applied sciences

MDPI

Review

Quercus suber: A Promising Sustainable Raw Material for Cosmetic Application

Sandra Mota [1,2,†], Cláudia Pinto [3,†], Sara Cravo [3,4], Joana Rocha e Silva [5], Carlos Afonso [3,4], José Manuel Sousa Lobo [1,2], Maria Elizabeth Tiritan [3,4,6], Honorina Cidade [3,4,*] and Isabel Filipa Almeida [1,2,*]

[1] UCIBIO—Applied Molecular Biosciences Unit, MedTech, Laboratory of Pharmaceutical Technology, Department of Drug Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal; up201608486@up.pt (S.M.); slobo@ff.up.pt (J.M.S.L.)

[2] Associate Laboratory i4HB—Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal

[3] Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal; elsaferreira1971@hotmail.com (C.P.); scravo@ff.up.pt (S.C.); cafonso@ff.up.pt (C.A.); beth@ff.up.pt (M.E.T.)

[4] CIIMAR–Interdisciplinary Centre of Marine and Environmental Research, Terminal de Cruzeiros do Porto de Leixões, Avenida General Norton de Matos, S/N, 4450-208 Matosinhos, Portugal

[5] Dimas & Silva, Lda. Industry, Rua Central de Goda 345, 4535-167 Mozelos, Portugal; joanasilva@dimas-silva.pt

[6] CESPU-Cooperativa de Ensino Superior Politécnico e Universitário, Institute of Research and Advanced Training in Health Sciences and Technologies (IINFACTS), Rua Central de Gandra, 1317, 4585-116 Gandra, Portugal

* Correspondence: hcidade@ff.up.pt (H.C.); ifalmeida@ff.up.pt (I.F.A.)

† These authors contributed equally to this work.

check for updates

Citation: Mota, S.; Pinto, C.; Cravo, S.; Rocha e Silva, J.; Afonso, C.; Sousa Lobo, J.M.; Tiritan, M.E.; Cidade, H.; Almeida, I.F. *Quercus suber*: A Promising Sustainable Raw Material for Cosmetic Application. *Appl. Sci.* **2022**, *12*, 4604. https://doi.org/10.3390/app12094604

Academic Editors: Giuseppe D'Orazio and Biagia Musio

Received: 7 March 2022
Accepted: 29 April 2022
Published: 3 May 2022

Abstract: There is a drive within the cosmetic industry towards the development of more sustainable products, supported by consumer awareness of the environmental footprint. The cosmetic industry is rising to meet consumer demand by following practices, such as the use of by-products from agro-industrial waste. *Quercus suber* is a tree prevalent in the Mediterranean basin. The extraction of cork is considered sustainable, as this process does not harm the tree, and the amount of cork produced increases with the number of extractions. Beyond this, the cork industry produces by-products that are used to sustain the industry itself, such as cork powder, which is reused for generating energy. Additionally, cork and cork by-products contain bioactive compounds mainly with antioxidant activity that can be of use to the cosmetic industry, such as for antiaging, anti-acne, anti-inflammatory, and depigmenting cosmetic products. We provide the reader with an overview of the putative cosmetic applications of cork and its by-products as well as of their bioactive compounds. It is noteworthy that only a few cork-based cosmetic products have reached the market, namely antiaging and exfoliant products. Clearly, the use of cork upcycled cosmetic ingredients will evolve in the future considering the wide array of biological activities already reported.

Keywords: *Quercus suber*; cork; cosmetics; sustainability; by-products; circular beauty; upcycling

1. Introduction

For several years now, planet Earth has been facing a significant increase in human activity, reaching worrying levels regarding the consumption of natural resources and other environmental issues, such as climate change, pollution, destruction of forests, and consequently, a decrease in biodiversity [1,2]. Sustainable development is defined by the United Nations as meeting the needs of the present without compromising the ability of future generations to meet their own needs, which is directly related to the preservation of natural resources [1,3]. Many industries started to adopt this concept following the rising interest of consumers in eco-friendly natural products, and the cosmetic industry was no exception [4–6]. Sustainability has been a challenge for this industry since formulating products with new eco-friendly ingredients can lead to stability, aesthetics, and effectiveness issues [7].

With the growing environmental concerns about climate change and sustainability, consumers expect cosmetic products to contain ingredients of natural origin from sustainable and renewable resources [8]. Thus, cosmetic industries have created innovative green products and have increasingly focused on strategies to reduce their environmental footprint using a life cycle assessment (LCA) [9]. The LCA is an approach that takes into account the environmental impact, namely resources and emissions at all stages of the production of a product [9]. The stages analyzed go from the sourcing of the raw materials to a post-consumer phase, where recycling and waste disposal take place [9]. Also, the reuse of by-products that are considered waste for the agronomic industry has gained increasing attention from the cosmetic industry, adopting the concept of circular beauty [10]. The use of these upcycled raw materials are one of the great pillars to reduce the environmental impact [9,10].

2. *Quercus suber* and the Cork Industry

Quercus L. is a genus that belongs to the Fagaceae family and includes several species of trees, around 450 different species scattered throughout the world [11,12]. This genus can be divided into two subgenera: one composed of species that live in temperate regions generally in the Northern Hemisphere, named *Quercus*, and another group that includes trees typical from subtropical regions in Asia, mostly in the east and southeast, called *Cyclobalanopsis* [13].

Quercus suber, the cork oak, is a slow-growing evergreen tree that can live up to 200 years or more and is native to Mediterranean countries, such as European-like Portugal, Spain, France, Italy and North-African-like Tunisia, Algeria, and Morocco [14,15]. *Q. suber* has a unique bark, thick and porous and with fissures, that protects the tree cells from the aggressions of the outside environment, such as forest fires [16]. This bark, known as cork, is exploited by humans without endangering the tree vitality since it has the ability to regenerate as it is being harvested through the years [17]. Additionally, cork oak has the capacity to prevent soil erosion and desertification, to regulate the hydrological cycle, and to reduce CO_2 emissions, protecting the biodiversity around it. For those reasons, this tree is part of an agroforestry system called "montado" in Portugal and "dehesa" in Spain that brings together forests, livestock, and agriculture [17–20].

Cork oak was highly used for its wood to build ships or manufacture tools, although nowadays, the primary use of this tree is the extraction of cork, the common name given to the cork oak outer bark that has outstanding properties, making it an important raw material for numerous applications [12,16]. Cork is a light material, is impermeable and compressible, is a good acoustic insulator, has low thermal conductivity, and has a high capacity to absorb energy and to resist impact and friction [17]. Thus, the main applications of cork are insulation, flooring, cork agglomerates and natural cork stoppers [21,22]. As several studies have shown, cork is also a source of bioactive compounds [13,23–29]. Cork extracts revealed the presence of substances with biological activity that could be incorporated in pharmaceutical and cosmetic formulations [4,13,27–36]. Therefore, we can consider that cork is a renewable and sustainable resource, currently gaining more interest as a raw material [7,9]. Nowadays, the cork industry is important in the economy of countries, such as Portugal and Spain. Portugal detains about 55% of the world production of cork [22]. The whole process begins with the first cork harvest. When the tree reaches between 25 and 30 years, the process of extraction of cork starts [12,16,17,22]. The first harvested cork is called "virgin cork", has poor quality, and cracks easily; thus, it is not used in most applications [16,37]. Then it takes 9 to 12 years to extract subsequent layers of cork from the same tree; thus, the bark obtains the adequate thickness [16,37]. The second extracted cork is called "first reproduction cork" and has better quality; however, it is used essentially to produce cork agglomerates [16,37]. Only in the third extraction, the "second reproduction cork", cork is used for its major purposes, such as to produce cork wine stoppers [16,22,37]. To avoid any damage to the tree, cork stripping is only done manually when the tree has perfect physiological conditions to remove the cork, being a seasonal activity in the transition from spring to summer [17]. On the other hand, as can be seen, this process is fully sustainable since the tree remains intact, and throughout each extraction it produces more and more cork [19].

Subsequently, the cork industry produces a lot of waste to manufacture the final products. However, this industry is sustainably developed since, for example, the cork powder is used as a fuel in generators to produce heat and energy in the factories that process cork [17,19,25,38]. Cork waste is often reused, and it is increasingly valued both for the production of new materials and for incorporation in pharmaceutical and cosmetic products since its chemical composition is being highly studied, revealing interest in certain bioactive compounds that it presents [19,25]. Therefore, this industry presents high ecological, economic, and social value; thus, cork oak forests and cork waste need to be correctly managed to continue to be sustainable [17].

3. Cork By-Products and Applications

One of the main problems inherent in the cork industry is related to the amount of waste that is generated by the processes of cork production and transformation, reaching values close to 50,000 tons per year [4]. Therefore, it is important to overcome this situation to reduce waste through its valorisation on many industrial applications. Figure 1 show the main by-products of the cork industry.

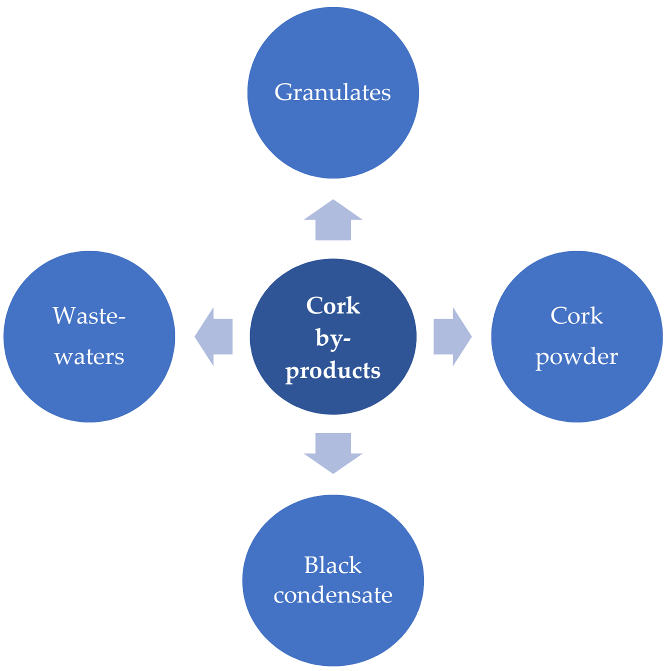


Figure 1. Main cork by-products.

In the production of cork disks and stoppers, some of these remnants are appropriate to obtain agglomerates through the application of high pressure and temperature in autoclaves [24]. Agglomerates, as the final product, keep some characteristics from the natural cork, such as elevated resistance and low thermal, acoustic and vibrational conductivity [39]. As expanded agglomerates result from exposure to superheated steam without using synthetic adhesives, this material is considered an environmentally sustainable by-product [19,39].

Accompanying industrial transformation processes, cork powder emerges from the granulometric separation once these particles are not viable to produce agglomerates [25]. This by-product is considered the main waste, representing about 25% of the raw materials that gather particles with dimensions lower than 0.25 mm [40]. Cork powder has a high heating value which is commonly used as a combustion on boilers for energy production [24,41]. Furthermore, cork powder can also be used as a filling agent to improve the quality of cork stoppers, incorporated in agglomerates and briquettes, on linoleum production, in agriculture, in the fabrication of explosives, and as a source of relevant chemicals [4,41,42]. Recent studies point to the pertinent ability of cork waste to prepare biomass materials [43]. Activated carbon can be prepared from the chemical or physical activation of cork where its adsorption properties are improved [44]. This transformation has proven to be effective to control the atmospheric levels of CO_2, storing carbon for long periods and reducing their release to the atmosphere [45]. In addition, cork-based activated carbon has been shown to be able to remove some pharmaceuticals from water, such as paracetamol, isoprofen, or iopamidol, and is a relatively fast adsorber of methylene blue [46,47]. This biosorbent has begun to gain some notoriety, constituting a sustainable alternative for contaminants removal, including heavy metals, such as Cu (II), Zn (II), Cr (VI), and Ni (II), due to the low costs, great efficacy, and environmental protection legislation [41,47,48].

Black condensate is another by-product that comes from the production of black agglomerate in the insulation corkboard industry. These corkboards result from the treatment of cork particles under elevated pressure and temperature conditions (250–500 °C) which originates a dark liquid that works as an adhesive and vapours that condensate in autoclave pipes, and black condensate that is removed as a pasty solid [24,49]. It is currently used to produce energy from its combustion, although its hydrophobic character can be used as a potential protective coating [49].

In one of the initial stages of cork stopper production, cork planks are boiled in water to increase its elasticity and to remove impurities, where cooking wastewaters are obtained. Usually, industries reuse these waters for several cycles resulting in a dark effluent known as cork-boiling wastewaters, with a high content of water-soluble compounds [50]. Although the composition of these waters is dependent on the type of cork and the number of boiling cycles, the main components that are present include phenolic compounds, tannins, and 2,4,6-trichloroanisol without suberin [51]. This by-product needs a previous treatment before disposal because it exceeds the legal limits of contaminants imposed for residual wastewaters [50]. Therefore, several methodologies, essentially based on chemical, physical, and even biological processes, have been tested over the years to decrease the level of contaminants [50]. For cork industry applications, gamma radiation treatment values this effluent by increasing the antioxidant potential of phenolic compounds whose recovery can be beneficial to other industries [51].

4. Bioactive Compounds on Cork and Cork By-Products

The composition of cork includes a variety of compounds from different chemical families, namely terpenes, sterols, saccharides, suberin, lignin, and other phenolic compounds, whose concentrations are dependent on several factors, such as climate, region, age, or the part of the tree [23,52]. Cork extractives are constituted by compounds with low molecular weight that are not connected to structural elements [33]. Aliphatic extractives, also known as waxes, are originated using nonpolar solvents, such as hexane or dichloromethane, while phenolic extractives are obtained from polar solvents, such as water or ethanol [53].

Suberin is the major component found on cork cell walls (30–50%), responsible for the low permeability and elasticity of this material, working as a protective barrier from the environment [54]. Cork suberin is a lipophilic polyester macromolecule, where monomers, such as long-chain fatty components, glycerol, hydroxyfatty, and phenolic acids are connected by ester groups [54–56]. The analysis of its monomeric fractions is possible thanks to depolymerization methods, concluding that suberin is constituted by an aromatic and an aliphatic domain. Among them, long-chain ω-hydroxyfatty acids and α,ω-dicarboxylic acids are the main aliphatic components, while ferulic acid is the principal aromatic component [57]. Despite being normally discarded due to its poor quality, virgin cork usually has more suberin than reproduction cork. In addition, cork powder is another rich source of suberin that can be valued in new applications [58]. For example, the aliphatic components from suberin are scarce in nature and can favour their industrial interest for the synthesis of polymeric materials [56,59]. Suberin extracts also showed antimutagenic properties and skin-firming properties [36] and acted in a desmutagenic manner [60].

Lignin is another hydrophobic polymer present on cork which works as the mechanical support of cell walls, believed to be the principal aromatic fraction of cork [61,62]. Studies indicate that lignin appears in the three layers from cork cell walls, although at different concentrations [63]. Cork powder often contains greater amounts of lignin than the original cork [64]. Additionally, lignin contains UV-absorbing properties which make it interesting to incorporate in sunscreens [65].

The minor components, cellulose and hemicellulose, are hydrophilic polysaccharides that confer structural rigidity to cork cells [66]. Even so, the bark of *Q. suber* L. is essentially composed of the monomeric units of glucose, xylose, and arabinose, contrary to what happens with other species [23].

Waxes include lipophilic, aliphatic, and aromatic compounds that along with suberin contribute to cork impermeability [67]. Triterpenes are the most abundant compounds found on waxes in addition to still having n-alkanes, n-alkanols and fatty acids [53]. Cerin (**1**), friedelin (**2**), betulin (**3**), betulinic acid (**4**), and sterols are examples of triterpenes that can be used as bioactive components (Figure 2) [68,69]. Dichloromethane cork extracts have been found to have a high amount of friedelin (**2**), betulin (**3**), betulinic acid (**4**), and β-amyrin (**5**), as well as sterols, such as sitost-4-en-3-one (**6**) (Figure 2) [28]. However, a higher number of sterols can be obtained using supercritical CO_2 as a solvent. Cork extraction using a dichloromethane/methanol mixture demonstrated that the most abundant triterpenes on cork are cerin (**1**) and friedelin (**2**), while betulinic acid (**4**) and friedelin (**2**) are the main components from cork powder and black condensate, respectively [59,67].

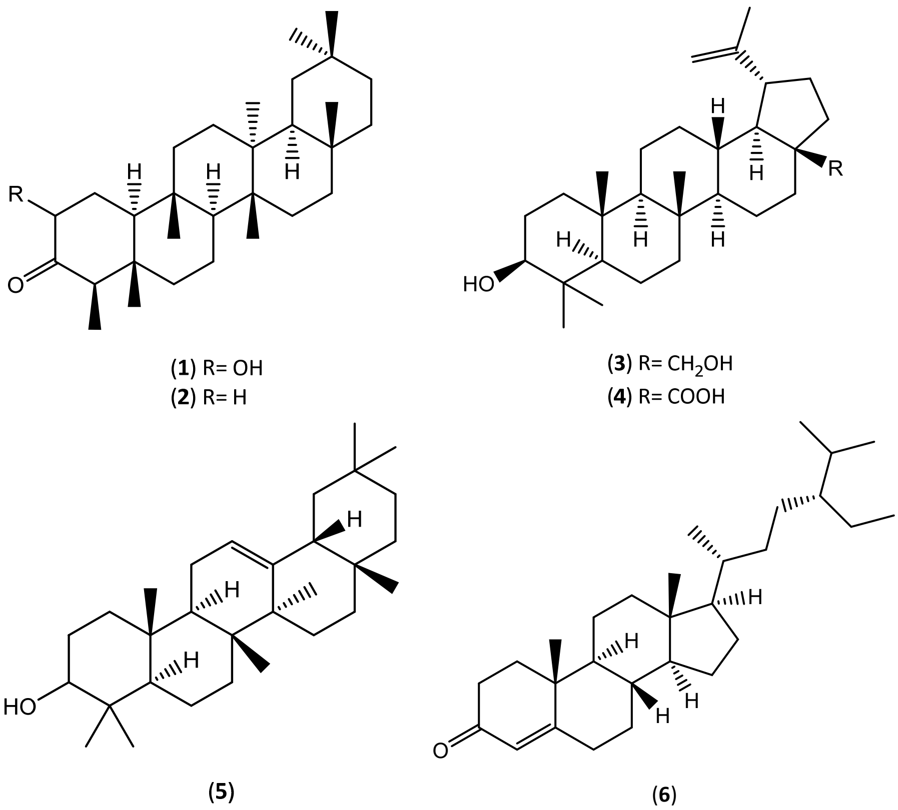


Figure 2. Chemical structures of bioactive triterpenes found on cork extracts.

Phenolic compounds are important secondary metabolites that present a wide range of biological activities [70]. In fact, many epidemiological studies point to the health benefits of fruit and vegetable intake, owing to the presence of many antioxidant phytochemicals [71]. They represent the second most abundant group of organic compounds in the plant kingdom produced as a response to the influence of biotic and abiotic factors and whose main functions include support, hormonal regulation, seed gemination, protection against pathogens, with herbivores and UV radiation also being involved in flavour, smell and colour [72].

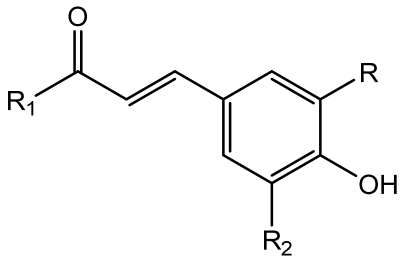
These compounds have at least one hydroxyl group attached to the aromatic ring with great structural diversity ranging from simple to complex structures obtained through the shikimate pathway [73]. Phenolics, also known as phenylpropanoids, can be classified into essentially two large groups named as flavonoids and nonflavonoids. Chemically, flavonoids have a fifteen-carbon backbone (C6-C3-C6) with two phenyl rings, A and B, attached through a three-carbon chain that normally arises as a heterocyclic pyran ring [74]. On the other hand, nonflavonoids encompass phenolic compounds, usually with a relatively simpler structure than flavonoids, such as phenolic acids, coumarins, stilbenes, hydrolysable, and condensed tannins and lignans [75].

The antioxidant, anti-inflammatory, antimicrobial, and anticancer properties of phenolic compounds make them very attractive for pharmaceutical, cosmetic, or food applications [76]. Hence, the valuation of this raw material and its by-products increasingly involves the identification of their phenolic composition [27].

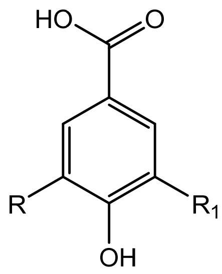
Cork phenolics are obtained by polar solvent extraction, and even though its composition is variable within trees and geographic location, it essentially includes phenolic acids and aldehydes, coumarins, flavonoids, and tannins [31]. Methanol/water mixtures are the most frequently employed methods to extract cork phenolics, often followed by an organic solvent [32,76]. The cork extracts can also be prepared through sequential extraction with increasing polarity solvents [77]. In 2015, Bouras and co-workers reported a microwave-assisted extraction method, using different proportions of water, methanol, and ethanol, demonstrating that the use of these alcohols promotes a significant improvement of polyphenol recovery. Among them, p-coumaric (**7**), syringic (**8**), and sinapic (**9**) acids are the major compounds on bark extracts (Figure 3) [78]. In the same year, a new method for the extraction of phenolic compounds from cork granulates using a mixture of water with propylene glycol was reported [76,79].

Hydrolysable tannins and low molecular weight phenolic compounds are suggested as the potential bioactive compounds from *Quercus suber* bark [27]. The most common phenolic acids in cork are ellagic (**10**), protocatechuic (**11**), gallic (**12**), vanillic (**13**), ferulic (**14**), and caffeic (**15**) acids, whereas phenolic aldehydes include vanillin (**16**), protocatechuic aldehyde (**17**), and coniferyl aldehyde (**18**) (Figure 3) [80,81].

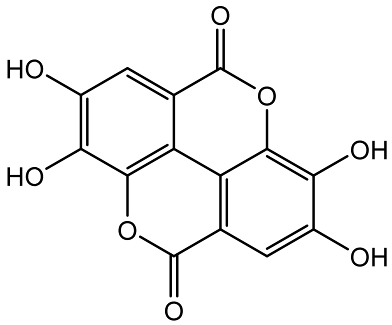
Tannins can be monomeric or polymeric and even condensed or hydrolysable, which are related to bitterness and astringency of wines as a result of binding to salivary proteins [82]. Several studies indicate that these phenolics, namely castalagin (**19**), grandinin (**20**), vescalagin (**21**), and roburin (**22**) are capable of migrating from cork stoppers to wine solutions after bottling and may interfere with its organoleptic properties, such as taste, colour, or bitterness or participate on wine oxidation (Figure 4) [83–85].



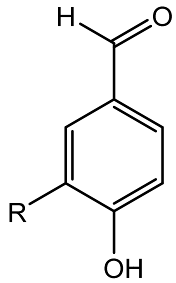
(**7**) R=R_2= H; R_1= OH
(**9**) R=R_2= OCH_3; R_1= OH
(**14**) R= OCH_3; R_1= OH; R_2= H
(**15**) R= R_1= OH; R_2= H
(**18**) R= OCH_3; R_1=R_2= H



(**8**) R=R_1= OCH_3
(**11**) R= H; R_1= OH
(**12**) R=R_1= OH
(**13**) R= H; R_1= OCH_3
(**25**) R=R_1= H

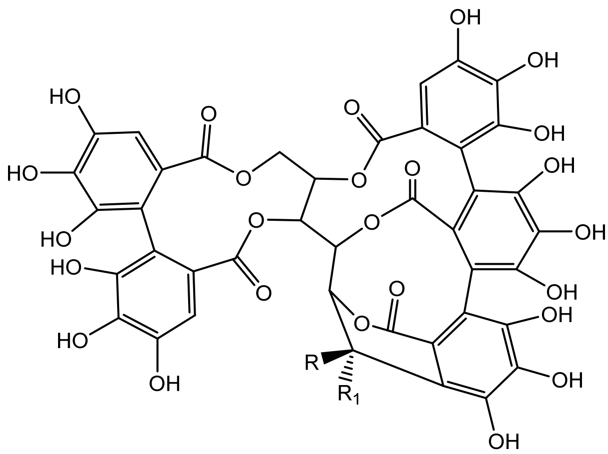


(**10**)



(**16**) R= OCH_3
(**17**) R= OH

Figure 3. Chemical structures of bioactive phenolic and aldehyde acids from *Quercus suber* bark.

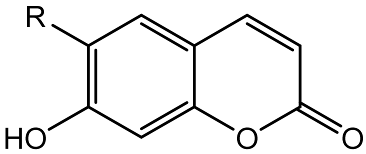


(**19**) R= OH; R_1= H
(**20**) R= H; R_1= Lyxose
(**21**) R= H; R_1= OH
(**22**) R= H; R_1= Xylose

Figure 4. Chemical structures of major ellagitannins from *Quercus suber* bark.

The first reported HPLC analysis of cork extract prepared with a methanol/water mixture showed that the most abundant phenolic compounds are the phenolic acids, ellagic (**10**), and protocatechuic (**11**) [32]. Aldehydes, such as protocatechuic aldehyde

(**17**), coniferyl aldehyde (**18**), and vanillin (**16**) and coumarins, such as scopoletin (**23**) and aesculetin (**24**), also appear, although in much smaller amounts (Figure 5) [24,32].



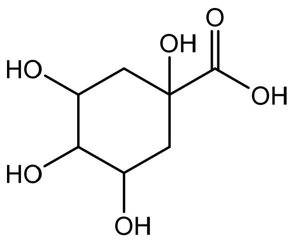
(**23**) R= OCH_3
(**24**) R= OH

Figure 5. Chemical structures of coumarins extracted by a mixture of 20% methanol in water.

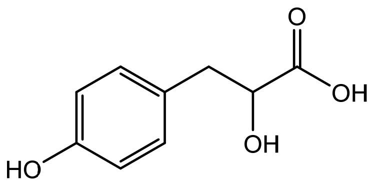
Santos et al. prepared cork extracts by two distinct extraction routes using a mixture of methanol 20% followed by diethyl ether fractionation and sequential extraction with methanol and water and analysed the differences in the phenolics extracted according to the solvent [80]. Thus, even though the aqueous extract had the higher phenol and p-hydroxybenzoic acid (**25**) (Figure 3) contents, the amount of ellagic acid (**10**) was vestigial, while some compounds, such as coumaric (**7**), vanillic (**13**), or ferulic (**14**) acids did not appear [4].

The cork hydroglycolic extract prepared by Batista and co-workers was shown to be mainly constituted by ellagic acid (**10**) and ellagitannins, such as castalagin (**19**), vescalagin (**21**), and roburin (**22**), as well as protocatechuic acid (**11**) and gallic acid (**12**) [79].

In 2013, Santos and co-workers extended the identification of cork phenolics to extracts prepared from cork powder and black condensate using methanol/water mixture (50%). Ellagic acid (**10**), gallic acid (**12**), protocatechuic acid (**11**), quinic acid (**26**) (Figure 6), and aesculetin (**24**) were present in all extracts. However, ferulic acid (**14**) only appears on cork powder extract, while coumaric acid (**7**), vanillin (**16**), coniferyl aldehyde (**18**), and p-hydroxyphenyllactic acid (**27**) (Figure 6) emerged on black condensate extract [24]. The major compounds on cork extract were ellagic (**10**) and gallic (**12**) acids, while on cork powder extract they were gallic acid (**12**) and aesculetin (**24**), and finally on black condensate they were gallic acid (**12**), coniferyl aldehyde (**18**), and aesculetin (**24**).



(**26**)



(**27**)

Figure 6. Chemical structures of phenolic acids present on cork powder and black condensate extracts.

As mentioned before, cork-cooking wastewaters are also rich in phenolic acids, mostly ellagic (**10**) followed by gallic (**12**), protocatechuic (**11**), and ferulic (**14**) [26,86].

Biological Activity of Cork Extracts and Cork By-Products

Cork and its by-products constitute a source of bioactive compounds with antioxidant activity that can be of use to the cosmetic industry [87]. In the scientific literature, some studies have already described the extraction of compounds from cork, cork acorns, and cork by-products, such as cork powder, black condensate, and cork-cooking wastewater. These extracts showed the presence of phenolic acids, such as ellagic (**10**), protocatechuic (**11**), gallic (**12**), vanillic (**13**), ferulic (**14**), and caffeic (**15**) and ellagitannins with antioxidant and protective DNA activity as well as collagenase and elastase inhibitory activity that can be interesting for antiaging cosmetics (Table 1) [4,79,88,89].

Table 1. Chemical composition and biological activity of cork extracts and cork by-products.

Extraction Solvent and Source Material	Composition		Quantification	Biological Activity	References
methanol/water (80:20); diethylether *granulated cork from Spain*	Ellagic acid (**10**)	228.4	μg of compound/g of dry cork	——	[32]
	Protocatechuic acid (**11**)	48.8			
	Vanillic acid (**13**)	27.4			
	Gallic acid (**12**)	18.3			
	Scopoletin (**23**)	12.7			
	Vanillin (**16**)	16.1			
	Coniferaldehyde (**18**)	11.2			
	Protocatechuic aldehyde (**17**)	8.1			
	Caffeic acid (**15**)	12.1			
	Ferulic acid (**14**)	10.7			
	Aesculetin (**24**)	7.5			
	Sinapaldehyde	4.5			
supercritical CO_2 *granulated cork*	Friedelin (**2**)	30.6	mg of compound/extract	——	[28]
	Sitost-4-en-3-one (**6**)	22.5			
	β-Sitosterol	6.59			
	Betulinic acid (**4**)	4.93			
	Betulin (**3**)	3.13			
dichloromethane *granulated cork*	Friedelin (**2**)	30.2	mg of compound/extract	——	[28]
	Sitost-4-en-3-one (**6**)	4.1			
	Betulinic acid (**4**)	10.5			
	Betulin (**3**)	3.9			
wine solution (12% ethanol, 5.0 g/L tartaric acid, pH = 3.2); ethyl acetate *granulated cork*	Protocatechuic aldehyde (**17**) Vanillin (**16**) Protocatechuic acid (**11**) Gallic acid (**12**) Conyferaldehyde (**18**) Caffeic acid (**15**) Ferulic acid (**14**) Ellagic acid (**10**) Ellagic acid-pentose Ellagic acid-deoxyhexose Ellagic acid-hexose Valoneic acid dilactone HHDP-glucose Valoneic acid Dehydrated tergallic-C-glucoside HHDP-galloyl-glucose Trigalloy-glucose Di-HHDP-glucose HHDP-digalloyl-glucose Tetragalloyl-glucose Castalagin (**19**) Vescalagin (**21**) Di-HHDP-galloyl-glucose Trigalloyl-HHDP-glucose Pentagalloyl-glucose Mongolicain A and B		——	——	[31,83,84]

Table 1. *Cont.*

Extraction Solvent and Source Material	Composition	Quantification		Biological Activity	References
water; water/ethanol (50:50) *granulated cork*	Castalagin (**19**) Ellagic acid (**10**) Vescalagin (**21**) Gallic acid (**12**)	46.9 26.7 22.4 2.9	mg of compound/g extract	Antioxidant activity (DPPH (EC_{50}) = 5.32 ± 0.45 µg of extract/mL; ORAC = 2.11 ± 0.24 $mgT_{eq}/g_{extract}$)	[29]
dichloromethane; methanol/water *cork powder*	Betulinic acid (**4**) Cerin (**1**) Friedelin (**2**) Ellagic acid (**10**) Betulin (**3**) β-Sitosterol Ursolic acid Lupeol	11719 2060 2009 1347 875 254 104 60	mg of compound/kg of cork powder	——	[67]
subcritical water *granulated cork*	Gallic acid (**12**) Ferulic acid (**14**) Caffeic acid (**15**)	4.9 ± 0.9 0.6 ± 0.1 0.5 ± 0.1	mg of compound/g extract)	Antioxidant activity (EC_{50} = 0.25 mg extract/mg DPPH)	[76]
water/propylene glycol (40:60) *granulated cork*	Ellagic acid (**10**) Roburin (**22**) and Grandinin (**20**) Castalagin (**19**) Vescalagin (**21**) Protocatechuic acid (**11**) Gallic acid (**12**)	6800–8200 500–3200 1800–2100 800–1900 100–130 60–100	µg of compound/g of dry cork	Antioxidant activity (ORAC = 22,603 ± 2097 ymolET/L; HORAC = 15,712 ± 1419 µmolEAC/L; HOSC = 22,678 ± 3225 pmolET/L; DPPH = 1.68 (IC_{50}) mL/L; O_2^- = 11.08 (IC_{50}) mL/L) Antiaging activity: inhibition of MMP-1, MMP-3, MMP-9 activity; inhibition of ROS formation in keratinocytes and fibroblasts. Depigmenting activity: inhibition of tyrosinase activity; inhibition of melanin production in melanocytes. Anti-inflammatory activity: inhibition of NO production; reduction of IL-6, TNF-α, CCL5 levels; reduction of the activation of NF-kB. Inhibition of lipid accumulation in keratinocytes (inhibition of SREBP-1 gene expression)	[79]
methanol/water (80:20); diethyl ether *granulated cork from Portugal*	Ellagic acid (**10**) Caffeic acid (**15**) Salicylic acid Gallic acid (**12**) Eriodictyol Protocatechuic acid (**11**) Vanillin (**16**) Aesculetin (**24**) Naringenin Vanillic acid (**13**) p-coumaric acid (**7**) Ferulic acid (**14**)	2031.5 57.6 32.7 30.6 27.4 17.5 14.3 4.9 2.6 Trace Trace Trace	mg of compound/kg of dry cork	Antioxidant activity (DPPH (IC_{50}) = 2.79 ± 0.15 µg of extract/mL)	[80]

Table 1. *Cont.*

Extraction Solvent and Source Material	Composition	Quantification		Biological Activity	References
methanol *granulated cork from Portugal*	Ellagic acid (**10**) Aesculetin (**24**) Protocatechuic acid (**11**) Gallic acid (**12**) Vanillin (**16**) Vanillic acid (**13**) Quinic acid (**26**)	1576.9 106.7 59.0 48.1 Trace Trace Trace	mg of compound/kg of dry cork	Antioxidant activity (DPPH (IC_{50}) = 3.58 ± 0.20 µg of extract/mL)	[80]
water *granulated cork from Portugal*	Ellagic acid (**10**) Gallic acid (**12**) Protocatechuic acid (**11**) Caffeic acid (**15**) p-hydroxybenzoic acid (**25**) p-hydroxyphenyllactic acid (**27**)	526.5 241.6 118.3 12.9 1.0 Trace	mg of compound/kg of dry cork	Antioxidant activity (DPPH (IC_{50}) = 5.84 ± 0.29 µg of extract/mL)	[80]
methanol/water (50:50) *granulated cork*	Ellagic acid (**10**) Ellagic acid-pentoside Gallic acid (**12**) Aesculetin (**24**) Quinic acid (**26**) Methyl gallate Brevifolin-carboxylic acid Protocatechuic acid (**11**) Ferulic acid (**14**) Coniferyl aldehyde (**18**) p-hydroxyphenyllactic acid (**27**) Valoneic acid dilactone Caffeic acid isoprenyl ester Isorhamnetin-rhamnoside Eriodictyol Isorhamnetin	1246.46 ± 0.18 770.16 ± 0.15 736.48 ± 1.63 391.59 ± 1.10 372.86 ± 1.94 251.43 ± 0.06 102.03 ± 0.08 79.26 ± 0.10 Trace Trace Trace 168.01 ± 0.70 127.98 ± 0.28 Trace Trace Trace	of dry cork mg of compound/kg	Antioxidant activity (DPPH (IC_{50}) = 4.77 ± 0.02 µg of extract/mL)	[24]
methanol/water (50:50) *cork powder* *(by-product)*	Ellagic acid (**10**) Gallic acid (**12**) Aesculetin (**24**) Quinic acid (**26**) Methyl gallate Ellagic acid-pentoside Valoneic acid dilactone Protocatechuic acid (**11**) Ferulic acid (**14**) Coniferyl aldehyde (**18**) Caffeic acid isoprenyl ester Brevifolin-carboxylic acid Isorhamnetin-rhamnoside Isorhamnetin	527.59 ± 1.70 263.04 ± 0.52 176.80 ± 0.60 137.02 ± 0.50 96.93 ± 0.56 46.18 ± 0.15 46.05 ± 0.11 16.44 ± 0.01 14.77 ± 0.02 Trace 82.47 ± 0.29 53.72 ± 0.15 Trace Trace	mg of compound/kg of dry cork powder	Antioxidant activity (DPPH (IC_{50}) = 3.33 ± 0.02 µg of extract/mL)	[24]

Table 1. *Cont.*

Extraction Solvent and Source Material	Composition	Quantification		Biological Activity	References
methanol/water (50:50)*black condensate* *(by-product)*	Coniferyl aldehyde (**18**) Aesculetin (**24**) Gallic acid (**12**) Quinic acid (**26**) Ellagic acid (**10**) p-hydroxyphenyllactic acid (**27**) p-coumaric acid (**7**) Vanillin (**16**) Caffeic acid (**15**) Protocatechuic acid (**11**) Ferulic acid (**14**) Eriodictyol	194.34 ± 0.56 125.28 ± 0.65 118.46 ± 0.61 117.17 ± 0.30 52.52 ± 0.18 49.36 ± 0.12 35.76 ± 0.22 32.47 ± 0.25 17.68 ± 0.05 9.97 ± 0.03 Trace Trace	mg of compound/kg of dry black condensate	Antioxidant activity (DPPH (IC_{50}) = 1.57 ± 0.01 µg of extract/mL)	[24]
water/ethanol *granulated cork*	Castalagin (**19**) Vescalagin (**21**) Ellagic acid (**10**) β-O-ethylvescalagin Gallic acid (**12**)	47.2 22.8 26.5 24.4 0.6	mg of compound/g of extract	Antioxidant activity (DPPH (EC_{50}) = 7.9 ± 0.02 µg of extract/mL; ORAC = 1533 ± 147 $mgT_{eq}/g_{extract}$; FRAP = 1963 ± 126 $mgT_{eq}/g_{extract}$; TEAC = 802 ± 8 $mgT_{eq}/g_{extract}$)	[90]

HHDP—hexahydroxydiphenyl. ——: unreported biological activity.

In addition to the in vitro studies that already exist and prove the biological activity of these extracts, there is also an in vivo study that proves the tensor and smoothing effect that cork extracts have on human skin [36]. Additionally, due to the presence of these phenolic compounds in cork and its by-products, there is the possibility of incorporating these ingredients in sunscreens, as it has been proven that these compounds, namely lignin [65], can absorb UV radiation.

Another known activity of phenolic compounds and flavonoids is the inhibition of tyrosinase in melanocytes by in vitro and in vivo studies [4]; hence, its interest in the development of depigmenting cosmetics is predictable. Thus, correlating the existence of these compounds in cork, namely ellagic (**10**) and gallic (**12**) acids, protocatechuic aldehyde (**17**) and ellagitannins, with their depigmenting activity, one of the possible cosmetic applications of cork is in depigmenting products for the treatment of skin blemishes [4,79,91].

Polyphenols can also inhibit the accumulation of lipids in keratinocytes and inhibit the expression of the SREBP-1 gene, which makes them promising in combating acne [92]. A cork hydroglycolic extract has also been studied for this activity, with favourable results [79]. In addition, cork powder has bioabsorbent properties, removing pollutants and oily substances. For this fact, it is being studied for protection of the environment and for the treatment of acne, absorbing the accumulated sebum on the skin [4,41,79]. In addition, for skin problems, such as acne, anti-inflammatory and antimicrobial cosmetics can be used. Compounds present in cork, such as suberin, friedelin (**2**), polysaccharide, and phenol (gallic acid (**12**) and ellagitannins) extracts have also demonstrated anti-inflammatory activity by the NO inhibitory activity in the presence of a pro-inflammatory stimulus and inhibitory activity of NF-kB transcription factor activation of a cork hydroglycolic extract [4,79]. On the other hand, cork extracts present bioactive compounds, namely protocatechuic (**11**) and gallic (**12**) acid, as well as ellagitannins, that have antimicrobial properties [80,93,94]. The antimicrobial activity of cork was also proven by preliminary studies, mainly against Staphylococcus aureus, with a MIC value of 6 mg/mL [4,95].

5. Current Cosmetic Applications of Cork

Cork and its by-products have been increasingly sought as a source of new ingredients for pharmaceutical and cosmetic use (Figure 7). In terms of commercial applications, cork is the main ingredient in a brand of anti-aging cosmetics which claims that the suberin present in the cork extract has a lifting effect on the skin [4,96]. There is only one cork cosmetic ingredient with established in vitro [79] and in vivo [36] activity on human skin described in the "CosIng" database, namely *Quercus suber* bark extract. This ingredient may be used alone as a unique ingredient or combined with other ingredients, such as plant extracts. The "CosIng" database is a cosmetic ingredients database from the European Commission, and it provides information on cosmetic ingredients, including their regulatory status according to the Regulation (EC) No 1223/2009 [97]. Several cork-based ingredients are available from different suppliers. The ACTISCRUB™ Cork by Lipotec is a cosmetic raw material constituted by a *Q. suber* bark extract and has exfoliant and peeling activity [98]. The Suberlift™ by Ashland Specialty Chemical is another cork raw material containing *Q. suber* bark extract with tensor and firming effects on human skin [99]. One last example, the DIAM Oléoactif® by Hallstar, is a raw material constituted by a mixture of Cocos nucifera oil, oak root extract, and *Q. suber* bark extract with soothing, antiaging, anti-redness, and anti-inflammatory effects [100].

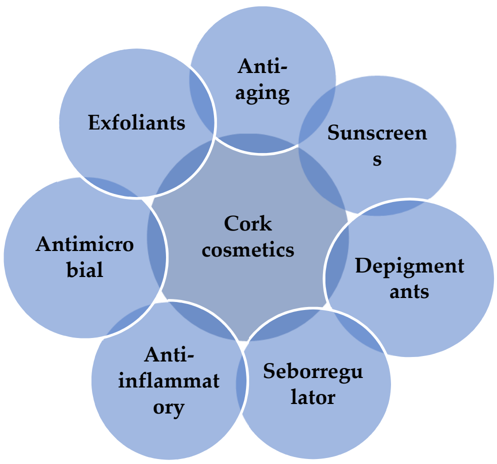


Figure 7. Potential cork cosmetic applications.

Furthermore, cork was also studied to be used in skin exfoliants. A granulated cork was studied and considered suitable as a mild exfoliant due to its morphology and properties. Cork particles were also tested as stabilizers of a Pickering emulsion for topical application with antioxidant and anti-elastase activity [4,34].

6. Conclusions

Cork obtained from *Q. suber* bark represents a natural and sustainable resource for various applications since its extraction does not harm the tree. The cork industry is also considered sustainable since most of the cork by-products that are formed during the process are reused to self-sustain the factory. However, the main problem inherent to this industry is the amount of waste generated throughout the process. For this reason, a new perspective on the potentialities of cork by-products aroused to take full advantage of its properties. Cork and its by-products are currently being studied for pharmaceutical and cosmetic application. Cork extract composition encompasses several compounds from different chemical families, thus attracting attention due to the different biological activities, translating into a variety of possible applications.

The growing concern for the environmental footprint is also reflected on the skin care market where consumers started to demand more natural and sustainable products. Cork extracts have a considerable number of bioactive compounds, especially phenolics. Cork phenolics, such as caffeic, gallic, ellagic, ferulic, vanillic, and protocatechuic acids, show remarkable antioxidant activity, owing to their radical-scavenging properties. Currently, cork and some cork extracts are already used in antiaging cosmetics and as mild exfoliants and are registered as cosmetic ingredients in official databases.

Even taking into account all the studies already carried out regarding cork and its by-products and their current applications, there is still room for innovation in this area. Although the results of in vitro studies on cork extracts are promising, they are still very preliminary, and it is necessary to conduct more studies to prove their effectiveness and safety for skin applications, namely studies to support skin depigmentation and anti-acne and antimicrobial claims as well as toxicological studies, according to the European Cosmetics Regulation No 1223/2009, "The SCCS Notes of Guidance for the Testing of Cosmetic Ingredients and their Safety Evaluation" and "Technical Document on Cosmetic Claims" [101–103]. In addition, more specific studies are needed regarding the analysis of bioactive compounds in cork by-products, such as cork powder, "black condensate", and cork-cooking wastewater. Clearly, cork is an important resource for the cosmetic industry, but further studies are needed to unveil and confirm the full spectrum of its potentialities.

Author Contributions: S.M. and C.P.: investigation, data curation, writing-original draft preparation; S.C., J.R.e.S., C.A. and J.M.S.L.: writing—review and editing, project administration; H.C., M.E.T., and I.F.A.: supervision, conceptualization, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financed by national funds from the European Regional Development Fund (ERDF) through the Northern Regional Operational Programme (NORTE2020) under the project 47239—Cork2Cosmetic (NORTE-01-0247-FEDER-047239). S. Mota and C. Pinto acknowledges the research fellowship (NORTE-01-0247-FEDER-047239), fully supported by national funding from project 47239-Cork2Cosmetic (NORTE-01-0247-FEDER-047239).

Acknowledgments: This work was supported by national funds from FCT—Fundação para a Ciência e a Tecnologia, I.P. in the scope of the projects, UIDP/04378/2020 and UIDB/04378/2020 of the Research Unit on Applied Molecular Biosciences—UCIBIO, and the project LA/P/0140/2020 of the Associate Laboratory Institute for Health and Bioeconomy—i4HB. This research was also supported by national funds from FCT though the projects, UIDB/04423/2020 and UIDP/04423/2020 (Group of Natural Products and Medicinal Chemistry-CIIMAR), and the European Regional Development Fund (ERDF) through the COMPETE—Programa Operacional Fatores de Competitividade (POFC) program in the framework of the program, PT2020.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hay, L.; Duffy, A.; Whitfield, R.I. The Sustainability Cycle and Loop: Models for a more unified understanding of sustainability. *J. Environ. Manag.* **2014**, *133*, 232–257. [CrossRef] [PubMed]
2. Kurnaz, M.L.; Kurnaz, I.A. Commercialization of medicinal bioeconomy resources and sustainability. *Sustain. Chem. Pharm.* **2021**, *22*, 100484. [CrossRef]
3. Mori, K.; Christodoulou, A. Review of sustainability indices and indicators: Towards a new City Sustainability Index (CSI). *Environ. Impact Assess. Rev.* **2012**, *32*, 94–106. [CrossRef]
4. Carriço, C.; Ribeiro, H.M.; Marto, J. Converting cork by-products to ecofriendly cork bioactive ingredients: Novel pharmaceutical and cosmetics applications. *Ind. Crops Prod.* **2018**, *125*, 72–84. [CrossRef]
5. Patnaik, A.; Tripathy, S.; Dash, A. *Identifying the Features Influencing Sustainable Products: A Study on Green Cosmetic*; Pant, P., Mishra, S.K., Mishra, P.C., Eds.; Springer Science and Business Media Deutschland GmbH: Berlin/Heidelberg, Germany, 2021; pp. 631–640.
6. Bom, S.; Ribeiro, H.M.; Marto, J. Sustainability Calculator: A Tool to Assess Sustainability in Cosmetic Products. *Sustainability* **2020**, *12*, 15. [CrossRef]
7. Born, S.; Jorge, J.; Ribeiro, H.M.; Marto, J. A step forward on sustainability in the cosmetics industry: A review. *J. Clean. Prod.* **2019**, *225*, 270–290.
8. Kumar, S. Exploratory analysis of global cosmetic industry: Major players, technology and market trends. *Technovation* **2005**, *25*, 1263–1272. [CrossRef]
9. Environmental Sustainability-The European Cosmetics Industry's Contribution 2017–2019. Available online: https://cosmeticseurope.eu/files/3715/6023/8402/Environmental_Sustainability_Report_2019.pdf (accessed on 10 January 2022).

10. NATRUE. Circular Beauty: Upcycled Ingredients in Cosmetic Products. Available online: https://www.natrue.org/circular-beauty-upcycled-ingredients-in-cosmetic-products/ (accessed on 10 January 2022).
11. Burlacu, E.; Nisca, A.; Tanase, C. A Comprehensive Review of Phytochemistry and Biological Activities of *Quercus* Species. *Forests* **2020**, *11*, 904. [CrossRef]
12. Sousa, V.B.; Leal, S.; Quilho, T.; Pereira, H. Characterization of Cork Oak (*Quercus suber*) Wood Anatomy. *IAWA J.* **2009**, *30*, 149–161. [CrossRef]
13. Şöhretoğlu, D.; Renda, G. The polyphenolic profile of Oak (*Quercus*) species: A phytochemical and pharmacological overview. *Phytochem. Rev.* **2020**, *19*, 1379–1426. [CrossRef]
14. Bugalho, M.N.; Caldeira, M.C.; Pereira, J.S.; Aronson, J.; Pausas, J.G. Mediterranean cork oak savannas require human use to sustain biodiversity and ecosystem services. *Front. Ecol. Environ.* **2011**, *9*, 278–286. [CrossRef]
15. Petroselli, A.; Vessella, F.; Cavagnuolo, L.; Piovesan, G.; Schirone, B. Ecological behavior of *Quercus suber* and *Quercus ilex* inferred by topographic wetness index (TWI). *Trees-Struct. Funct.* **2013**, *27*, 1201–1215. [CrossRef]
16. Gil, L.; Varela, M.C. *EUFORGEN-Technical Guidelines for Genetic Conservation and Use for Cork Oak (Quercus suber)*; EUFORGEN: Barcelona Spain, 2008; p. 6.
17. Pereira, H. *Cork: Biology, Production and Uses*; Elsevier: Amsterdam, The Netherlands, 2007.
18. Joffre, R.; Rambal, S.; Ratte, J.P. The dehesa system of southern Spain and Portugal as a natural ecosystem mimic. *Agrofor. Syst.* **1999**, *45*, 57–79. [CrossRef]
19. Gil, L. Cork: Sustainability and New Applications. *Front. Mater.* **2015**, *1*, 38. [CrossRef]
20. Gil, L. Cork: A strategic material. *Front. Chem.* **2014**, *2*, 16. [CrossRef]
21. Houston Durrant, T.; de Rigo, D.; Caudullo, G. *Quercus suber* in Europe: Distribution, habitat, usage and threats. In *European Atlas of Forest Tree Species*; San-Miguel-Ayanz, J., de Rigo, D., Caudullo, G., Houston Durrant, T., Mauri, A., Eds.; Publications Office of the EU: Luxembourg, 2016; pp. 164–165.
22. Branco, D.G.; Santiago, C.; Lourenço, A.; Cabrita, L.; Evtuguin, D.V. Structural Features of Cork Dioxane Lignin from *Quercus suber* L. *J. Agric. Food Chem.* **2021**, *69*, 8555–8564. [CrossRef]
23. Pereira, H. Chemical composition and variability of cork from *Quercus suber* L. *Wood Sci. Technol.* **1988**, *22*, 211–218. [CrossRef]
24. Santos, S.A.O.; Villaverde, J.J.; Sousa, A.F.; Coelho, J.F.J.; Neto, C.P.; Silvestre, A.J.D. Phenolic composition and antioxidant activity of industrial cork by-products. *Ind. Crops Prod.* **2013**, *47*, 262–269. [CrossRef]
25. Reis, S.F.; Lopes, P.; Roseira, I.; Cabral, M.; Mateus, N.; Freitas, V. Recovery of added value compounds from cork industry by-products. *Ind. Crops Prod.* **2019**, *140*, 111599. [CrossRef]
26. Madureira, J.; Melo, R.; Botelho, M.L.; Leal, J.P.; Fonseca, I.M. Effect of ionizing radiation on antioxidant compounds present in cork wastewater. *Water Sci. Technol.* **2013**, *67*, 374–379. [CrossRef]
27. Mislata, A.M.; Puxeu, M.; Ferrer-Gallego, R. Aromatic potential and bioactivity of cork stoppers and cork by-products. *Foods* **2020**, *9*, 133. [CrossRef] [PubMed]
28. Castola, V.; Marongiu, B.; Bighelli, A.; Floris, C.; Laï, A.; Casanova, J. Extractives of cork (*Quercus suber* L.): Chemical composition of dichloromethane and supercritical CO_2 extracts. *Ind. Crops Prod.* **2005**, *21*, 65–69. [CrossRef]
29. Araújo, A.R.; Pereira, D.M.; Aroso, I.M.; Santos, T.; Batista, M.T.; Cerqueira, M.T.; Marques, A.P.; Reis, R.L.; Pires, R.A. Cork extracts reduce UV-mediated DNA fragmentation and cell death. *RSC Adv.* **2015**, *5*, 96151–96157. [CrossRef]
30. Khennouf, S.; Benabdallah, H.; Gharzouli, K.; Amira, S.; Ito, H.; Kim, T.H.; Yoshida, T.; Gharzouli, A. Effect of tannins from *Quercus suber* and *Quercus coccifera* leaves on ethanol-induced gastric lesions in mice. *J. Agric. Food Chem.* **2003**, *51*, 1469–1473. [CrossRef] [PubMed]
31. Fernandes, A.; Sousa, A.; Mateus, N.; Cabral, M.; Freitas, V. Analysis of phenolic compounds in cork from *Quercus suber* L. by HPLC-DAD/ESI-MS. *Food Chem.* **2011**, *125*, 1398–1405. [CrossRef]
32. Conde, E.; Cadahia, E.; García-Vallejo, M.C.; de Simon, B.F.; Adrados, J.R.G. Low molecular weight polyphenols in cork of *Quercus suber*. *J. Agric. Food Chem.* **1997**, *45*, 2695–2700. [CrossRef]
33. Bejarano, I.; Godoy-Cancho, B.; Franco, L.; Martínez-Cañas, M.A.; Tormo, M.A. *Quercus Suber* L. Cork Extracts Induce Apoptosis in Human Myeloid Leukaemia HL-60 Cells. *Phytother. Res.* **2015**, *29*, 1180–1187. [CrossRef]
34. Carriço, C.; Pinto, P.; Graça, A.; Gonçalves, L.M.; Ribeiro, H.M.; Marto, J. Design and characterization of a new *Quercus suber*-based pickering emulsion for topical application. *Pharmaceutics* **2019**, *11*, 131. [CrossRef]
35. Hunt, K.J.; Hung, S.K.; Ernst, E. Botanical extracts as anti-aging preparations for the skin: A systematic review. *Drugs Aging* **2010**, *27*, 973–985. [CrossRef]
36. Coquet, C.; Bauza, E.; Oberto, G.; Berghi, A.; Farnet, A.M.; Ferré, E.; Peyronel, D.; Dal Farra, C.; Domloge, N. *Quercus suber* cork extract displays a tensor and smoothing effect on human skin: An in vivo study. *Drugs Exp. Clin. Res.* **2005**, *31*, 89–99.
37. Diaz-Maroto, I.J.; Diaz-Maroto, M.C. Cork from *Quercus suber* L.: Forest certification system for sustainable management of cork oak forests. *Wood Res.* **2020**, *65*, 855–864. [CrossRef]
38. Montero, I.; Miranda, T.; Sepúlveda, F.J.; Arranz, J.I.; Nogales, S. Analysis of pelletizing of granulometric separation powder from cork industries. *Materials* **2014**, *6*, 6686–6700. [CrossRef] [PubMed]
39. Ferreira, R.; Pereira, D.; Gago, A.; Proença, J. Experimental characterisation of cork agglomerate core sandwich panels for wall assemblies in buildings. *J. Build. Eng.* **2016**, *5*, 194–210. [CrossRef]
40. Gil, L. Cork powder waste: An overview. *Biomass Bioenergy* **1997**, *13*, 59–61. [CrossRef]

41. Pintor, A.M.A.; Ferreira, C.I.; Pereira, J.C.; Correia, P.; Silva, S.P.; Vilar, V.J.; Botelho, C.M.; Boaventura, R.A. Use of cork powder and granules for the adsorption of pollutants: A review. *Water Res.* **2012**, *46*, 3152–3166. [CrossRef] [PubMed]
42. Fernandes, E.M.; Correlo, V.M.; Chagas, J.A.M.; Mano, J.F.; Reis, R.L. Cork based composites using polyolefin's as matrix: Morphology and mechanical performance. *Compos. Sci. Technol.* **2010**, *70*, 2310–2318. [CrossRef]
43. Gil, L. New cork-based materials and applications. *Materials* **2015**, *8*, 625–637. [CrossRef]
44. Silva, S.P.; Sabino, M.A.; Fernandes, E.M.; Correlo, V.M.; Boesel, L.F.; Reis, R.L. Cork: Properties, capabilities and applications. *Int. Mater. Rev.* **2005**, *50*, 345–365. [CrossRef]
45. Cardoso, B.; Mestre, A.S.; Carvalho, A.P.; Pires, J. Activated Carbon Derived from Cork Powder Waste by KOH Activation: Preparation, Characterization, and VOCs Adsorption. *Ind. Eng. Chem. Res.* **2008**, *47*, 5841–5846. [CrossRef]
46. Duarte, A.P.; Bordado, J.C. Cork–A Renewable Raw Material: Forecast of Industrial Potential and Development Priorities. *Front. Mater.* **2015**, *2*. [CrossRef]
47. Novais, R.M.; Caetano, A.P.F.; Seabra, M.P.; Labrincha, J.A.; Pullar, R.C. Extremely fast and efficient methylene blue adsorption using eco-friendly cork and paper waste-based activated carbon adsorbents. *J. Clean. Prod.* **2018**, *197*, 1137–1147. [CrossRef]
48. Wang, Q.; Lai, Z.; Mu, J.; Chu, D.; Zang, X. Converting industrial waste cork to biochar as Cu (II) adsorbent via slow pyrolysis. *Waste Manag.* **2020**, *105*, 102–109. [CrossRef] [PubMed]
49. Pires, R.A.; Mano, J.F.; Reis, R.L. Surface properties of extracts from cork black condensate. *Holzforsch. Int. J. Biol. Chem. Phys. Technol. Wood* **2010**, *64*, 217–222. [CrossRef]
50. Ponce-Robles, L.; Miralles-Cuevas, S.; Oller, I.; Agüera, A.; Trinidad-Lozano, M.J.; Yuste, F.J.; Malato, S. Cork boiling wastewater treatment and reuse through combination of advanced oxidation technologies. *Environ. Sci. Pollut. Res.* **2017**, *24*, 6317–6328. [CrossRef] [PubMed]
51. Madureira, J.; Pimenta, A.I.; Popescu, L.; Besleaga, A.; Dias, M.I.; Santos, P.M.P.; Melo, R.; Ferreira, I.C.F.R.; Cabo Verde, S.; Margaça, F.M.A. Effects of gamma radiation on cork wastewater: Antioxidant activity and toxicity. *Chemosphere* **2017**, *169*, 139–145. [CrossRef]
52. Ferreira, J.P.A.; Miranda, I.; Sousa, V.B.; Pereira, H. Chemical composition of barks from *Quercus faginea* trees and characterization of their lipophilic and polar extracts. *PLoS ONE* **2018**, *13*, 18. [CrossRef]
53. Touati, R.; Santos, S.A.O.; Rocha, S.M.; Belhamel, K.; Silvestre, A.J.D. The potential of cork from *Quercus suber* L. grown in Algeria as a source of bioactive lipophilic and phenolic compounds. *Ind. Crops Prod.* **2015**, *76*, 936–945. [CrossRef]
54. Lopes, M.H.; Gil, A.M.; Silvestre, A.J.D.; Neto, C.P. Composition of Suberin Extracted upon Gradual Alkaline Methanolysis of *Quercus suber* L. Cork. *J. Agric. Food Chem.* **2000**, *48*, 383–391. [CrossRef]
55. Santos, S.; Cabral, V.; Graça, J. Cork Suberin Molecular Structure: Stereochemistry of the C18 Epoxy and vic-Diol ω-Hydroxyacids and α,ω-Diacids Analyzed by NMR. *J. Agric. Food Chem.* **2013**, *61*, 7038–7047. [CrossRef]
56. Graça, J. Suberin: The biopolyester at the frontier of plants. *Front. Chem.* **2015**, *3*, 62. [CrossRef]
57. Silvestre, A.J.D.; Neto, C.P.; Gandini, A. Chapter 14-Cork and Suberins: Major Sources, Properties and Applications. In *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M.N., Gandini, A., Eds.; Elsevier: Amsterdam, The Netherlands, 2008; pp. 305–320.
58. Menager, C.; Guigo, N.; Vincent, L.; Sbirrazzuoli, N. Suberin from Cork as a Tough Cross-Linker in Bioepoxy Resins. *ACS Appl. Polym. Mater.* **2021**, *3*, 6090–6101. [CrossRef]
59. Pinto, P.C.R.O.; Sousa, A.F.; Silvestre, A.J.D.; Neto, C.P.; Gandini, A.; Eckerman, C.; Holmbom, B. *Quercus suber* and *Betula pendula* outer barks as renewable sources of oleochemicals: A comparative study. *Ind. Crops Prod.* **2009**, *29*, 126–132. [CrossRef]
60. Križková, L.V.; Lopes, M.H.; Polónyi, J.; Belicová, A.; Dobias, J.; Ebringer, L. Antimutagenicity of a suberin extract from *Quercus suber* cork. *Mutat. Res.-Genet. Toxicol. Environ. Mutagen.* **1999**, *446*, 225–230. [CrossRef]
61. Pereira, H. The Rationale behind Cork Properties: A Review of Structure and Chemistry. *Bioresources* **2015**, *10*, 6207–6229. [CrossRef]
62. Marques, A.V.; Rencoret, J.; Gutiérrez, A.; del Río, J.C.; Pereira, H. Ferulates and lignin structural composition in cork. *Holzforschung* **2016**, *70*, 275–289. [CrossRef]
63. Jové, P.; Olivella, M.À.; Cano, L. Study of the variability in chemical composition of bark layers of cork from different production areas. *BioResources* **2011**, *6*, 1806–1815.
64. Fernandes, E.M.; Aroso, I.M.; Mano, J.F.; Covas, J.A.; Reis, R.L. Functionalized cork-polymer composites (CPC) by reactive extrusion using suberin and lignin from cork as coupling agents. *Compos. B Eng.* **2014**, *67*, 371–380. [CrossRef]
65. Sadeghifar, H.; Venditti, R.; Jur, J.; Gorga, R.E.; Pawlak, J.J. Cellulose-Lignin Biodegradable and Flexible UV Protection Film. *ACS Sustain. Chem. Eng.* **2016**, *5*, 625–631. [CrossRef]
66. Asensio, A. Polysaccharides from the Cork of *Quercus suber*, II. Hemicellulose. *J. Nat. Prod.* **1988**, *51*, 488–491. [CrossRef]
67. Sousa, A.F.; Pinto, P.C.R.O.; Silvestre, A.J.D.; Neto, C.P. Triterpenic and Other Lipophilic Components from Industrial Cork Byproducts. *J. Agric. Food Chem.* **2006**, *54*, 6888–6893. [CrossRef]
68. Castola, V.; Bighelli, A.; Rezzi, S.; Melloni, G.; Gladiali, S.; Desjobert, J.M.; Casanova, J. Composition and chemical variability of the triterpene fraction of dichloromethane extracts of cork (*Quercus suber* L.). *Ind. Crops Prod.* **2002**, *15*, 15–22. [CrossRef]
69. Moiteiro, C.; Curto, M.J.M.; Mohamed, N.; Bailén, M.; Martínez-Díaz, R.; González-Coloma, A. Biovalorization of Friedelane Triterpenes Derived from Cork Processing Industry Byproducts. *J. Agric. Food Chem.* **2006**, *54*, 3566–3571. [CrossRef]

70. Teplova, V.V.; Isakova, E.P.; Klein, O.I.; Dergachova, D.I.; Gessler, N.N.; Deryabina, Y.I. Natural Polyphenols: Biological Activity, Pharmacological Potential, Means of Metabolic Engineering (Review). *Appl. Biochem. Microbiol.* **2018**, *54*, 221–237. [CrossRef]
71. de la Rosa, L.A.; Moreno-Escamilla, J.O.; Rodrigo-García, J.; Alvarez-Parrilla, E. Chapter 12-Phenolic Compounds. In *Postharvest Physiology and Biochemistry of Fruits and Vegetables*; Yahia, E.M., Ed.; Woodhead Publishing: Sawston, UK, 2019; pp. 253–271.
72. Sharma, A.; Shahzad, B.; Rehman, A.; Bhardwaj, R.; Landi, M.; Zheng, B. Response of Phenylpropanoid Pathway and the Role of Polyphenols in Plants under Abiotic Stress. *Molecules* **2019**, *24*, 2452. [CrossRef] [PubMed]
73. Cheynier, V.; Comte, G.; Davies, K.M.; Lattanzio, V.; Martens, S. Plant phenolics: Recent advances on their biosynthesis, genetics, and ecophysiology. *Plant Physiol. Biochem.* **2013**, *72*, 1–20. [CrossRef] [PubMed]
74. Kumar, S.; Pandey, A.K. Chemistry and Biological Activities of Flavonoids: An Overview. *Sci. World J.* **2013**, *2013*, 162750. [CrossRef] [PubMed]
75. Kumar, N.; Goel, N. Phenolic acids: Natural versatile molecules with promising therapeutic applications. *Biotechnol. Rep.* **2019**, *24*, 370. [CrossRef] [PubMed]
76. Cunha, M.; Lourenço, A.; Barreiros, S.; Paiva, A.; Simões, P. Valorization of Cork Using Subcritical Water. *Molecules* **2020**, *25*, 4695. [CrossRef] [PubMed]
77. Şen, A.; Miranda, I.; Santos, S.; Graça, J.; Pereira, H. The chemical composition of cork and phloem in the rhytidome of *Quercus cerris* bark. *Ind. Crops Prod.* **2010**, *31*, 417–422. [CrossRef]
78. Bouras, M.; Chadni, M.; Barba, F.J.; Grimi, N.; Bals, O.; Vorobiev, E. Optimization of microwave-assisted extraction of polyphenols from *Quercus* bark. *Ind. Crops Prod.* **2015**, *77*, 590–601. [CrossRef]
79. Batista, M.; Rosete, M.; Ferreira, I.; Ferreira, J.; Duarte, C.; Matias, A.; Poejo, J.; Crespo, J.; Valério, R.; Fraga, M.; et al. Extracto Hidro-Glicólico de Cortiça, Processo para a sua Preparação, Formulações Compreendendo o Referido Extracto e sua Utilização. 2015. Available online: https://patentimages.storage.googleapis.com/9f/01/2a/9d81e00f9817b0/WO2015152746A1.pdf (accessed on 4 January 2022).
80. Santos, S.A.O.; Pinto, P.C.R.O.; Silvestre, A.J.D.; Neto, C.P. Chemical composition and antioxidant activity of phenolic extracts of cork from *Quercus suber* L. *Ind. Crops Prod.* **2010**, *31*, 521–526. [CrossRef]
81. Santos, S.A.; Freire, C.S.R.; Domingues, M.R.M.; Silvestre, A.J.D.; Neto, C.P. Characterization of phenolic components in polar extracts of *Eucalyptus globulus* Labill. bark by high-performance liquid chromatography-mass spectrometry. *J. Agric. Food Chem.* **2011**, *59*, 9386–9393. [CrossRef] [PubMed]
82. Reis, S.F.; Coelho, E.; Evtuguin, D.V.; Coimbra, M.A.; Lopes, P.; Cabral, M.; Mateus, N.; Freitas, V. Migration of Tannins and Pectic Polysaccharides from Natural Cork Stoppers to the Hydroalcoholic Solution. *J. Agric. Food Chem.* **2020**, *68*, 14230–14242. [CrossRef] [PubMed]
83. Fernandes, A.; Fernandes, I.; Cruz, L.; Mateus, N.; Cabral, M.; Freitas, V. Antioxidant and Biological Properties of Bioactive Phenolic Compounds from *Quercus suber* L. *J. Agric. Food Chem.* **2009**, *57*, 11154–11160. [CrossRef]
84. Azevedo, J.; Fernandes, A.; Oliveira, J.; Brás, N.F.; Reis, S.; Lopes, P.; Roseira, I.; Cabral, M.; Mateus, N.; Freitas, V. Reactivity of Cork Extracts with (+)-Catechin and Malvidin-3-O-glucoside in Wine Model Solutions: Identification of a New Family of Ellagitannin-Derived Compounds (Corklins). *J. Agric. Food Chem.* **2017**, *65*, 8714–8726. [CrossRef]
85. Gabrielli, M.; Fracassetti, D.; Tirelli, A. Release of phenolic compounds from cork stoppers and its effect on protein-haze. *Food Control* **2016**, *62*, 330–336. [CrossRef]
86. Mota-Panizio, R.; Hermoso-Orzáez, M.J.; Carmo-Calado, L.; Lourinho, G.; de Brito, P.S.D. Biochemical Methane Potential of Cork Boiling Wastewater at Different Inoculum to Substrate Ratios. *Appl. Sci.* **2021**, *11*, 3064. [CrossRef]
87. Igueld, S.B.; Abidi, H.; Trabelsi-Ayadi, M.; Chérif, J.K. Study of physicochemicals characteristics and antioxidant capacity of cork oak acorns (*Quercus Suber* L.) grown in three regions in Tunisia. *J. Appl. Pharm. Sci.* **2015**, *5*, 26–32. [CrossRef]
88. Aroso, I.M.; Fernandes, E.M.; Pires, R.A.; Mano, J.F.; Reis, R.L. Cork extractives exhibit thermo-oxidative protection properties in polypropylene–cork composites and as direct additives for polypropylene. *Polym. Degrad. Stab.* **2015**, *116*, 45–52. [CrossRef]
89. Mukherjee, P.K.; Maity, N.; Nema, N.K.; Sarkar, B.K. Bioactive compounds from natural resources against skin aging. *Phytomedicine* **2011**, *19*, 64–73. [CrossRef]
90. Aroso, I.M.; Araújo, A.R.; Fernandes, J.P.; Santos, T.; Batista, M.T.; Pires, R.A.; Mano, J.F.; Reis, R.M. Hydroalcoholic extracts from the bark of *Quercus suber* L. (Cork): Optimization of extraction conditions, chemical composition and antioxidant potential. *Wood Sci. Technol.* **2017**, *51*, 855–872. [CrossRef]
91. Passi, S.; Nazzaro-Porro, M. Molecular basis of substrate and inhibitory specificity of tyrosinase: Phenolic compounds. *Br. J. Dermatol.* **1981**, *104*, 659–665. [CrossRef] [PubMed]
92. Sinha, P.; Srivastava, S.; Mishra, N.; Yadav, N.P. New Perspectives on Antiacne Plant Drugs: Contribution to Modern Therapeutics. *BioMed Res. Int.* **2014**, *2014*, 301304. [CrossRef] [PubMed]
93. Subhashini, S.; Begum, S.F.M.; Rajesh, G. Antimicrobial characterisation combining spectrophotometric analysis of different oak species. *Int. J. Herb. Med.* **2016**, *4*, 32–35.
94. Rattanata, N.; Klaynongsruang, S.; Daduang, S.; Tavichakorntrakool, R.; Limpaiboon, T.; Lekphrom, R.; Boonsiri, P.; Daduang, J. Inhibitory Effects of Gallic Acid Isolated from *Caesalpinia mimosoides* Lamk on Cholangiocarcinoma Cell Lines and Foodborne Pathogenic Bacteria. *Asian Pac. J. Cancer Prev.* **2016**, *17*, 1341–1345. [CrossRef]
95. Goncalves, F.; Correia, P.; Silva, S.P.; Almeida-Aguiar, C. Evaluation of antimicrobial properties of cork. *FEMS Microbiol. Lett.* **2016**, *363*, 6. [CrossRef]

96. Birkenstock-Natural Cosmetics. Available online: https://www.birkenstock.com/gb/natural-cosmetics/ (accessed on 4 January 2022).
97. CosIng-Cosmetics. Available online: https://ec.europa.eu/growth/tools-databases/cosing/index.cfm?fuseaction=search.simple (accessed on 4 January 2022).
98. ACTISCRUB™ Cork. Available online: https://cosmetics.specialchem.com/product/i-lubrizol-actiscrub-cork (accessed on 4 January 2022).
99. Suberlift™ Biofunctional. Available online: https://cosmetics.specialchem.com/product/i-ashland-suberlift-biofunctional (accessed on 4 January 2022).
100. DIAM Oléoactif®. Available online: https://cosmetics.specialchem.com/product/i-hallstar-diam-oleoactif (accessed on 4 January 2022).
101. The SCCS Notes of Guidance for the Testing of Cosmetic Ingredients and their Safety Evaluation-11th Revision. Available online: https://ec.europa.eu/health/system/files/2021-04/sccs_o_250_0.pdf (accessed on 6 January 2022).
102. Regulation (EC) No 1223/2009 of the European Parliament and of the Council. Available online: https://ec.europa.eu/health/system/files/2016-11/cosmetic_1223_2009_regulation_en_0.pdf (accessed on 6 January 2022).
103. Technical Document on Cosmetic Claims. Available online: https://ec.europa.eu/docsroom/documents/24847 (accessed on 6 January 2022).