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Converting cork by-products to ecofriendly cork bioactive ingredients: Novel pharmaceutical and cosmetics applications

C. Carriço[a], H.M. Ribeiro[b], J. Marto[b,*]

[a] Faculty of Pharmacy, Universidade de Lisboa, 1649-003 Lisboa, Portugal
[b] Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Lisbon, Portugal

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ABSTRACT

Quercus suber forests are very important, both economically and ecologically, in countries from the Mediterranean basin. *Quercus suber* bark or cork is obtained from the outer bark of this tree and it is the base of many commercial and profitable products. The industry around cork extraction and transformation leads to the production of considerable amounts of by-products, some of them considered as waste. Cork and its by-products can be an important source of multiple bioactive components, such as phenolic acids, terpenoids and tannins. These natural products present a wide variety of relevant properties, namely antioxidant, anti-inflammatory, antiaging, radical scavenger and depigmenting activity. Thus, cork and its by-products can be reused as promising ingredients in topical products. They may be used in different pharmaceutical and cosmetic applications, such as skin ageing prevention and skin depigmenting activity or as complements in acne treatment and skin inflammatory processes. The heterogeneity of its chemical composition and its extraordinary properties make cork a material with a lot of potential and considerable importance. Reusing and valorising cork by-products in the cosmetic field fits with the current sustainable perspective. In this literature review, the different cork by-products and their bioactive compounds are presented and the promising application of these wastes as cosmetic and pharmaceutical ingredients is analysed.

1. Introduction

Presently, with the growing environmental protection awareness, there is a strong market trend to formulate green and natural products. Sustainability is the new goal, increasingly pursued by professionals and consumers alike (Rastogi et al., 1996; Mestre and Gil, 2011; Gil, 2014; Csorba and Boglea, 2011). The aim is to reduce the environmental impact of products by creating value and rationally using the resources (Mestre and Gil, 2011; Sierra-Pérez et al., 2015). Customers are always demanding better, more sustainable alternatives and are actively seeking a more natural and healthy lifestyle. There is also an increased interest in biological activity of natural products (Rastogi et al., 1996; Batista et al., 2015; Silva et al., 2005; Nohynek et al., 2010). This way, companies are motivated to develop innovative products based on material derived from plants or microorganisms, that is, renewable resources. Moreover, it is suggested that bioactive ingredients from natural sources have greater biocompatibility when compared with to synthetic substances. Consequently, products that are natural or organic are regarded as healthy (Rastogi et al., 1996; Csorba and Boglea, 2011; Batista et al., 2015; Gonçalves et al., 2015; Philippe et al., 2012; Cervellon et al., 2011). The increasing use of natural plant ingredients in cosmetic products raised new safety issues that require novel approaches to their safety evaluation. Pragmatic approaches for quality and safety standards of botanical ingredients are needed (Antignac et al., 2011).

Quercus suber bark, commonly known as cork, is a natural material obtained from the outer bark of the oak tree *Quercus suber* L. (Jové et al., 2011; Gil, 2015). There are around 2 million hectares of cork forest in the western Mediterranean basin. *Q. suber* acts as a buffer to soil erosion, its forests avoid desertification and have a massive social and economic importance in their region. Portugal has 32% of cork forests and is the leading producer and exporter of cork, followed by Spain (Pereira, 2011; Parsons, 1962; González-García et al., 2013). Cork is a renewable and non-toxic material, used since ancient Egypt in multiple applications (Gil, 2014; Silva et al., 2005; Gil, 2015). The bark is obtained from the tree without endangering it, since the stripping process only means that the tree will rebuild a new cork layer (Jové et al., 2011; Gil, 2015).

* Corresponding author at: Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Av. Professor Gama Pinto, 1649-003 Lisboa, Portugal.
E-mail address: jmmarto@ff.ulisboa.pt (J. Marto).

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Cork goes through different transformation processes and can originate several high added-value products for different fields' applications (Silva et al., 2005; Gonçalves et al., 2015). This makes it a very promising area of study (Mestre and Gil, 2011; Gil, 2014). Cork is a light weight material, impermeable to liquids, a good thermal insulator, resistant to microbial activity, with high friction coefficient. Its best-known use is as stoppers for wine bottles, which has the greatest economic impact, despite the severe competition from substitutes and synthetic materials (Parsons, 1962; Pereira et al., 1987; Bejarano et al., 2015).

However, cork products and the waste from its production have a lot of potential and can be used in innovative ways (Parsons, 1962; Cordeiro et al., 1998). During the production processes, by-products of cork are originated. Ideally, all these by-products would be reused or valued in some way, consolidating their sustainable nature. For example, cork powder is nowadays burned to produce energy. New derivative cork products are used in different fields, such as the construction industry, and its diversity of uses is likely to increase due to its multiple by-products and attractive properties. The future holds many possibilities for this multifunctional material (Gil, 2015; Sousa et al., 2006). There is a need and an opportunity to rethink and upgrade the by-products applications and value them further as important sources of oleochemicals (Pereira, 1988). Cosmetic and topical pharmaceutical application could be a new way to reuse *Q. suber* by-products.

Cork consists essentially of suberin, lignin and cellulose, containing also smaller amounts of extractives, fatty acids, terpenes, long chain aliphatic compounds and saccharides. The presence of several extractable phenolic acids was also identified. The interest on these natural phenolic compounds relies on the wide variety of relevant properties shown by this family, namely, their antioxidant, anti-inflammatory, radical scavenger, enzyme inhibitor and antimicrobial properties. Several studies demonstrate that the extracts obtained from *Q. suber* bark have in fact antioxidant, antiaging, anti-inflammatory and anti-fungal properties all from a naturally occurring and sustainable material (Fernandes et al., 2011; Santos et al., 2010). The heterogeneity of chemical composition and its extraordinary properties make cork a material with a lot of potential and considerable importance in several industries, namely in the cosmetic and pharmaceutical field (Santos et al., 2010; Castola et al., 2005; Subhashini et al., 2016; Khennouf et al., 2003).

Cosmetics are a common type of product that people apply on the skin. Cosmetics do not penetrate through the deeper layers of the skin, meaning there is no significant systemic exposure. However, it cannot be excluded that, in some circumstances, its components might cause a reaction (Nohynek et al., 2010). Consequently, before placing a cosmetic product on the market, a safety assessment must be performed, because as stated in the European legislation, cosmetic products must be safe for the consumer. Cosmetic products follow the requirements of the EC Cosmetics Regulation 1223/2009, where product exposure estimates and toxicological evaluation are essential for the safety assessment, as well as skin compatibility studies (EC, 2009). In particular, it is possible to assess the safety of pharmaceutic, cosmetic and other chemical products, using literature data, *in vitro* studies, computational approaches and human tests, since animal testing is no longer permitted by European legislation (SCCS et al., 2010; Domingo et al., 2016; Villaverde et al., 2017). It is expected that the right balance of *in vivo*, *in vitro* and computational toxicology predictions applied as early as possible will help to reduce the number of safety issues. Many computational approaches are available to predict the toxicity induced by a small molecule from its chemical drawing. In silico techniques like knowledge-based expert systems (quantitative) structure activity relationship tools and modeling approaches may therefore help to predict adverse reactions in preclinical studies. In the future the overall hazard and risk assessment strategy will likely include the standardization of analytical approaches, more complete and reliable data collection methods, and a better understanding of toxicity mechanisms (Merlot, 2010; Leist et al., 2012).

Nowadays, there is a huge preoccupation with skin ageing, skin pathologies, such as skin cancer and acne, or any kind of skin imperfections. Some of these concerns are related to sun exposure due to the UV radiation. Its absorption by the skin originates reactive oxygen species (ROS), causing "oxidative damage" to cellular components (Mukherjee et al., 2011; Marto et al., 2016; Matsuoka et al., 2006; Leyden, 1997). UV radiation is carcinogenic and accelerates skin ageing and photodermatoses (Nohynek et al., 2010). Besides UV radiation, other environmental factors, like pollution, also promote skin ageing. These factors lead to the formation of free radicals that polymerize collagen and reduce skin elasticity and skin capacity to hold water, causing wrinkles (Mukherjee et al., 2011; Momtaz and Abdollahi, 2012). Acne vulgaris, also mentioned, affects a great number of people and their quality of life. This pathology involves excessive amounts of sebum and inflammatory lesions that can seriously affect the appearance of the skin (González-García et al., 2013; Gil, 1997).

Taking this into account, it is easy to understand the importance of cosmetic products. Particularly, natural products lead to an ample variety of phytomolecules, with properties like scavenging free radicals from skin cells, preventing trans-epidermal water loss, inhibiting lipogeneses and preventing wrinkles (Mukherjee et al., 2011). *Q. suber* bark is one of such products. It is a multifunctional ingredient full of relevant properties that together with its by-products, can be used as a constituent of skin care products (*e.g.* cork granulates can be used as exfoliant particles and cork extracts as antioxidant and antiaging agents).

In this review, the possible new applications of *Q. suber* by-products as bioactive ingredients for cosmetic and topical pharmaceutical products were discussed, analysing the main compounds responsible for their activity and evidencing their effects on skin.

2. *Quercus suber* bark and its by-products

2.1. Characterizing cork

Q. suber, commonly known as cork oak, belongs to the Fagaceae family (Parsons, 1962; González-García et al., 2013). It has a narrow geographical range, growing in the Western part of the Mediterranean basin and along the Atlantic coast of North Africa and South-Western Europe, mainly in the Iberian Peninsula (Mestre and Gil, 2011; Sierra-Pérez et al., 2015; Pereira, 2011; Lumaret et al., 2005). These regions have ideal weather conditions, with dry summers and mild winters, for oak trees' growth (Jové et al., 2011; Touati et al., 2015). *Q. suber* can grow to 15–20 m height and live 200–250 years (González-García et al., 2013; Touati et al., 2015). Its forests are very important, both economically and ecologically, in countries from the Mediterranean basin (Mestre and Gil, 2011; Santos et al., 2013).

Cork is the suberose parenchyma from the outer bark of *Q. suber*, obtained both from the trunk and branches of the tree. The tree has the ability to regenerate it, by producing a suberose thick layer from its inner bark. This bark tissue is formed by the phellogen of the cork oak, responsible for the formation of new cells due to its meristematic nature, which means cell generation ability (Mestre and Gil, 2011; Silva et al., 2005; Pereira et al., 1987; Pereira, 1988). As such, the cork itself can be extracted without endangering biodiversity or causing damage to the tree. In other words, it is a natural, recyclable, non-toxic, renewable resource with high environmental qualities that plays a relevant role in sustainability (Sierra-Pérez et al., 2015; Pereira, 2011; González-García et al., 2013; Touati et al., 2015). Its forests play a key role in ecological processes and its use remotes to Antiquity, to times before Egyptian, Greek and Roman civilisations, where it was firstly used in fishing floats and other maritime devices (Mestre and Gil, 2011; Pereira, 2011; Santos et al., 2013).

Q. suber outer bark is a barrier between the cortex of the tree and the atmosphere. It is elastic, light, impermeable to liquids and gases, it does not absorb water and can absorb energy, showing chemical and