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Review

Cistus ladanifer as a Potential Feedstock for Biorefineries: A Review

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Abstract: *Cistus ladanifer* (rockrose) is a widespread shrub species in the Mediterranean region well known due to its production of labdanum gum, especially in the hot season. Its leaves and branches can be subjected to different extraction and distillation processes to produce various types of extracts. The natural extracts of *C. ladanifer* have several applications, especially in the perfumery and cosmetics sector. *C. ladanifer* extracts, in addition to presenting interesting odoriferous properties, are also known for their bioactive properties, such as antioxidant and antimicrobial. Use of this species in animal feed or phytostabilisation of mining areas has also been successfully applied. On the other hand, the lignin and polysaccharides that are the major fractions from *Cistus* residues can be relevant sources of high-value products in a biorefinery framework. Recently, it has been reported that the residues obtained from the essential oil industry can sustain production of significant amounts of other marketable products, namely phenolic compounds, oligomeric and monomeric sugars, lignin, and lactic acid. All these applications show the potential of *C. ladanifer* as a raw material to be fully valued in a biorefinery context, contributing to important revenues and generating an associated marketable biobased product portfolio.

Keywords: added-value products; bioeconomy; biofuels; essential oils; integrated upgrade; rockrose

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1. Introduction

Cistus ladanifer L. (crimson-spot rockrose) is a wild perennial shrub species of the *Cistaceae* family and the *Cistus* genus that is mainly distributed in Mediterranean countries, such as France, Greece, Spain, Portugal, Morocco, Algeria, and Cyprus [1–6].

The *C. ladanifer* species includes three subspecies: *ladanifer* (. . .), *africanus* (Dans), and *sulcatus* (Demoly). The subsp. *ladanifer* is mainly distributed in the Iberian Peninsula, France, and northern Africa; the subsp. *sulcatus* is endemic to southwestern Portugal along the coastal cliff tops of Costa Vicentina; and the subsp. *africanus* is commonly found in northern Africa and also spread in southern Spain [7,8]. Subsp. *ladanifer* has an erect habit, generally with linear–lanceolate and lanceolate leaves [5,9]; subspecies *sulcatus* is a prostrated habit shrub (50 cm) when it grows near the sea or up to 200 cm and erect when protected from the wind, with white flowers and sessile leaves, generally elliptical or oblanceolate, with accentuated nervures in the upper surface [9]; and subsp. *africanus* has leaves with an apparent petiole, lanceolate–elliptic, or oblong to linear—generally

lanceolate—with little apparent nerves on the upper side, and other leaves oval or obovate, with well visible nerves on the upper side [10].

C. ladanifer is a shrub, generally erect, with a reddish-brown stem, hardwood, and sticky bark with striking vivid flowers (Figure 1). The 40–80 mm long leaves are impregnated by the labdanum, which makes them sticky and with a strong and specific smell [10]. It is considered a species of rapid growth and development that reproduces easily [11] by natural seed propagation during winter and autumn [5,12]. In gardening, *Cistus* spp. can be multiplied by stem cuttings and layering [13]. Vegetative propagation of *C. ladanifer* is carried out preferably in September and October using lateral cuttings of 1 to 15 cm in length (without flowering) with five or six pairs of leaves or also 8 to 12 cm long mature wooden stem stakes with a heel or knot [14]. Micropropagation by germinating seeds of *C. ladanifer* and other species of Cistus has also been successfully studied [15]. Exploitation of wild populations to produce essential oil and labdanum has been the main practice.

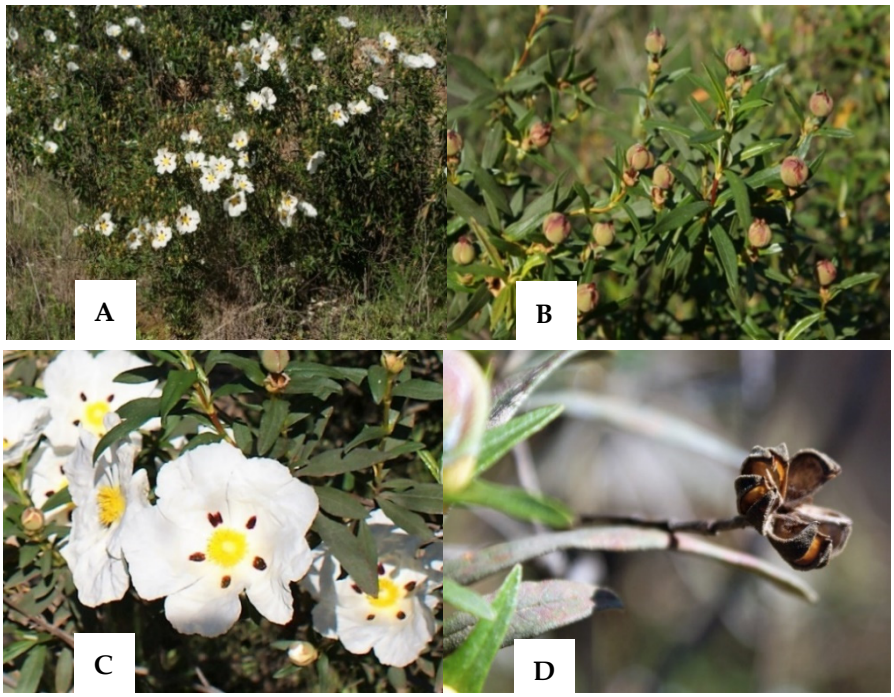

Figure 1. *Cistus ladanifer* L.: (**A**) whole plant; (**B**) flower buds; (**C**) flowers; (**D**) open cysts.

C. ladanifer occurs in a wide range of altitudes, latitudes, climates, and soil types, but it prefers acidic and siliceous soils [16,17] and dry areas with high insolation where it can give rise to large and dense populations. It has high-stress tolerance and, consequently, is competitive under various environmental conditions, including poor soils with low organic matter content, low pH, and high concentrations of trace elements, as well as hydric stress and high temperature and solar radiation [18]. This tolerance may be associated with activity of different isoenzymes, namely superoxide dismutase (SOD), peroxidase (POD), and catalase (CAT) [19], which are the major enzymes involved in detoxification of active oxygen species (AOS) [20]. An evaluation was made of As, Cu, Pb, and Zn concentrations and activity of the soluble and cell wall ionically bound forms of enzymes SOD, POD, and CAT in leaves of *C. ladanifer*. The enzymatic activity of these enzymes varied with populations of *C. ladanifer*, as well as with the seasons of the year, with specificity for each trace element and the location of the enzyme in the cells [19].

C. ladanifer shows an important adaptative mechanism in post-fire plant dynamics, and its recovery after burning is faster when compared with other shrub species (e.g., *Erica australis* and *Calluna vulgaris*) [21]. *Cistus* species tend to recover by an autosuccession process in areas affected by cutting and burning, being dominant after the first or second year [22]. Its strong heat resistance suggests that there is a break in seed dormancy by the

high temperatures during a fire; e.g., *Quercus* woodlands are occupied by *C. ladanifer* after fire [5]. A study under controlled conditions demonstrated an increase in the germination of seeds preheated at 100 °C when compared to seeds stored at room temperature [23]. *C. ladanifer* seeds and plantlets generally show rapid germination and growth [24].

The fruits are globular lignified capsules (cysts) that can produce 500 to 1000 seeds, and a single plant may produce 250 thousand seeds annually [25,26]. Mature fruits remain attached to the plant and release the seeds gradually when they open, allowing short-distance dissemination for a long time [5]. The seeds are small, allowing easy penetration and accumulation in the soil, and have a stiff and impermeable cover important for their longevity; however, they contain few nutrient reserves, which requires a quick start for the photosynthesis process [25]. The number of valves per fruit (five to twelve) can vary between populations, between plants, and within the same plant. Rockrose is a highly polymorphic plant and the only species of the *Cistaceae* family with a variable number of valves per fruit. This variation may be a result of natural selection, phenotypic plasticity, and developmental instability of the plant [27].

Rockrose flowers are white with a crimson spot on the base of the petals. There are two color varieties: *C. ladanifer* var. *albiflorus* with white petals and *C. ladanifer* var. *maculatus* with red stains at the petal base [28]. The flowers are large (ca. 64 mm in diameter), appear during spring (March–May), and produce abundant pollen and nectar [5,29]. The size and longevity of the flowers positively influence the incidence of folivores, mainly ants and beetles [30].

The ecosystem of *C. ladanifer* also provides high proliferation of edible mushroom species, some of which are in high demand due to their gastronomic interest [31]. Rockrose is also considered promising for phytoremediation and revegetation of contaminated soil in semi-arid climates as it is capable of colonizing these soils with a great capacity for tolerance and adaptability to adverse climatic conditions, e.g., droughts and high temperatures [17,32].

Cistus ladanifer (rock rose) is widespread throughout the Mediterranean basin, where it is a naturally occurring shrub. It is estimated that it extends to circa 2 million hectares in the south and southwest of the Iberian Peninsula [33], where it is the main shrub species with an important ecological role but also an actor in some challenging situations, such as regarding rural fires that take place in summer in these regions. Rockrose is an example of an underused species without any regular and complete exploitation, and it is currently mainly exploited by the perfumery industry or as an ornamental plant [14], generally associated with small family businesses or linked to rural organizations. There is still a lack of robust economic exploitation as well as developed value chains. Therefore, *C. ladanifer* is a natural and very relevant candidate to be considered as a biomass feedstock; furthermore, it also has an exploitation history, as reported as follows. This is the driving force for this work, which attempts to contribute to demonstrate the potential of rockrose to be fully valorized as a biorefinery feedstock.

2. Traditional Products from Rockrose

Rockrose plants have been traditionally used as an important resource for primary health care given their low cost, accessibility, and accumulated ancestral experience. The aerial parts of rockrose are used to produce extracts, obtaining exudates and essential oils with complex composition and pharmacological properties that make interesting further application targeted investigation [34]. Traditional use of rockrose has contributed to socio-economic development of rural communities [35]. Both labdanum and essential oil from *C. ladanifer* are much appreciated in perfumery, cosmetics, aromatherapy, and food flavors (restricted use), being used as ingredients in about 30% of modern perfumes due to their excellent fixative properties [36,37]. The *C. ladanifer* products are described in detail below.

2.1. Aromatic Extracts

Figure 2 summarizes the major conventional products obtained from rockrose for the perfumery/cosmetic industry and the main extraction methods used. Three main products can be obtained directly from the *C. ladanifer* plant: essential oil, using steam distillation or hydrodistillation, labdanum gum, employing hot alkaline extraction followed by acidulation, and cistus concrete, by extraction with apolar solvents, such as hexane and isopropanol. From these extracts, other products with interesting properties odoriferous and/or commercial can be further obtained, e.g., labdanum resinoid, labdanum oil, labdanum absolute from labdanum gum, and absolute from concrete. However, the portfolio of natural extracts obtained exclusively from *C. ladanifer* can still be more diversified for use in many applications, such as fragrance and flavoring ingredients, among which are hydrolate, labdanum resinoid 50%/DPG (dipropylene glycol synthetic), hydrocarboresine, dynamone, cistus absolute SIS, cistus by-absolute, cistus by-colorless, cistus organic oil, cistus water concentrate, and others [37].

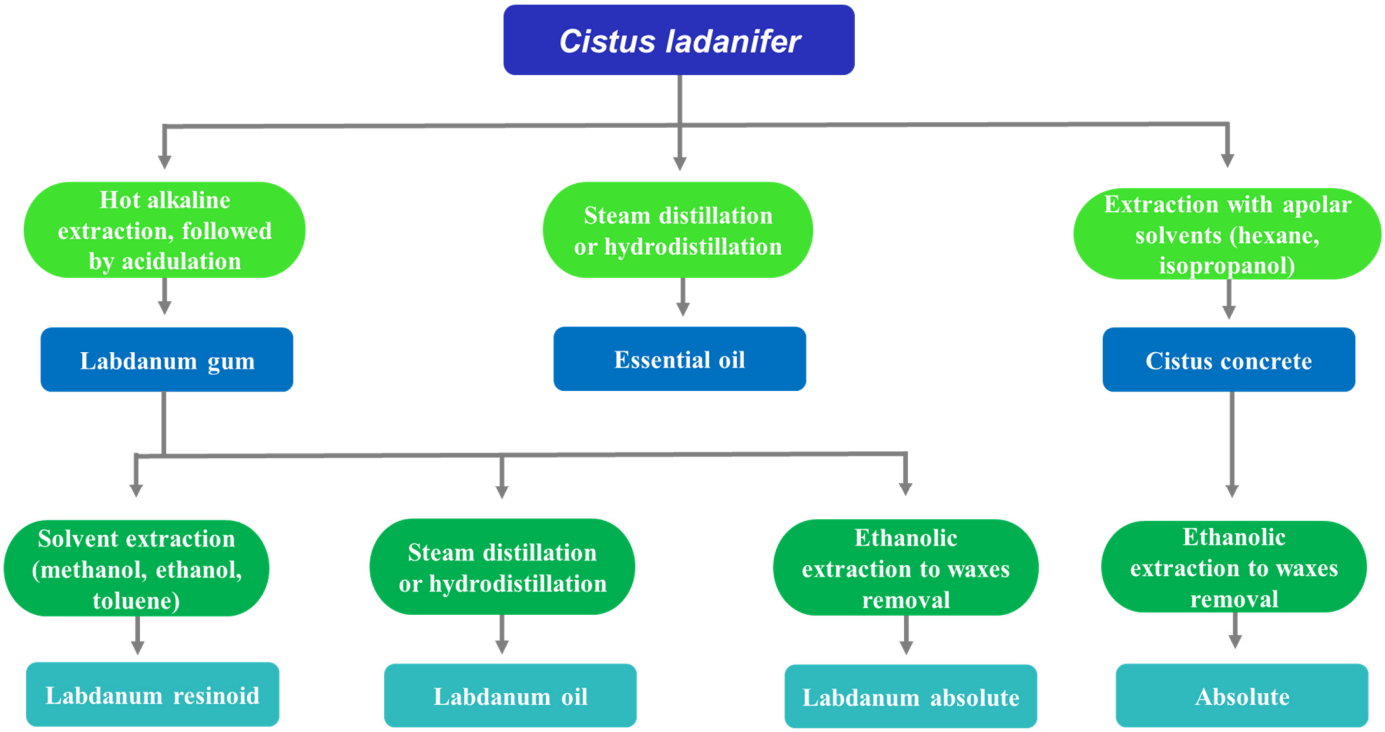

Figure 2. Main conventional aromatic extracts obtained from *C. ladanifer* and respective extraction methods.

2.1.1. Labdanum Gum

C. ladanifer produces a sticky resin or aromatic exudate known as labdanum, which has been used as a sedative, hemostatic, antiseptic, astringent, tonic, expectorant, and balsamic compound [38,39]. Labdanum has been studied mainly due to its interest in the perfumery industry. It is produced in the leaves and secreted by trichomes found in adaxial and abaxial leaf surfaces, especially in young leaves [11]. The subspecies *ladanifer* is the most important for obtaining labdanum since the other subspecies are not used for this purpose [35].

This resin makes rockrose highly flammable, which may cause problems in summer concerning the risk of fires since it is an abundant species in uncultivated areas and pastures [26,40,41]. On the other hand, *C. ladanifer* plays an important role as a bridge in recovery of forest stands after fire, providing mycorrhizal inoculum to colonize tree roots as the new stand develops [42].

There are reports of the presence of pollen from *C. ladanifer* and other *Cistaceae* species in 15th- and 16th-century cesspits in Belgium, suggesting their use for reducing bad smell [43]. The labdanum of *C. ladanifer* was also used as incense in Arabic countries [44].

Crude gum of labdanum is obtained from the surface of the plant leaves and branches by removing waxes, resinous matter, and oily materials by treatment with hot alkaline water (sodium carbonate), followed by acidification (sulfuric acid). Most of the water is removed from the crude labdanum gum by evaporation. Another way to obtain the raw gum is by boiling the leaves and young stems in water, purifying and drying the liquid mass. The yields of labdanum resin in dry weight to fresh weight of the plant are circa 7.4% obtained with alkaline extraction at bench scale [45] and 2–2.5% with water boiling (Zamorano method) (total fresh weight of the plant) [35]. The labdanum is dark brown, making up a pasty mass or a brittle solid.

The typical odor originates from several compounds formed by oxidative degradation of diterpenes with the labdane skeleton, which are the main constituents of labdanum gum [46].

In perfumery, it has been used as a technical ingredient due to its sticky mechanical properties, being suitable for incense sticks or other products to burn. In cosmetics, it can be used in masks, make-up removers, and creams [37].

Different products can be obtained from crude labdanum, where the main conventional ones are resinoid of labdanum, labdanum oil, and labdanum absolute. Labdanum resinoid is extracted from the crude gum by methanol, ethanol, or toluene solubilization, followed by concentration, in yields around 50% to 95%. It is a red–brown and pasty substance. This product consists mainly of nonvolatile and resinous compounds and is an excellent natural fixative; due to its high viscosity, it sometimes needs dilution for better processing [46]. Resinoid offers slightly resinous woody notes very faithful to the smell of the raw gum exuded by the twigs. Labdanum resinoid is particularly suitable for fumet and meat aromas [37].

Labdanum oil is obtained from the gum by steam distillation or hydrodistillation and represents the odoriferous principles of the gum in its most concentrated form with a warm and amber-like odor [2,46]. Weyerstahl et al. [2] identified 186 compounds from the neutral and acid fractions of a commercial labdanum oil. The main constituents from the neutral fraction were ledene (9.3%), viridiflorol (4.3%), and cubeban-11-ol (4.1%), while other neutral compounds with circa 1.2% were 1,5-cis-aromadendr-9-ene, allo-aromadendrene, eugenol, myrtenol, borneol, pinocamphone, bornyl acetate α-copaene, 1,2-dehydroviridiflorol, palustrol, ledol, copaborneol, and ambrox®. The main constituents of the acid fraction were dihydrocinnamate (6.5%), myrtenate (6%), palmitate (5.1%), labd-8(17)-enoate (5.1%), and labd-7-enoate (6.3%).

Labdanum absolute, an almost colorless oil, is also obtained from the gum by precipitating the waxes in cold using alcohol. Labdanum absolute represented ~70% of the resin, principally composed of labdane-type diterpenes (75%) and methylated flavonoids (15%), and its anti-inflammatory and UV protection properties demonstrate potential to be valued as a cosmetic ingredient for skincare [45].

2.1.2. Concrete

Concrete is a viscous product with a balsamic odor that is extracted from the whole plant using apolar solvents (hexane or isopropanol, for example). After evaporation of the solvent, the extract contains a volatile fragrance and waxy compounds. Thus, concrete is not completely soluble in alcohol, being occasionally used as a perfume ingredient and more appreciated for use in the perfume of soaps [46]. In cosmetics and compositions dedicated to candles, concrete provides a slightly woody, resinous, and soft touch [37]. Chemical analysis of *C. ladanifer* concrete showed high content of diterpenes, namely derivatives of the bicyclic diterpene labdane, with the major neutral compounds identified being pentyltricontane ($C_{35}H_{72}$) (18.1%), Iabd-14-ene-16, l8-diol (6.7%), 16-kaurene (4.6%), labda-8(20),13(16) (4.6%), labd-14-ene-8,13-diol (4.5%), and octadecane (4.5%), and the major acid

compounds were labda-8.14-dienoic acid (9.8%), labdanoic acid (8.9%), labda-7,8-dienoic acid (6.9%), and labda-8.20-dienoic acid (4.7%) [28].

Absolute is prepared from the concrete by extraction with polar solvents (e.g., ethanol) under continuous agitation and moderate heating [28]. After cooling the extract, the waxes are removed by filtration. Ethanol is evaporated and the wax-free residue is called absolute. Unlike concrete, absolute is completely soluble in ethanol and can be used as an ingredient in perfumes, especially as a fixative agent [46]. Analysis of the neutral fraction of absolute from concrete showed mainly $C_{13}H_{20}O$ (9.0%), labd-14-ene-8,13-diol (6.6%-), and labd-14-ene-16,18-diol (6.0%-), and it showed labdenoic acid (12.7%) and labdanoic acid (9%) from the acid fraction [28].

2.1.3. Essential Oils

Essential oils are organic compounds responsible for aroma and are involved in the defense mechanisms of several species [47]. They can be synthesized by any plant organ and are stored in secretory cells, cavities, canals, epidermic cells, or glandular trichomes. In general, their density is lower than that of water, and they are soluble in lipids and organic solvents. Essential oils are known for their antimicrobial, analgesic, sedative, anti-inflammatory, and spasmolytic properties [48]. They also attract insects, favoring dispersion of seeds and pollens, and simultaneously repel other undesirable insects [48].

Essential oils act as concentrated medicinal and aromatic sources, which have been widely utilized across industries in medical products, food and beverages, spa and relaxation, cleaning agents, and others. They are increasingly utilized as the main component in personal care products, including soaps and cosmetics. They are also used extensively by the perfumery industry in perfumes, room fresheners, and deodorants [49].

The main components of essential oils are hydrocarbons, especially terpenes, and oxygenated compounds, such as alcohols, aldehydes, esters, ketones, phenols, and oxides. Most of the compounds of essential oils are monoterpenes (corresponding to about 90%), followed by sesquiterpenes [47]. In general, commercial cistus oils have a high content of easily degradable monoterpenes and require further processing by the perfumery industry to obtain better-quality products [29].

The methods to obtain essential oils from plants are hydro distillation, steam distillation, solvent extraction, and supercritical extraction [50]. Drawbacks of distillation are the time required and loss of valuable water-soluble compounds. Solvent extraction is carried out at lower temperatures, but there is co-extraction of non-volatile compounds that requires a cleaning step that may cause loss of important volatile components. Supercritical fluid extraction, although still an expensive technique, is an interesting alternative once the operating conditions are adjusted towards extraction selectivity, although co-extraction of waxes is unavoidable, requiring their subsequent separation [51].

C. ladanifer is particularly interesting as a source of essential oils for the cosmetics and perfume industry [52]. The rockrose plants used in distillation are 2- to 5-year-old whole plants, and, although the plant harvest may putatively occur all year, the oil yield is higher in the warmer seasons. The *C. ladanifer* oil yield is in the order of 45 mL per 100 kg of fresh material, with a market value of 4–9 € per mL of essential oil. When the material is ground, the yield can increase to around 1%. Some authors have reported yields between 0.14 and 0.3% from dry plant material [29,52,53].

Table 1 shows the major constituents detected in *C. ladanifer* essential oil from plants grown in different regions. The diversity observed can be due to several factors, such as climatic and soil variations, the stage of the vegetative cycle, seasonal factors, part of the plant analyzed, and the method used to obtain the essential oil, among others [54].

Table 1. Chemical composition (relative % of the peak area) of *C. ladanifer* essential oils from plants grown in different countries: center-interior of Portugal [29], central Spain [52], Corsica with plants of Spanish origin [55], and eastern Morocco [53].

Component	Centre Interior of Portugal [a]	Central Spain [a]	Corsica (Spanish Origin) [b]	Eastern Morocco [a]
Monoterpene hydrocarbons				
Tricyclene	-	-	-	2.7
α-Pinene	2.1	4.70	39	4.2
Camphene	0.3	0.64	2.1	15.5
Pinocarvone	1.1	-	0.9	-
Limonene	-	0.37	1.7	-
γ-Terpinene	-	0.10	0.4	3.8
α-Terpinene	-	-	0.1	1.8
p-cymenene	-	1.17	1.7	2.3
Oxygenated monoterpenes				
Bornyl acetate	1.6	7.03	3.1	
Terpinen-4-ol	1.0	6.37	1.1	6.3
α-Terpineol	-	2.20	-	1.2
trans-pinocarveol	2.1	20.00	1.9	
Borneol	0.7	-	0.8	11.1
Myrtenal	0.7	2.26	0.5	-
cis-Pinocamphone	-	3.84	-	-
2 (10)-Pinen-3-one	-	5.05	-	-
Verbonene	-	0.85	0.3	0.8
Camphor	-	0.86	-	1.5
p-Mentha-1,5-dien-8-ol	-	4.78	-	-
Sesquiterpene hydrocarbons				
Viridiflorene	1.3	0.41	-	-
$C_{15}H_{26}O$ sesquiterpene alcohol	6.0	-	-	-
Cyclosativene	-	0.70	0.7	0.6
Aromadendrene	-	1.77	-	-
Allo-aromadendrene	0.8		1.9	-
α-Copaene	-	0.62	0.8	-
α-Cubebene	-	-	-	2.2
δ-cadinene	1.0	-	0.8	6.4
Oxygenated sesquiterpenes				
Viridiflorol	17.4	13.59	11.8	2.8
Spathulenol	0.8	0.53	0.5	-
Globulol	5.0	-	0.3	-
Ledol	-	4.36	3.3	-
Caryophyllene oxide	1.8	-	-	-
Palustrol	-	0.50	-	-
Others				
2,2,6-trimethylcyclohexanone	2.8	-	0.9	7.3
Phthalates				
Diethyl phthalate	-	-	-	2.9
Bis (2-ethylhexyl) phthalate	-	-	-	0.2
Material used for hydrodistillation	dry leaves and small branches	fresh leaves	leaves and stems	dry leaves

[a] components identified using gas chromatography (GC) and/or gas chromatography/mass spectrometry (GC/MS); [b] components identified by C-NMR spectroscopy and GC.

More than 400 compounds have already been detected in essential oil compositions of *C. ladanifer*, including those present in trace amounts [29]. It is noteworthy that the content of viridiflorol was high for *C. ladanifer* oil produced in Portugal, Spain, and France, reaching 17.4%, 13.6%, and 11.8% of the oil, respectively. Cistus oils from Portuguese plants present organoleptic advantages because they are rich in amber-like compounds and have

a low content of monoterpenes [29]. There are differences between Portuguese varieties of *C. ladanifer* even if grown in the same place. Populations of *C. ladanifer* var. *maculatus* have higher concentrations of α-pinene, β-pinene, γ-terpinene, and verbenone than populations of *C. ladanifer* var. *albiflorus* [56].

Trans-pinocarveol was the main compound in *C. ladanifer* essential oil obtained from plants grown in central Spain; viridiflorol, bornyl acetate and terpinen-4-ol also presented important concentrations, setting up an essential oil rich in oxygenated compounds. *C. ladanifer* grown in Corsica showed high percentages of α-pinene; viridiflorol was one of the main compounds identified in the oils of *C. ladanifer* grown in Portugal, Spain, and France, while the main components from *C. ladanifer* from Morocco were camphene and borneol, which presented small amounts in the samples from the other countries.

Viridiflorol and bornyl acetate are compounds that may be responsible for the antimicrobial power of the cistus oil against several pathogenic strains (*E. coli, B. megaterium*, *S. aureus*, *A. niger*, *B. cinerea*, *M. racemosus*) [28]. The potential of cistus oil to inhibit or block germination of weed species (e.g., *Amaranthus hybridus*, *Portulaca oleracea*, *Chenopodium album*, *Conyza canadensis*, and *Parietaria judaica*) was also demonstrated in vitro [52].

Zidane et al. [53] also found phthalates, esters of phthalic acid, mainly applied as plasticizers and which are considered hazardous to human health [57,58]. Losses in the manufacturing processes and leaching out from material can contaminate the environment [59]. Contamination of water and soil by phthalate derivatives can result in their absorption and accumulation by plants [58]. Due to this exposure, these compounds have been detected in essential oils and an aqueous phase from medicinal plants and food crops [58,60,61].

Many other compounds occurred in small amounts in the essential oils of *C. ladanifer*. The odors and flavor of the essential oil result from the combination of all these components, including the trace components [62].

Ecotoxicological evaluation of essential oils and hydrolates of *C. ladanifer* using *Daphnia magna* as a model organism in acute toxicity tests suggested that they do not present a toxic risk to the environment. The essential oil of *C. ladanifer*, for example, showed an EC50 value of 201.1 and 199.7 mg/L at 24 and 48 h, respectively [63]. However, the European Chemicals Agency (ECHA) classified an essential oil from *C. ladanifer* as toxic to *D. magna* with EC50 below 100 mg/L after 24 and 46 h of exposure [64]. This study does not report the details of the chemical composition of rockrose essential oil, nor the relationship of any chemical component with its toxicity. However, the safety data sheet for α-pinene (CDH—Central Drug House), one of the most abundant components of *C. ladanifer*, reports its toxicity to *D. magna* (EC50 of 41 mg/L—48 h). The differences in toxicity can be explained due to chemical variations that may occur in the composition of essential oils [63], taking into account the time of year when the plant was harvested and the extraction process [65]. In general, the relative amount of monoterpene hydrocarbons obtained by steam distillation was higher in March and lower in August (79.6% and 49.7%, respectively). On the other hand, the relative fraction of sesquiterpene hydrocarbons was higher in summer than in late winter (2.3%—March; 9.2%—August) [65].

2.2. Extractives

Both labdanum and essential oil are extractives obtained by selective extraction methods, but the extractives highlighted in this section correspond to a wider set of non-structural compounds that can be removed from the plant. Extractives comprise a wide variety of chemical compounds, generally of low molecular weight, that are not structural compounds of the plant cell walls [66]. They can come from two general sources: (1) primary metabolites that include sugars, amino acids, simple fats, and various carboxylic acids, among others; and secondary metabolites, which are generally more complex compounds, such as starch, sitosterol, simple terpenoids, chlorophyll, phenylpropanoids, and phenolics; and (2) artefacts arising from later modifications of the metabolites or even from external sources, such as metabolites of microorganisms or lichens [67].

The usual procedures for isolating extractives include traditional techniques (maceration, decoction, digestion, infusion, boiling under reflux, Soxhlet) and a wide range of modern techniques that have been introduced in recent decades (microwave-assisted extraction, ultrasound, fluid extraction supercritical, pressurized liquid extraction, enzyme-assisted extraction, among others) [68].

Table 2 shows the major phytochemical categories of volatile and non-volatile compounds isolated from extracts solubilized from different parts of *C. ladanifer* that were identified using various chromatographic and spectroscopic methods.

Table 2. Major phytochemical constituents of *C. ladanifer* extracts obtained from various parts of the plant.

Compound	Chemical Group	Part of the Plant	References
Volatile compounds			
α-Pinene	**Monoterpene hydrocarbons**	Aerial part; shoots	[6,32]
Camphene		Aerial part; shoots	[6,32]
Pinocarvone		Aerial part; shoots	[6,32]
Limonene		Aerial part	[6]
α-Phellandrene		Leaves	[69]
γ-Terpinene		Aerial part	[6]
α-Thujene		Aerial part	[6]
p-cymene		Aerial part	[6]
Bornyl acetate	**Oxygenated monoterpenes**	Aerial part; shoots	[6,32]
Terpinen-4-ol		Aerial part; shoots	[6,32]
α-Campholenal		Aerial part	[6]
trans-pinocarveol		Aerial part	[6]
Borneol		Leaves; aerial part	[6,69]
Myrtenal		Aerial part	[6]
(cis)-Verbenol		Leaves; shoots	[32,69]
Verbonene		Leaves; aerial part; shoots	[6,32,69]
Camphor		Leaves; shoots	[32,69]
Viridiflorol		Shoots	[32]
Globulol	**Oxygenated sesquiterpenes**	Shoots	[32]
Ledol		Leaves	[69]
Caryophyllene oxide		Shoots	[32]
Eugenol	**Phenylpropene**	Leaves	[69]
Benzenepropanoic acid	**Phenylpropanoid**	Shoots	[32]
2-Phenylethanol	**Alcohol**	Leaves; aerial part	[6,69]
Acetophenone	**Aromatic ketone**	Leaves	[69]
Thuja-2,4(10)-diene	**Others**	Aerial part	[6]
Rhododendrol		Shoots	[32]
2,2,6-trimethylcyclohexanone		Leaves; aerial part; shoots	[6,32,69]
Soluble compounds (phenolics)			
Apigenin	**Flavonoids**	Leaves; aerial part; whole plant	[4,70,71]
Apigenin-6-C-glucose-8-C-glucose		Leaves	[72]
Apigenin methylether		Whole plant	[4]
Kaempferol dimethylether		Aerial part; leaves; whole plant	[4,71,72]
Kaempferol diglycoside		Whole plant	[4]
4′(o)methyl-apigenin		Leaves	[70]
7(*o*)methyl-apigenin		Leaves	[70]
3-methyl-kaempferol		Leaves	[70]
4′-dimethyl-kaempferol		Leaves	[70]
3,7-dimethyl-kaempferol		Leaves	[70]
3,7,4′-trimethyl-kaempferol		Leaves	[70]
Kaempferol methylether		Aerial part; leaves	[71,72]
Quercetin-O-hexoside-Ohexoside		leaves	[72]
Epigallocatechin		Aerial part; leaves	[71,72]

Table 2. *Cont.*

Compound	Chemical Group	Part of the Plant	References
Gallic acid	**Phenolic acids and derivatives**	Aerial part	[71]
Glucogallin (isomer)		Aerial part	[71]
Gentisoyl glucoside		Aerial part; whole plant	[4,71]
Digaloil-*β*-D-glucopiranose		Aerial part	[71]
Galloyl glucose		Leaves	[72]
Mirciaphenone B		Aerial part	[71]
Punicalagin isomer 1	**Ellagic acid and derivatives**	Aerial part, leaves	[71,72]
Punicalagin isomer 2		Aerial part, leaves	[71,72]
Punicalagin gallate 1		Leaves	[72]
Punicalagin gallate 2		Leaves	[72]
Punicalin		Aerial part; whole plant	[4,71]
Cornusiin		Aerial part	[71]
Ellagic acid-7-xyloside		Aerial part	[71]
Ellagic acid		Aerial part	[71]
Ducheside A		Aerial part	[71]
Shikimic acid	**Others**	Aerial part Whole plant	[4,71]
Quinic acid		Aerial part Whole plant	[4,71]
Hexahydroxydiphenoyl-D-glucose (isomer)		Aerial part	[71]
Phenethyl-β-primeveroside		Aerial part	[71]

Extractives of *C. ladanifer* are rich in terpenoids, such as monoterpenes, sesquiterpenes, labdane-type, diterpenes, and phenylpropanoids, including flavonoids, phenolics, and tannins, and carbonylic compounds [44].

Phenolic compounds are considered one of the most important groups of plant secondary metabolites due to their large participation in development of morphological, physiological, and reproductive processes [73]. They comprise one or more aromatic rings with hydroxyl groups [74] and may be grouped into several categories, such as phenolic acids and analogs, flavonoids, tannins, and stilbenes, among others.

Flavonoids and diterpenes (C20-carbon) are the main secondary metabolites and can contribute to a variety of functions, such as defense purposes, and are also precursors of hormones, such as tocopherols and gibberellins [71]. Monoterpenes (C10-carbon) and sesquiterpenes (C15-carbon) are volatile compounds that contribute to plant odors and are repellants for herbivores, respectively [44]. Flavonoids may vary according to the season since their synthesis is induced by climatic factors [75]. Flavonoids such as apigenin, 4′-methyl-apigenin, 7-methyl-apigenin, 7,4′-dimethyl-apigenin, 3-methyl-kaempferol, 3,4-dimethyl-kaempferol, 3,7-dimethyl-kaempferol, and 3,7,49-trimethyl-kaempferol can be found in the leaf resin [70]. Phenolic compounds such as ferulic acid, *p*-hydroxybenzoic, vanillic, *p*-coumaric, and caffeic acids, in association with terpenes (α and β-pinene), have been detected not only in aqueous extracts but also on soil samples occupied by *C. ladanifer* [76]. Ellagitannins, in particular punicalagins derivatives, are the main compounds found in the aqueous extract of the aerial part of *C. ladanifer*, with 0.24% of the extract for gallic acid and 3.50% for all ellagitannins. Tannin content has a significant proportion of 6.8% of the total dry matter of the extract [77].

Diterpenes and flavonoid contents vary seasonally. The maximum concentration of diterpenes in the leaves occurs in winter and the minimum in spring–summer, but the maximum production of flavonoids is detected in summer and the minimum in winter. Low temperatures increase the amount of diterpenes, and higher temperatures increase the concentration of flavonoids [78]. Flavonoids are systematically lower in plants grown in shaded areas than in those grown in open areas. These compounds protect plants from the harmful effects of UV radiation, and irradiation is the main inductor in production of flavonoids. This induction may be synergistically increased by drought, where there is higher production of methylated flavonoids (kaempferols and 7-methylated apigenins),

suggesting that the methylated form is part of the defense mechanism of the plant against hydric stress [79]. Seasonal variations in the levels of phenolic compounds and condensed tannins have also been reported [80]. Accumulation of phenolic substances in various tissues and their deposition in cortical cells defend the plants from predators and protect the internal tissues against UV-B radiation, respectively [81].

Vitamins, reducing sugars, and polyunsaturated fatty acids (PUFA) were also detected in rockrose. *C. ladanifer* leaves presented a very high level of ascorbic acid (647.6 µg/g dry weight of the plant) and of sugars such as fructose, glucose, sucrose, and raffinose, fructose being the most abundant (48.2 mg/g of the dry weight of the plant). Fatty acids such as eicosadienoic acid, arachidic acid, and linolenic acid were identified in cistus extracts [82]. The highest concentration of PUFA occurs in winter and spring and that of branched-chain fatty acids (BCFA) in summer [83].

3. Bioactivity

Various compounds from different phytochemical groups identified in rockrose are associated with different biological activities, namely antibacterial, antiviral, and antioxidant activities (Table 3). The functional diversities presented by these compounds offer many opportunities for development of new drugs and represent excellent sources for production of food additives, functional foods, nutritional and nutraceutical products for pharmaceutical industries, and natural food companies [84].

Table 3. Biological activities of *C. ladanifer* extracts obtained with different solvents from different plant parts.

Plant Part	Type of Extract	Biological Activities	References
Fresh leaves from flowering stems	Methanol/water extract	Antifungal	[72]
Leaves	Aqueous extract	Autotoxicity	[12]
Wood/stalks, bark, and leaves	Ethanol extract and Acetone extract	Antioxidant	[85]
Leaves	Aqueous extract	Allelopathic	[76]
Aerial parts	Aqueous extract	Antihypertensive	[86]
Whole plant	Hydroalcoholic and spray-dried/spray-dried aqueous extract	Antibacterial	[4]
Leaves	Aqueous extract	Antioxidant Antimicrobial, Cytotoxic activity against human cancer cells	[77]
Leaves	Flavonoids extract	Allelopathic	[87]
Shoots	Water-soluble and volatile compounds	Phytotoxic	[88]
Leaves and small branches Whole plant	Essential oil Labdanum extracts	Antitungical, Antibacterial	[28]
Aerial parts	Essential oil	Herbicidal activity	[52]
Fruits, stems, flowers, and leaves	Essential oil water, ethanol, ethanol: water (50:50), methanol, methanol: water (50:50), acetonitrile	Antioxidant	[53]
Aerial parts	Hydrolates volatiles Essential oil	Antioxidant Anti-inflammatory Antimicrobial	[65]

3.1. Antimicrobial Activity

C. ladanifer is known for its antimicrobial properties due to the phenolic compounds that are present in the plant exudate [89]. Antifungal effects against species responsible for diseases such as *C. glabrata*, *C. parapsilosis,* and *C. albicans* (MIC < 0.05 mg/mL) were observed in rockrose phenolic extracts containing phenolic acids and their derivatives, ellagic acid derivatives, and flavonoids (catechins, flavonols, and flavones) [72]. Cistus extracts can be considered good antibacterial agents, in particular against Gram-positive bacteria (e.g., *Staphylococcus aureus*), possibly due to the combination of ellagitannins present in the extracts [77].

Hydroalcoholic and aqueous extracts obtained with different drying methods exhibited stronger antibacterial activity and higher levels of polyphenolic compounds compared to freeze-dried aqueous extracts, possibly due to degradation during extract preparation of some polar compounds that contribute to inhibition of Gram-positive bacteria (e.g., cyclohexane carboxylic acids, hexa-hydroxydiphenyl glucose, gallotannins, punicalin, and epigallocatechin) [4]. On the other hand, the inhibitory activity against Gram-negative bacteria is associated with the presence of galloylated flavonols and some specific flavonols [4]. Essential oils isolated from *C. ladanifer* showed weak antimicrobial activity against *E. coli*, *S. aureus*, and *C. albicans* [65], while Karkouri et al. [90] reported remarkable results regarding the antimicrobial power of *C. ladanifer* essential oil with inhibition of several bacteria species (*S. aureus*, *Salmonella typhi*, *E. coli*, and *Acinetobacter baumannii*), yeasts (*Candida* sp such as *C. tropicalis*, *C. glabrata*, *C. dubliniensis*, and *Rhodotorula rubra*, *Cryptococcus neoformans*), and fungi (*Penicillium* sp., *Fusarium* sp., and *Aspergillus niger*) that the authors believed to be mediated mainly by the presence of oxygenated sesquiterpenes, such as viridiflorol, pinocarveol, bornylacetate, and ledol. Concrete and absolute extracts have shown interesting inhibitory efficiency on growth of various strains (e.g., *E. coli*, *Bacillus megaterium*, *S. aureus*, *Aspergillus niger*, *Botrytis cinerea*, *Mucor racemosus*) [28].

3.2. Antioxidant Activity

The antioxidant power of *C. ladanifer* essential oil and different extracts has been determined by different methods, including DPPH and ABTS radical scavenging capacity assay, oxygen radical absorbance capacity (ORAC) assay, superoxide dismutase (SOD) assay, ferric reducing antioxidant potential (FRAP) assay, and xanthine method [53,65,77,85,91,92]. In general, the results revealed significant antioxidant activity of *C. ladanifer*. An ethanolic extract, for example, has displayed radical scavenging activity about two times higher than that of Trolox (antioxidant standard) [85]. An aqueous extract of leaves showed 5% of DPPH inhibition and 27% of ABTS inhibition [91]. Extracts from different *C. ladanifer* parts exhibited higher scavenging ability of DPPH radicals when compared to *C. ladanifer* essential oils [53]. Essential oil obtained by different extraction methods and from plants collected at different times of the year also showed strong inhibition (97–99%), determined by the xanthine method [65]. However, additional studies are needed to identify the chemical compounds that contribute to the antioxidant activities of these extracts and thus better understand their mechanism as radical scavengers [77,85].

Antioxidant properties of *C. ladanifer* essential oils, as well as their antibacterial and anti-quorum sensing inhibitor bioactivities, have also been explored to develop bioactive packaging for oxidation and rancidity susceptible foods by production of bioactive pullulan-based films containing rockrose essential oils [88].

3.3. Allelopathic Activity

The allelopathic ability of phytotoxic compounds present in *C. ladanifer* exudates is associated with decreased richness and diversity in species that share the same habitat [93], such as *Phillyrea angustifolia*, *Phillyrea latifolia*, *Rhamnus alaternus*, *Halimium ocymoides*, *Cistus populifolius*, *Erysimum lagascae*, *Brassica barrelieri*, *Silene tridentata*, and *Moricandia moricandioides* [76]. Direct incorporation of phenolic compounds into the soil occurs through falling

of the leaves, and, although present in low levels in the order of mg/g, they have high persistence (ca. 10 months) and a negative effect on regeneration [93].

The auto-allelopathic potential of *C. ladanifer* was also demonstrated by using an aqueous solution from leaves for inhibiting germination and cotyledon emergence of its seeds [12].

Due to its allelopathic properties, *C. ladanifer* may be an alternative to current herbicides used as pesticides in agriculture. The phytotoxic effect of *p*-cresol, 2-phenylethanol, and 3-phenyl-1-propanol, a phenolic component abundant in the labdanum of *C. ladanifer*, was evaluated in a static acute toxicity test using *Allium cepa* and *Lactuca sativa*, and the results showed that the three compounds, whether pure or in a mixture at 1mM, inhibited germination, germination rate, and seedling development of these species in paper tests, while soil tests attenuated their effect on the size of roots and cotyledons since physical, chemical, and biological soil factors can interfere with their activities [94].

The autotoxicity of *C. ladanifer* has been attributed to the presence of diterpene compounds in the exudate of the leaves since tested diterpenes solutions (0.26 g/L, 0.13 g/L, and 0.065 g/L) were able to negatively affect germination, seedling size, and seedling establishment of *C. ladanifer* [95]. However, additional studies are needed to better understand the action of these compounds, as well as their soil stability.

3.4. Antihypertensive Activity

A pharmacological study on *C. ladanifer* aqueous extracts demonstrated their antihypertensive effect. An aqueous extract of cistus leaves (500 mg/kg/day in oral administration) reduced the systemic blood pressure of two models of experimental hypertension, the L-NAME and renovascular 2K-1C, acting in a preventive and curative manner, and a reversal of the endothelial dysfunction in both animal models was also observed [86]. Further studies are needed to identify the chemical compounds involved in the process.

3.5. Antitumoral Activity

Cistus extracts were able to inhibit proliferation of pancreatic cancer cells M220 and MCF7/HER2 and JIMT-1 breast cancer cells, but this cytotoxic potential on cancer cells merits further investigation regarding their potential mechanism [77].

Flavonoids are generally nontoxic and associated with diverse biological activities, including prevention of cancer. Some epidemiological studies have associated the high dietary intake of flavonoids present in fruits and vegetables with low cancer prevalence in humans; in vivo and in vitro assays demonstrated action in carcinogen inactivation, antiproliferation, cell cycle arrest, induction of apoptosis and differentiation, inhibition of angiogenesis, antioxidation, and reversal of multidrug resistance, or a combination of these mechanisms [96].

3.6. Hypoglycemic and Hypolipidemic Activities

Treatment using cistus aqueous extract was applied in diabetic rats: a dose of 500 mg/kg body weight administered orally for 28 days occasioned a reduction in the levels of blood glucose, alanine aminotransferase, aspartate aminotransferase, urea, and creatinine while also reducing total cholesterol, triglycerides, and low-density lipoprotein–cholesterol levels [97].

4. Novel and Potential Applications

Other potential applications have been suggested for *C. ladanifer* besides traditional use of extracts in their already well established application in the perfumery industry as a fixative of perfumes. Some of the new directions regarding valorization of rockrose include phytoremediation of soils contaminated by heavy metals, use of the plant for feed with nutritional benefits for animal health, and use as a lignocellulosic raw material for added value products, namely production of bioethanol.

4.1. Phytoremediation

Phytoremediation is an emerging environmentally friendly and low-cost technology that uses plants and their associated microorganisms to remove pollutants from contaminated sites, especially heavy metals [98]. *C. ladanifer* was reported to survive and grow in soils with high concentrations of toxic elements, such as Mn, Cu, Zn, Pb, and As [99–101]. Observations in mining areas suggest selectivity in absorption and translocation of metals. Therefore, the tolerant behavior of this species in soils with toxic elements can expand the possibilities of phytoremediation in environments with significant rates of contamination [99].

One study on rockrose resistance to heavy metals was conducted in hydroponic experiments [16]. Higher tolerance to metals, such as Cd, Co, Cr, Mn, and Ni, was observed in plant populations originating from ultramafic soils or soils developed on basic rock, while populations originating from acid rock soils exhibited higher tolerance to Cu and Zn. Different patterns were observed in accumulation of metals in the plant: Cd, Co, and Mn accumulated in the aerial part, while Cu and Pb were not transported efficiently through the roots up to the shoots. In general, *C. ladanifer* can accumulate heavy metals in the aerial parts without inhibiting plant growth [16].

Thus, its potential for phytostabilization in mines soil can be considered suitable considering trace element concentrations in leaves and seeds and seed germination rates [101]. Beyond immobilization of chemical elements, phytostabilization with autochthonous species also increases organic matter and water retention capacity, improving soil structure and reducing erosion [102].

It is worth mentioning that hexane extracts from *C. ladanifer* plants growing in mining areas did not exhibit potentially hazardous heavy metals, suggesting no human health risks [32]. Therefore, the high resistance of *C. ladanifer* to nutrient unbalanced soils, with potentially toxic elements and adverse climatic conditions, makes this species appropriate for phytoremediation and revegetation of contaminated soils [17].

4.2. Animal Feed

Use of *C. ladanifer* (soft stems and leaves or extracts) as a food supplement for animal nutrition and productivity increase has shown interesting results. Inclusion of leaves and soft stems of *C. ladanifer* in diets of lambs supplemented with an oil blend (sunflower and linseed oils) increased intramuscular fatty acids content [103]. The fatty acids provided by the diet with *C. ladanifer* benefited health and did not jeopardize animal performance.

Another approach using a *C. ladanifer* diet, with or without oil supplementation, reduced lipid oxidation of lamb meat in pro-oxidant conditions and did not affect the meat's sensory properties [104].

Incorporation of ethanolic *C. ladanifer* extracts in rabbit feed showed also to be possible since it did not affect productivity, although the consumption rate was higher due to excess fiber and low protein [105]. Phenolic crude extracts from *C. ladanifer* were also employed in treatment of soybean meal to reduce rumen degradation, which may be advantageous to increase the flux of potential feed protein into the post-ruminal compartments [106].

Several studies evaluated the effect of adding rockrose-condensed tannins in diets for lambs, showing that they can improve the digestive efficiency of soybean meal protein without compromising growth performance, blood metabolites, carcass characteristics, and meat quality, thus being able to reduce feed costs by reducing the content of protein used in diets [107]. Inclusion of low levels of *C. ladanifer* extracts of condensed tannins (1.25%) in the diet of lambs also showed favorable results in the pattern of ruminal biohydrogenation, while addition of 2.5% of condensed tannins negatively affected lamb growth, with no beneficial effect on the fatty acids composition of intramuscular and subcutaneous fat [108]. An increase in the α-tocopherol content in the muscle, with a reduction in the lipid oxidation of the meat, has also been reported in studies with incorporation of leaves and soft stems of *C. ladanifer* in lamb diets [109].

4.3. Added-Value Products from Lignocellulosic Material

Development of industrial activity, fluctuations in the fossil fuel markets, and the need to minimize global climate change impacts have led to increasing interest in use of natural resources, in particular lignocellulosic residues and byproducts in the context of a transition to a circular bio-based economy. In this sense, valorization of biomass within the biorefinery concept has been gaining increasing relevance since a biorefinery integrates biomass conversion processes to obtain energy, materials, and chemical products, namely of added value [110]. These include biofuels, biochemical, and biobased compounds. Among these, organic acids, as well as bioactive compounds, are quite relevant. The phenolic compounds, both derived from extractives and from lignin, have strong potential for application in various industries, such as cosmetics, pharmaceuticals, and food, due to their potential functional activities.

Oligosaccharides, in particular xylooligosaccharides (XOS), are potential functional products that can be obtained from hydrolysis of hemicelluloses. These compounds have already been used as food ingredients (sweetener, weight control agents, humectants, etc.) and pharmacological supplements (prebiotic, anti-cariogenic, immunostimulant, antioxidant, antibiotic alternative, glycemic regulators, etc.), as well as in the cosmetic industry, animal and fish food, and agriculture [111]. In a study involving the techno-economic and environmental assessment of lignocellulosic-based small-scale biorefineries, it was demonstrated that the market price for products, such as XOS (USD 4.05/kg), for example, can give rise to significant economic profits, taking into account that the associated production costs are rather competitive (USD 1.18/kg) [112].

Rockrose lignocellulosic residues, from production of essential oils and labdanum gum, are produced in significant amounts as these traditional products represent a small percentage of the total raw material. Thus, the products to be derived from the lignocellulosic fraction, even if they have a cheaper commercial cost, can be obtained in larger quantities. These residues are rich in polysaccharides and lignin, and, when they result from distilleries as extracted solid residues, they still contain an important fraction of extractives [113–115]. According to the literature, the chemical composition of *C. ladanifer* presents some variations depending on the plant parts and plant age. In whole plants with ten years of age, contents of polysaccharides, Klason lignin, and extractives of 41.5%, 15.6%, and 6.2%, respectively, were reported [116]. For distillery residues, composed mainly of the aerial part of the plant, the polysaccharide values are around 29.2–33.3%, Klason lignin 17–19.2%, and extractives 39.2–43.7% [113,115]. For extractive-free biomass, polysaccharide and lignin values increase to about 50% and 30%, respectively. Some abundant agro-industrial residues, such as olive pomace, sugar cane bagasse, or rice straw, have lower lignin contents than those found in extractive-free cistus biomass (16–26% vs. 29%) but higher polysaccharide contents (55–67% vs. 50%) [117].

Some studies have reported use of *C. ladanifer* as a lignocellulosic feedstock to obtain value-added products. For bioethanol production, for example, lignocellulose materials need to be pre-treated (e.g., with acids), followed by subsequent enzymatic hydrolysis and fermentation [118]. Some studies reported rockrose residues as a potential source for bioethanol production. Gil et al. [119] reported that dilute acid pre-treatment was effective for carbohydrate solubilization from *C. ladanifer* residues, achieving a maximum concentration of 302.2 mg of total sugars/g of dry material. Subsequent enzymatic hydrolysis of the solid fractions resulting from the acid hydrolysis pretreatment was enhanced and varied with temperature, cellulase concentration, and incubation time [120]. Another study using steam explosion followed by alkaline extraction was also an effective pretreatment of 10-year-old rockrose, collected from the field, leading to a 75% higher glucose yield than the untreated raw material. Use of simultaneous saccharification and fermentation (SSF) for bioethanol production reached a yield of 22.1 g bioethanol/100 g of rockrose residues and proved more efficient than separate enzymatic hydrolysis and fermentation (SHF) [116]. Mixtures of rockrose and other lignocellulosic biomass have been studied to produce solid

biofuel, oligosaccharides, glucose, and L-lactic acid, aiming to contribute to the circular and sustainable bioeconomy concept [121,122].

Recently, a set of works suggested an integrated upgrading strategy for *C. ladanifer* distillery biomass residues obtained after essential oil steam distillation. The strategy started with removal of extractives (40% of the dry biomass), producing an extract rich in phenolic compounds (mainly gallic acid and flavonoids) with antioxidant properties [114,115]. The remaining lignocellulosic material, containing mainly polysaccharides (51%) and lignin (33%), was subjected to selective fractionation processes for sequential recovery of hemicelluloses by an autohydrolysis process [114] and lignin by organosolv and alkaline processes [123], producing a solid enriched in cellulose that had increased enzymatic digestibility (approximately four times more compared to the initial feedstock) [124].

Optimization of the autohydrolysis process enabled obtaining XOS with potential prebiotic activity, in a maximum concentration of 16 g/L, corresponding to a yield of 10.2 g/100 g extracted feedstock [114]. The alkaline and organosolv delignification processes affected the monomeric composition of the residual lignin, with a decrease in the S/G ratio (quantified by analytic pyrolysis, Py-GC/MS) and solubilization and recovery of several phenolic compounds with high added value, namely vanillic acid, *p*-coumaric acid, and epicatechin [123]. The alkaline treatments lead to higher delignification (87%) and subsequent higher cellulose enzymatic saccharification yields (79%) [123]. Glucan-rich solids and pentoses-rich hemicellulosic hydrolysates were used, separately or together, for selective production of the D-lactic acid isomer (D-LA) by recombinant strain *E. coli* JU15 in different fermentation modes: simultaneous saccharification and co-fermentation (SSCF), SHF, and SSF. The results achieved for lactic acid yield were around 92–99 g $_{\text{D-LA}}$/100 g sugars [125]. These are very promising results considering that lactic acid (LA) is an organic acid widely used in food and non-food industries (cosmetic, pharmaceutical, and chemical), and it is a precursor for production of biodegradable and biocompatible polylactic acid (PLA) polymers. A study on steam gasification of *C. ladanifer* biochar prepared by wood pyrolysis showed good results with a gas mixture of CO, CO_2, and especially H_2 as the main product of gasification, presenting a high calorific value of 10 MJ/m^3N, thereby suggesting that rockrose may be a suitable raw material for this purpose [126]. Other studies also approached use of extracted rockrose for obtaining active carbon after heat treatment [127,128].

Even though these targeted products are mainly intended low-price biofuels or bulk products, some of these products, e.g., XOS, also present high market value, and, as they can be produced in significant amounts, they will surely positively affect revenue streams.

5. Future Perspectives

Use of rockrose, not only as a source of essential oils or labdanum gum but also as a source to obtain other products, namely from its industrial residues, can be strategic in expansion of essential oil distilleries and consequently in development of rural areas where endogenous biomass potential is still poorly explored, promoting the bioeconomy and circular economy models.

Figure 3 presents a possible integration of processes and products for valorization of *C. ladanifer* in a biorefinery framework, with full resource use and exploitation to obtain added-value products or novel applications, conveying the biorefinery goals, i.e., integral and sustainable use of biomass for concomitant production of biofuels, energy, materials, and chemicals, preferably with added value [110]. Non-structural chemical components (essential oils, labdanum gum, concrete, phenolics) from *C. ladanifer* can be obtained using different extraction methods. Each of these extracts can be used as raw material, especially for the perfumery, cosmetics, and pharmaceutical industries, to obtain a variety of products. Extracts of condensed tannins can be used as a feed supplement for animals. Considering the structural chemical fractions of the plant (cellulose, hemicelluloses, and lignin), use of different technologies for fractionation of the lignocellulosic material is mandatory. The first step is to optimize the extraction by targeting the phenolic compounds. For most

of the lignocellulosic feedstocks, this is usually economically unfeasible due to their low content, but, for some types of biomasses, such as *C. ladanifer*, the amount and composition of these compounds is very interesting [114,115]. Furthermore, extraction is beneficial for the subsequent stages. Selective fractionation of hemicelluloses can be carried out using hydro-thermal processes (autohydrolysis) that produce hemicellulose-derived sugars (mainly XOS) with high yield, besides organic acids, furfural, and phenolics, whereas cellulose and lignin are retained in the remaining solid phase.

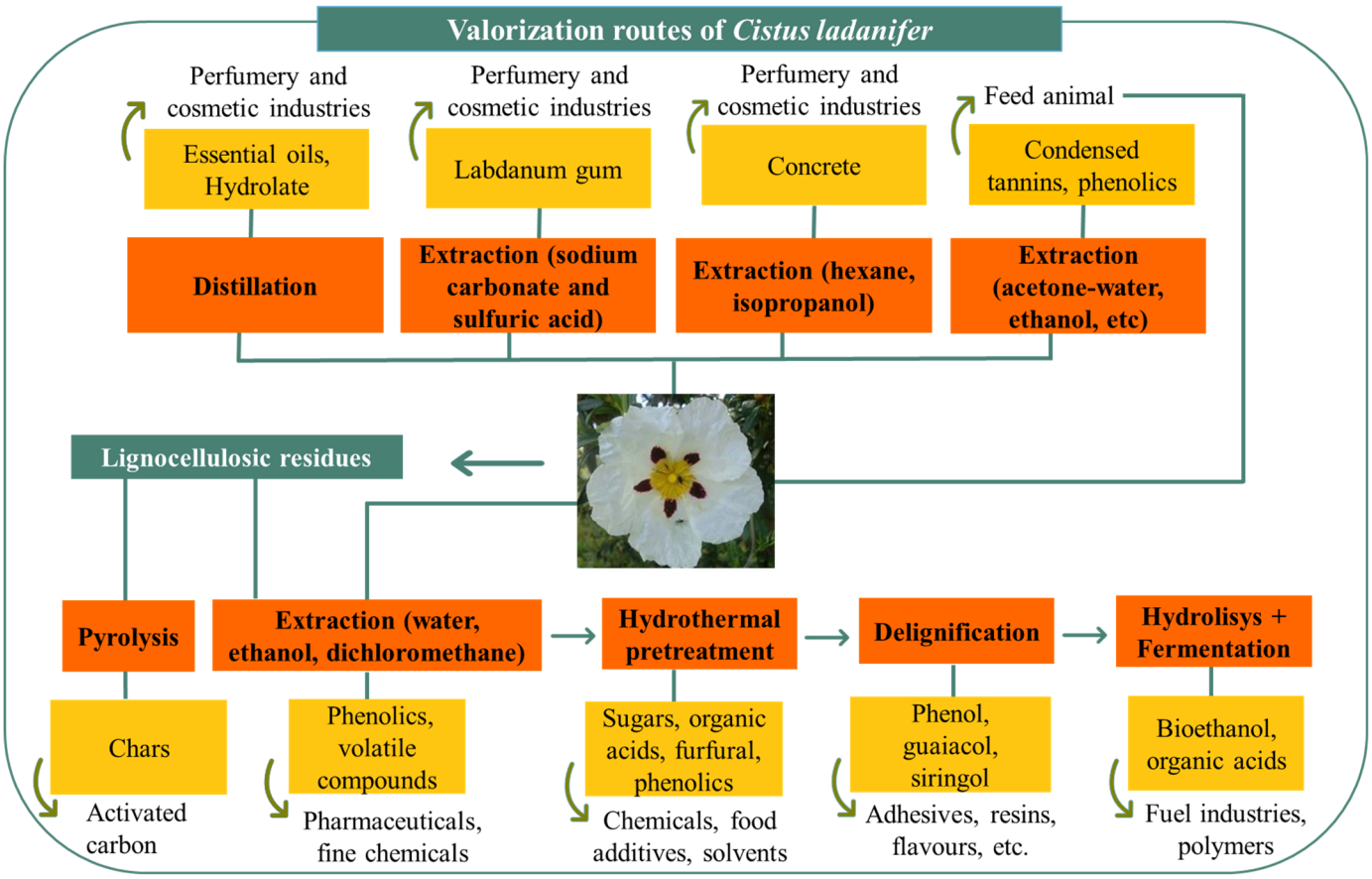

Figure 3. Potential path for use of *C. ladanifer* with an integrated valorization in a biorefinery framework for obtaining different added-value products.

The following step for removal of lignin (delignification) and its valorization is crucial to increase the sustainability of the biorefinery. Alkali processes are the most used but are also highly polluting and yield low-quality lignins, while the organosolv processes have been shown to be important alternatives [129–131]. Aside from other applications, lignin-derived products can also be used in several applications (i.e., adhesives, resins, flavors, etc.) due to their bioactive properties.

The remaining solid fraction is enriched in cellulose and putatively easily hydrolyzed by enzymes. Glucose can then be fermented and used in many industrial applications, such as bioethanol and organic production. All the extraction processes, whether to obtain essential oil, labdanum, or phenolic compounds, as well as the lignocellulosic fractionation processes, can be applied to plants harvested directly from the field. However, sequential processing (extraction of phenolics, hemicellulose hydrolysis, delignification, enzymatic hydrolysis, and fermentation) using residues after removing essential oils or labdanum is more advantageous since these products already have an established market.

Most plants processing *C. ladanifer* for the cosmetics and perfume industry are usually small, although there are important companies in countries such as Japan, Netherlands, France, and especially in Spain [35] where this species extends to a total of 2,106,717 ha in

shrub formations and as an understory in sparse forests [33]. In general, the *C. ladanifer* biomass resulting from the extraction process (steam distillation or solvent extraction) is considered waste or a by-product and is used only for burning. The yields of essential oils and labdanum are considerably small (usually, essential oils represent $\leq$1% and labdanum gum $\leq$6% of the dry biomass), and the amount of residual biomass remaining after the extraction process is very large, thereby requiring adequate management or valorization.

As the extraction processes to obtain essential oil are relatively soft, the solid residues remain largely unaltered and have the potential to be used for a wide range of other products. The chemical composition, in particular their extractives, polysaccharides, and lignin, are favorable for valorization in a biorefinery framework [113]. These industrial units, now focused only on labdanum gum and essential oil, may, therefore, grasp this possibility to produce novel products.

The specific characteristics of the biomass raw material are important, and selection of fractionation methods, which include physical, chemical, and biological processes, should be optimized [132] and integrated also considering the economic viability of biomass-based transformation.

In addition, extractive fractions can be targeted as potential valuable chemicals, namely bioactive products, providing another pathway for use of this species, namely in pharmaceutical, food, and feed industries. The products obtained from *C. ladanifer* extraction have varied composition, and determination of the compounds responsible for its bioactivity is complex; however, several bioactivities of its extracts are demonstrated (antioxidant, antimicrobial, allelopathic, antihypertensive, antitumoral, hypoglycemic, and hypolipidemic), although the synergistic action of compounds seems to outweigh the isolated action of each constituent. Therefore, additional studies are needed to determine which compounds are responsible for the pharmacological activities, as well as the mechanisms of action involved, their toxicity, possible interactions, and secondary effects [34].

In conclusion, valorization of *C. ladanifer* may contribute to better use of an underexploited endogenous resource while promoting residues management, reducing pressure on the environment, and promoting sustainable development through creation of new products and generation of new jobs. Nevertheless, to shift biorefineries into industrial reality, development of a distribution map highlighting local potential availability and aspects related to logistics of transport must be taken into consideration to build a complete sustainability analysis. Additionally, a comparative techno-economic analysis of the different processes, namely with the help of modelling tools, as well as a life cycle assessment in terms of environmental, social, and economic sustainability should also be carried out before selecting biomass commercial valorization pathways.

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