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Chitin and Lignin: Natural Ingredients from Waste Materials to Make Innovative and Healthy Products for Humans and Plant

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In a globalized world, plants are continually cut to obtain free land for intensive farming without remembering their important function in the planet ecosystem. They produce oxygen eliminating the carbon dioxide excess, contributing to reduce the pollution thus giving a great support to our health. According to the World Health Organization (WHO), air pollution -both outdoor and indoor- is nowadays "the biggest environmental risk to health carrying responsibility for about one in every nine deaths" (WHO, 2016). Outdoor pollution alone, in fact, kills around 3 million people each year. At this purpose however, it is necessary to remember that indoor emission of nanoparticles (NP) represent 50-80% of human exposure, calculated from 10.000 to 249.000 NP/mL air-while in polluted air NP are from ~10.000 to 50.000 NP/mL (Nohynek, 2011). Thus, there is a strict necessity "to consider air pollution as a global health priority in the sustainable development agenda" (WHO, 2016). Moreover, plants, multicellular organisms, as well as humans have evolved several mechanisms of defense and sensor systems to detect danger and prevent entry of most foreign material (Janeway et al, 2001). The sensors can direct and assist the host defenses by the use of specialized cells that ingest and digest foreign material. This protective non-specific method is called innate immune system, also connected with certain specific molecular patterns recognition associated with invading microbes or tissue damage (Nurnberger et al., 2004). In addition to innate immunity, vertebrates have evolved an adaptive immune system that relies on many antigen receptors, expressed by specialized immune cells. Unlike vertebrates, plants lack mobile defender cells and respond to infection by a two-branched immune system (Jones et al., 2006). The first branch recognizes and responds to all the common microbial molecules, while the second responds to pathogen virulence factors only. However, both plants and mammals have as first-line defense a barrier that, separating and shielding the interior of the body from the surrounding environment, represents the initial obstacle to be overcame from any pathogenic microorganisms. This barrier not only provides a physical separation, but releases also substances with antimicrobial properties. Moreover, when the first-line barrier has been breached, sensor systems are activated to give information to other components of the host defenses. Thus, while mammals activate, for example, the toll-like receptors capable to recognize families of compounds unique to microbes, plants release specialized compounds known as elicitors, signaling molecules able to induce their defense systems (Trouvelot et al., 2014). Examples of common ingredients, used from both plant and mammal as elicitors and defense-related compounds, are chitin and lignin.
In this work, these materials will be briefly reviewed and results of chitin nanofibrils production and usage is reported. Finally, possible usage of combined chitin-lignin nanofibrils in commercial products will be pointed out.

1.State of the art

1.1.Chitin

Chitin is a cationic amino polysaccharide which, isolated prevalently from crustacean waste, is composed of N-acetyl-D-glucosamine and D-glucosamine unit linked with Beta-(1-4) glycosidic bond. Moreover, due to its

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widespread distribution in fungi, crabs, shrimps and insects, this sugar-like polymer, with the same backbone of hyaluronic acid, represents the second-most abundant polysaccharide in nature, after cellulose. However, it is to remember that crustacean waste makes up ~45% by weight of the shellfish with a discard estimated to be more than 20 million tons per year, equivalent of 25% of the total annual fishery's production. Chitin and its derivative chitosan is forecast to reach to 155,5 thousand metric tons by 2022, with a value of US$ 4.2 billion and an increased annual growth rate of 15.4% from 2017-2021 (Buyer, 2017). Moreover, this waste is considered hazardous for their high perishability and pollution effect. When disposed off-shore, it leads to sea eutrophication with a high biochemical oxygen demand, while on land it becomes colonized by pathogens causing environmental and public health concerns (Brunch et al., 2011). Thus the necessity to use chitin and chitosan as much as possible to produce innovative products to be used in medicine, cosmetics and food due also to their healthy character. At this purpose, it is interesting to underline the striking similarities of chitin's immune activity recovered both in animals and plants, where lectins, for example, seem to play the same role as pattern recognition receptors. These proteins, in fact, recognize the pathogen aggression, initiating the stress response in plants as well as in animals and humans (Van Damme et al, 2004; Manikandan and Ramar, 2012).

Lectins are carbohydrate-binding macromolecular structures of non-immune origin, displaying on cell surfaces. They, serving as interaction sites between cells and their environments, play many roles in biological recognition phenomena (Berg et al., 2002). These complex molecules not only interact with the glycan structures on proteins, but recognize and bind carbohydrate chains on glycolipids, proteoglycans, and free sugars also (De Schutter and Van Damme, 2015).

However, the binding of a lectin with a specific carbohydrate-recognition domain (CRD) is mediated through hydrophobic interactions and hydrogen bonds to key hydroxyl groups, both in plants and humans (Drickamer, 1997). In any way CRDs are important for many cellular processes such as cell-cell interactions, self/non-self recognition, the glycoprotein quality control, as well as in the recognition of invaders, as part of a non-specific immune system. They, in fact, are capable to detect a wide variety of pathogenic agents, distinguishing them from the own healthy cells of the organisms. Thus, differently from adaptive immune system, in the innate immune system, pathogenic microorganisms are recognized through the specialized structures, known as pathogen associated molecular patterns (PAMPs). These structures, subsequently are bound to the pattern recognition receptors (PRRs), that will trigger phagocytosis or can activate the complement system, further activating the chemokine and cytokine production together with the adaptive immune response, when necessary (Delaloye and Calandra, 2014). Thus both plants and mammals, evolved the same defense systems by the use of comparable mechanisms with similar regulator modulus such as lectins and PRRs capable to recognize and interact with carbohydrate structure, coming from the invaders microorganisms or derived from the cell wall damage.

As previously reported, chitin is used by both plants and mammals to protect their respective structures from the harsh conditions in their environment and host/antiparasitic/pathogen immune responses. Its biosynthesis and accumulation is regulated and balanced by the enzymatic activity of chitinase (see Figure 1), produced as part of immune response to chitin containing pathogens where they induce chitin fragmentation (Elias et al., 2005; Da Silva et al, 2009). Chitin, in fact, is a PAMP capable to induce pro- and anti-inflammatory responses, depending on its size: large chitin fragments are inert, fragments of 40-70 μm size have a pro-inflammatory activity, while fragments with a small size < 40 um possess an anti-inflammatory effectiveness inducing a release of IL-10, and regulating the intensity and chronicity of local inflammation.

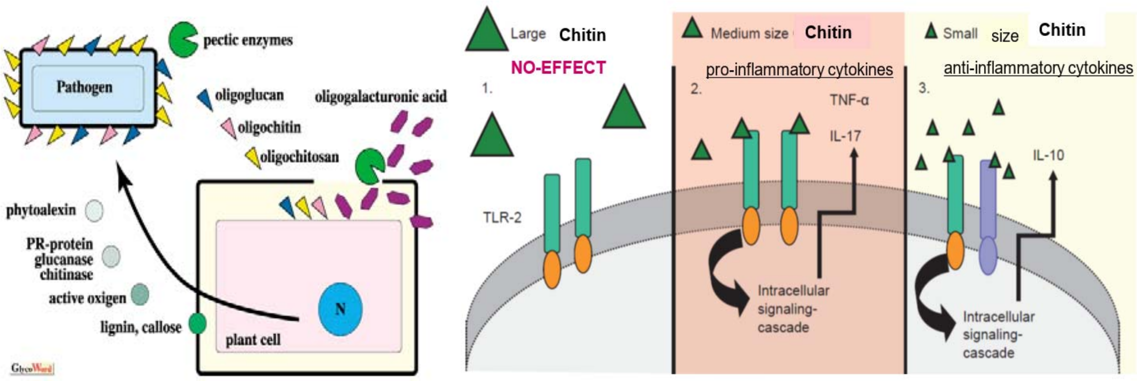

Figure 1: Some chitin mechanisms (left: pathogen response; right: anti-inflammatory properties as a function of dimensions).

Also in plants chitin and its derived compounds seem effective against bacterial, fungi and viruses attack because capable to induce its defenses and stimulate the growth and activity of beneficial microbes. The last activity in stimulating the beneficial plant microbiota in controlling pathogens, promoting plant growth, and remediation soil pollutants seem to be particularly impressive, giving the possibility in the near future to reduce the consume of the toxic chemicals used today (Sharp et al., 2013). It is to remember that in a world of human-made chemicals, pesticides are second only to fertilizer in their extent of use, being dangerous for both the warmers, if improperly used, and the environment. The consume topped 2.4 billion kilograms in 2007 and unfortunately more toxic chemicals are still used causing more harm in the developing countries where basic safety equipment is often lacking. Moreover, despite many studies on wildlife toxicology, ecosystem-wide impacts are poorly understood. Thus the necessity to use natural and biodegradable ingredients human environmentally-friendly, such as chitin and its derivatives. As for humans, these compounds, triggering the plant's own defense mechanisms, represent a pathogen- or microbe-associated molecular pattern (PAMP or MAMP), acting as general elicitors of nonspecific, long-lasting and systemic immunity by binding to a PRR in the plant cell (Iriti and Varoni, 2017). Its use represents, therefore, a novel and promising strategy for a future alternative to conventional toxic agrochemicals.

1.2.Lignin

Lignin, responsible of the strength and rigid structure of the cell walls, is the second most abundant natural polymer of wood and annual plants, making up 10-25% of lignocellulosic biomass. It is a macromolecule highly cross-liked composed of phenolic polymers, which include coniferyl, synaptyl and p-coumaryl alcohols. Lignocellulose is a complex polymer composed of mainly three parts: cellulose, made by D-glucose units, hemicellulose, containing pentose and hesose compounds, and lignin, containing aromatic compounds. It is obtainable by an organosolv pulping-process, prevalently organized to produce paper and ethanol from agricultural waste from bagasse (~90%) and leaves (~75%) with a total free bleaching sequence and a purity level higher than 75% (Fernandez-Rodrigues et al., 2017). The global lignin market was estimated at US$ 732,7 million in 2015 and it is expected to exceed a revenue of US$ 6.2 billion by 2022 with a value in EU of over US$ 1.6 billion and a production from 50 to 280 million tons/year (Hodasova et al., 2015). Due to the different source (jute, hemp, banana pseudo stem, sugarcane bagasse, cotton, wood pulp, etc.) and extraction method used, the lignin's physicochemical behaviour will result different (Watkins et al., 2015). Their by-products, in fact, contain highly branched phenolic macromolecules, the structure of which is depending on botanic origin, harvesting period and extraction process. However, it seems interesting to remember that today the global biomass from the agricultural waste is estimated to be over 150 billion tons/year,10% of which is still utilized, first of all, for producing energy (Morganti, 2015; Morganti, 2016).

Thus, it could be useful the consume of a major quantity of this by-product for producing goods, also because lignocellulose and lignin-derived compounds are obtained from a low cost biomass with a price for lignin that can go from US$ 180 to US$ 500/MT, depending on its purity. Unfortunately, today, this biomass is used prevalently for the production of biofuels, also if lignin hydrolysates contain many different chemical species such as ferulic acid, coumaryc acid, vanillic acid, vanillin and furfural all compounds useful for food, cosmetic and medical use. Only 2% of technical lignins are used, in fact, to produce low added value products, while the remaining are burned to produce energy (Gargulack and Lebovic, 2000; Lora, 2008) while it is underutilized to produce functional molecules. At this purpose, it is interesting to underline the activity of pure lignin that, involved in bacterial cell-to-cell signaling, may be considered a natural antioxidant, antimicrobial, antifungal and photoprotective compound for pharmaceutical, food and cosmetic use (Espinoza-Acosta et al, 2016), as well as for polymeric formulations as plasticizer, hydrophobizing agent, flame retardants, optical modifier or stabilizer (Domenek, 2013) and as antioxidant agent to avoid the polymer's photo- or thermo-oxidation also. However, it is to be remembered the interesting activity pure lignin has shown that, as nontoxic macromolecule, protects also living organisms against damage from different genotoxic compounds.

As consequence it could find potential applications in biomedicine as antimutagenic agent in chemoprevention (Labaj et al., 2003; Kusalova et al., 2003). The hydrolyzed lignin portion of plant biomass, in fact, releases different phenolic acid-derivatives of hydroxybenzoic acid, such as the p-hydroxybenzoic and vanillic acids as well as the hydroxycinamic acid-derivatives, such as p-coumaric and cerulic acid, as previously reported.

All these ingredients have interesting antioxidant properties due to their free radical scavenging capabilities, so that they have been proposed for the neurodegenerative diseases, such as Alzheimer's or Parkinson's diseases, characterized by oxidative stress in brain, or diabetes and cardiovascular diseases caused by an over production of free radicals, as well as for protection from UV-radiations and against several diseases associated with oxidative deterioration (Lee et al., 2012). Recently, about the UV protection it has been shown as lignin seems to be a natural broad-spectrum sun blocker, being active against both UVB and UVA rays so that it could be used to produce innovative antiaging sunscreens (Qian et al., 2015).

2. Results and discussion

As reported, both chitin and lignin can have interesting applications as natural ingredients to be used in substitution of toxic chemicals for the production of innovative and healthy products, skin-friendly and environmentally-friendly. While chitin represents the world's most abundant renewable resource from fishery's industrial by-product, lignin is abundant in plant biomass. Both the ingredients, recovered in great quantity, represent available raw materials at low cost and give us the possibility to preserve the precious natural materials of our planet for the incoming generations, helping to maintain its biodiversity also. At this purpose, by different new methodologies, it is now possible to obtain, characterize and control chitin and lignin in their crystalline and purest form at their nanodimension, so that their effectiveness is notably increased (see Figure 2). These data are in agreement with our results, showing both in vitro and in vivo the interesting antibacterial, antiinflammatory (Morganti et al., 2016), cicatrizing (Morganti et al., 2013) and antiaging effectiveness (Morganti et al., 2014) of chitin nanofibrils (CNs) used alone or in combine with nanolignin (Morganti et al., 2017). CNs, in fact, have a very low size of 240x7x5 and seem useful not only as cicatrizing agent embedded into emulsion or non-woven tissues, but could be also an antiinflammatory agent in asthma, because of its capability to depress the development of adaptive type 2 allergic responses due to its particular chemical/biochemical characteristics of purity and crystallinity (Morganti et al., 2014).
Additionally, our group has patented the technology to complex the electropositive Chitin nanofibril with the electronegative hyaluronan and/or lignin to obtain micro/nanoparticles capable to entrap different active ingredients hydrosoluble or liposoluble (Morganti, 2014). These nanoparticles, made in water solution without the use of toxic organic solvents, have also been obtained in powder by the spray drier methodology. By this new technology it has been possible to embed these activated nanoparticles into: (1) emulsions and gels, obtaining innovative Cosmetics or (2) to entrap them into biodegradable non-woven-tissue used to made Advanced medications or Beauty masks. Thus, for example, by new enzymatic hydrolytic methodologies it is possible the conversion of agricultural wastes into valuable products and, for example, rice and wheat bran, sugarcane, bagasse and corncob became the cheapest and plentifully available carbon sources for the production of industrially important enzyme (Bharathiraja et al., 2017).
Another example is skin photo-aging recovery: sunlight, by the activity UVB and UVA rays is, in fact, the most harmful external component threatening the skin, inducing overlapping biological responses in the epidermal and dermal layers by cumulative damage and increased oxidative stress, evidenced as photoaging (Morganti, 2014), as reported in Figure 2.

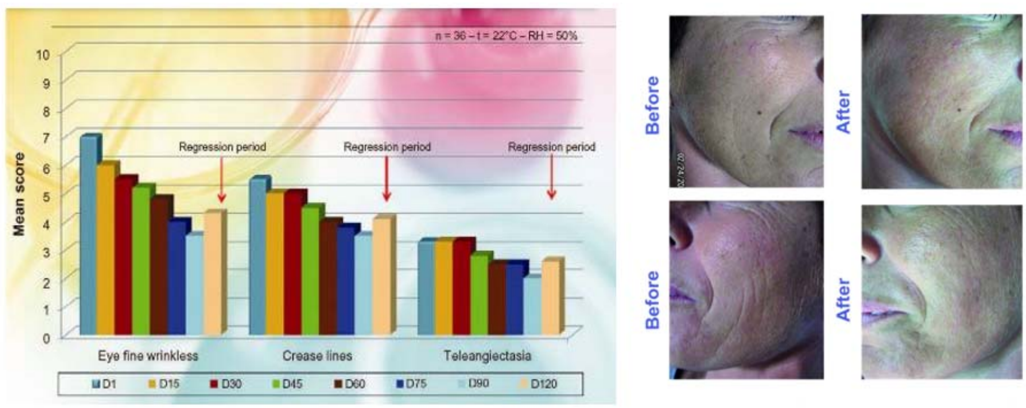

Figure 2: Activity of Nanochitin-based cosmetics on a photoaged skin.

Naturally the characterization and effectiveness of the obtained products is due to the different active ingredients selected and embedded into the respective matrices: emulsions or tissues. At this purpose, it is interesting to underline that the complex CN-LG, for example, acts not only as a carrier, but also as active ingredient. When metabolized from the human Chitotriosidases, in fact, CN is hydrolyzed to obtain glucosamine and acetyl glucosamine, which present in the fluid around joints, is utilized from the human cells to lubricate the bones preserving the formation of osteoporosis also, while LG could be used as potent antioxidant compound to combat the formation of the free radicals in excess. On the other hand, CN and its derivatives alone or complexed with nanolignin, sprayed on the plant leaves or poured directly in the land-roots may be used to stimulate the production of elicitors capable to increase both the plant growth and its natural defenses against the pathogenic aggression of microbes, fungi and yeasts (Jia et al, 2015). Moreover, due the film forming and barrier properties of these biopolymers, they could be used for other applications, such as food containers, soil retention sheeting, agricultural film, waste bags and packaging material in general as well as for automotive development, hazardous waste removal, paper industries and development of new building materials (Sampath et al, 2016).

3. Conclusions

This work is a brief review about new possibilities in the next future, in particular on the use of both chitin and lignin.

Nanochitin exhibited enhanced properties against pathogens, and aids the healing of skin. The production of pure nanochitin starts from the reuse of wastes. In this respect, this reuse permits green process application promoting novel circular economy establishments. On the other hand, pure lignin has similar properties and the use of nanolignin appears to be advantageous.

Combining the two materials appears to be synergic, and opens an interesting research topic to be exploited: together these materials may give rise to superior products, such as innovative ones for human use and natural elicitors for the plants, reducing or eliminating the actual use of toxic chemicals and safeguarding the human health and the environment. All these aspects will be tested in the very next future at our facilities.

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