,16] but which, at present, are mainly burned for energy production. Among bark components the suberin hydroxy and epoxy derivatives of fatty acids, some of which are relatively rare in nature, may constitute interesting chemical precursors for many applications.

This brief review deals with the essential literature on suberin bioavailability, structure and composition, with the specific purpose of emphasizing its potential (modestly exploited thus far) as a precursor to original macromolecular materials, particularly in terms of its long-chain aliphatic units.

2. Natural occurrence

It is practically impossible to estimate the real content of suberin in suberized plant tissues because of its complex macromolecular nature and the structural similarity between the suberin aromatic domains and lignin [1–5]. Typically, the analysis of suberin containing substrates involves a preliminary solvent extraction of low molecular weight components, followed by the chemical scission of the various ester moieties in the network and the isolation as well as the qualitative and quantitative characterization, of the ensuing fragments [2].

The outer bark of higher plants and tuber periderms constitute the major sources of suberin in nature (Table 1). Its content and composition in outer barks is quite variable, depending on the wood species and the isolation method used. In hardwoods of industrial relevance, suberin represents typically between 20% and 50% of the extractive-free bark weight. The industrial transformation of such woods (papermaking, construction, furniture, etc.) generates enormous amounts of outer barks as by-product. Several examples show the relevance of this point. Thus *Betula pendula* (birch), one of the most important industrial hardwood species in Northern European countries, is used predominantly for pulp and paper production. A birch kraft pulp mill, with a typical yearly pulp production of 400,000 ton, generates about 28,000 ton of outer bark, corresponding to a potential annual production of about 8000 ton of suberin “aliphatic monomers” [17]. Yet another

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