Rev Environ Sci Biotechnol (2022) 21:583–633
https://doi.org/10.1007/s11157-022-09624-1

REVIEW PAPER

Chemical composition and industrial applications of Maritime pine (*Pinus pinaster* Ait.) bark and other non-wood parts

José Ignacio Alonso-Esteban · Marcio Carocho · Diana Barros · Manuela Vaz Velho · Sandrina Heleno · Lillian Barros

Received: 8 February 2022 / Accepted: 11 May 2022 / Published online: 14 June 2022

Abstract Maritime pine (*Pinus pinaster* Ait.) is native to the western Mediterranean basin and has an economic importance in southwestern Europe. This importance is based on the use of its wood in the construction, furniture, and paper industries. Bark and other parts of the plant, such as resin, needles, and cones, are by-products with potential industrial application. These parts of the tree stand out because of the presence of secondary metabolites, the main ones being phenolic compounds and terpenes. Bark contains both, while other parts of the plant are mainly composed of terpenes. All these compounds have biological potential, mainly antioxidant and antimicrobial properties. The bark has the widest range of industrial applications, and it can be used to obtain dietary supplements and functional foods, adsorbents, and bio-based resins and foams. Resin has a prominent industrial role too, especially in chemical industry. In this manuscript, an overview of these applications is described, opening an innovation opportunity for enterprises to use the by-products and residue of maritime pine. Still, albeit the described application, maritime pine has further applications that are right now being studied under the premises of circular economy.

Keywords *Pinus pinaster* · Phytochemistry · Sustainable industrial applications · Bark · Needles · Cones · Oleoresin

1 Introduction

Maritime pine (*Pinus pinaster* Ait.) is a 20–30 m tall medium-sized pine, although some specimens can reach 40 m of height. It has a deep taproot with well-developed secondary roots, and a thick, bright reddish-brown and deeply fissured bark. Young trees have a regular ovoid or conic crown, while adult trees have an irregular and open crown with branches with close-packed branches at the ends. Needles are 10–25 cm long and are mostly grouped by pairs. They have shiny green and well-marked lines of stomata on both faces. Cones have a moderately asymmetrical ovoid-conic shape and are 8–22 cm long, being

---

J. I. Alonso-Esteban · M. Carocho (✉) · S. Heleno · L. Barros (✉)
Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
e-mail: mcarocho@ipb.pt

L. Barros
e-mail: lillian@ipb.pt

D. Barros · M. V. Velho
Centro de Investigação em Sistemas Agroalimentares e Sustentabilidade (CISAS), Instituto Politécnico de Viana do Castelo, Rua Escola Industrial e Comercial Nun'Álvares, 34, 4900-347 Viana do Castelo, Portugal

D. Barros
Escuela de Doctorado Internacional de la USC, Universidade de Santiago de Compostela, Santiago de Compostela, Spain

light brown and persistent, usually grouped in clusters. Their scales present broad ridge and up-curved prickles, while seeds are shiny black to brown above, and grey below, with an easily removable wing (Abad Viñas et al. 2016; Correia et al. 2007; de las Heras et al. 2012; Eckenwalder 2009).

This pine species is native to the western Mediterranean basin, especially southwestern Europe, as well as some places of northwestern Africa, in smaller proportion. In Europe, it occurs in the Iberian Peninsula, southern France, including the island of Corsica, and western Italy (Abad Viñas et al. 2016). As seen in Fig. 1, there are several areas in Europe with a relative presence of maritime pine higher than 70%, corresponding to wide extensions of pine forests. These pine forests are located in the west coast of Portugal and Galicia (Spain), some areas of the middle basin of the Douro river (Portugal), in Castile and Leon (Spain), where an area called *Tierra de Pinares* (Pine Woodlands) ows its name to the dense pine forests that abund there; and southwestern France, in Landes de Gascogne, where the largest continuous plantation forest of maritime pine exists (Abad Viñas et al. 2016; Rodríguez-García et al. 2015). This forest is unique because it was almost entirely planted by humans and is managed for specific industrial purposes (Layton et al. 2021). This species has also been cultivated in non-native Mediterranean regions, such as Turkey, where it was imported in 1970's (Kurtca and Tumen 2020), and in the southern hemisphere, where it was introduced for environmental and economical purposes and became a highly invasive species, especially in South Africa (Abad Viñas et al. 2016).

Maritime pine is considered ecologically versatile because it shows diverse growth characteristics, namely frost resistance and adaptation to drought and various types of substrates. It exhibits preference for warm temperate areas with an annual rainfall higher than 600 mm, although it can survive with 400 mm if there is sufficient atmospheric moisture. It dwells well in siliceous soils with coarse textures, especially sandy soils, dunes, and other poor substrates (Abad Viñas et al. 2016). Due to its adaptability to different environmental conditions, it has become a study model for studies in coniferous forest management and functional genomics (Arrillaga et al. 2019), although main conifer models for functional genomic studies are loblolly pine (*Pinus taeda* L.) and Norway spruce (*Picia abies* L.) (Nystedt et al. 2013; Zimin et al. 2017). Additionally, pine trees can be bio-monitors of the occurrence of persistent organic pollutants (POPs) in the environment, mainly through the

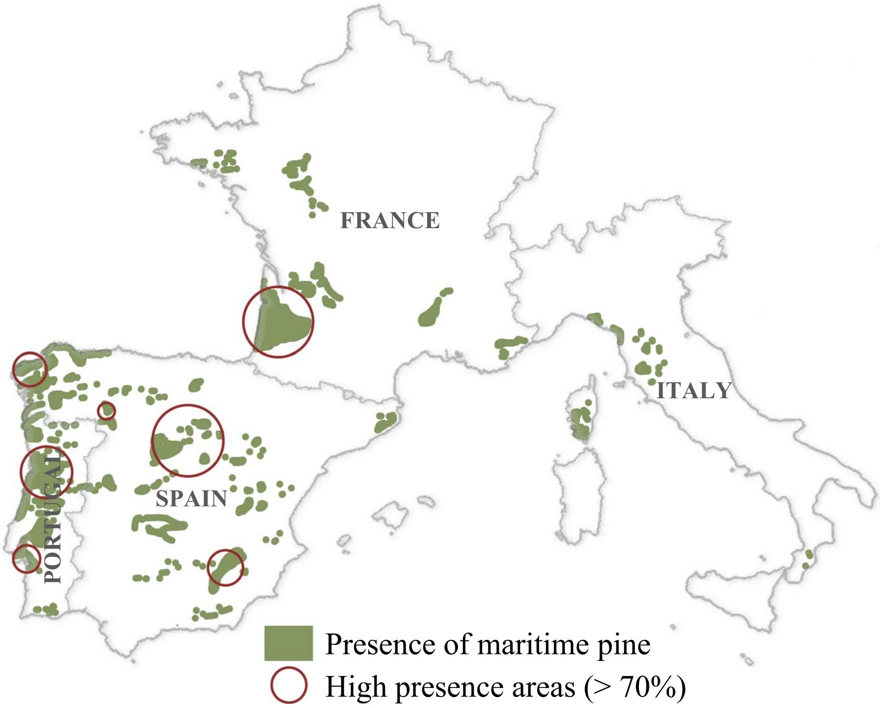

Fig. 1 Geographical distribution of maritime pine (*Pinus pinaster* Ait.) in southwestern Europe. Adapted from Abad Viñas et al. (2016)

needles, because of the retention properties of their waxy layer, however, the bark can accumulate airborne contaminants, due to its porosity. The presence of POPs, specifically polycyclic aromatic hydrocarbons, such as phenanthrene, fluoranthene, pyrene and fluorene, have been observed in maritime pine needles and bark (Ratola et al. 2009).

The regeneration of maritime pine forests is often unsuccessfully in the Mediterranean basin and the problem is worsening due to climate change (Vergarechea et al. 2019). Maritime pine has been used to cover burned areas after wildfires and has shown a high resistance to low and moderate fires (Aguiar et al. 2021; Molina et al. 2021). However, wildfires are expected to increase due to land use changes, which result in biomass accumulation that contribute to the surface fuel-complex in the tall and dense shrub layer of maritime pine forests (Fernández-Guisuraga et al. 2022).

From an economic point of view, maritime pine is one of the most important trees in the Iberian Peninsula forests, especially *Pinus pinaster* subsp. *atlantica* (Vieto et al. 2019), together with eucalyptus (*Eucalyptus* sp.), and poplar (*Populus* sp.), which are other relevant species. In Portugal it stands out as one of the three economically dominant species, which are eucalyptus, maritime pine, and cork oak (*Quercus suber* L.), which are used for wood, agglomerates of wood, pulp, biomass pellets, and cork industries (Nunes et al. 2019; Santos et al. 2021). These three species represent 75% of Portuguese forests, which currently represent in turn 35% of the total Portuguese area, with maritime pine representing roughly a third of all forestry area in Portugal (Fradinho et al. 2002; Nunes et al. 2019).

Economic importance of maritime pine consists in the use of its wood as construction wood and as raw material for manufacturing furniture, poles and posts (Abad Viñas et al. 2016). It is widely used by wood-based panel industry, pulp and paper industry too (Santos et al. 2021). Besides, maritime pine is the most used pine species for nutritive and medicinal purposes (Mármol et al. 2019). It is used to prevent landslides in sandy and slope areas, to preserve soils, and for afforestation of deserted agricultural lands because they are fast-growing trees, and their roots go deep into the soil. They have been used as a windbreak in the western coast of the Iberian Peninsula to protect agricultural crops against salt spray. Additionally, they are common shade trees in European recreational areas (Abad Viñas et al. 2016; Kurtca and Tumen 2020).

It is worth stressing that maritime pine, unlike eucalyptus, is a native species and this fact shows environmental considerations, such as patterns of lichen abundance and diversity. Maritime pine plantations provide a more suitable habitat for lichens in the Iberian Peninsula because they have higher lichen abundance and diversity than eucalyptus plantations (Calviño-Cancela et al. 2020). Maritime pine forests, as for other pines, are suitable ecosystems to produce edible fungi of the genera *Boletus*, *Hygrophorus*, *Lactarius*, *Macrolepiota*, and *Tricholoma* (Abad Viñas et al. 2016; Herrero et al. 2019). Although maritime pine shows an ecological adaptation to fire, fungi could be strongly affected, especially mycorrhizal taxa. Fungal communities of Mediterranean maritime pine forests seem to be more adapted to fire than those of boreal pine species, where only saprotrophic taxa are observed in the year following fire (Franco-Manchón et al. 2019).

Taking into account the relevance in forestry of this pine species in Portugal, as well as in the rest of the Iberian Peninsula and other European regions, and the forest sustainability, it is important to know all potential uses beyond wood industry, thus moving up the value chain to exploit all parts of the tree. This is closely related to circular economy, which is an economic system linked to sustainability, as it is based on the maximum use of resources and the minimum waste generation (Deutz 2020). Industrial potential of non-wood parts of several pine species has been previously studied (Neis et al. 2019). In maritime pine, the scientific production associated to "*Pinus pinaster*" topic has been almost constant in the last six years, as seen in Fig. 2, and many different research areas were covered. Depending on the database, it ranged from 113 to 136 or from 192 to 222, and the maximum values were achieved in 2021 in both cases. Besides these last articles, there are older articles that provide valuable knowledge about maritime pine, which were also consulted. This review aims to provide a wide view of the chemical composition of maritime pine bark and other parts of the tree which cannot be used by wood industry, such as needles, cones or resin, particularly secondary metabolites, as well as their industrial applications, especially those of bark, which is the most studied part.

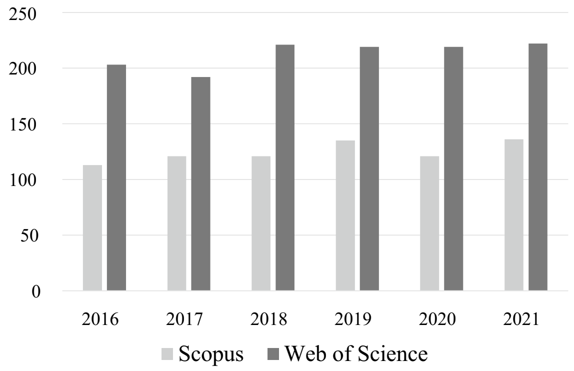

Fig. 2 "*Pinus pinaster*" topic related research articles produced from 2016 to 2021

2 Chemical composition of bark and other parts of maritime pine

Several parts of maritime pine have been studied by different authors and their data were summarised in Table 1. Bark composition was described by Ferreira-Santos et al. (2020) and more than 70% corresponded to fibres, being lignin the major one and represented about 42%, followed by cellulose and hemicellulose, with 17 and 12%, respectively. The percentage of fibre reported by Santos et al. (2021) was even higher, 85.5%, because lignin, cellulose and hemicellulose contents were higher, 46%, 23%, and 16%, respectively. Hemicelluloses of maritime pine bark were studied by Fradinho et al. (2002), who reported that xylose was the major component and that they also contained mannose, arabinose, glucose, uronic acids, and a small quantity of galactose and fucose. According to Santos et al. (2021), hemicellulose content in cones and needles were similar to barks, but cellulose content was higher, 34% and 29%, respectively. Lignin was the major fibre in cones and needles, but their content was lower than barks, close to 36%. Chemical composition of maritime pine knots and stumps was described by Celhay et al. (2014), and fibres were also the major compounds in both cases, especially cellulose, which represented 51% in knots and 58% in stumps. Lignin content was similar in both parts of the tree, 15%, while hemicellulose content was much higher in knots, 25%, 2.5 times higher than in stumps.

Ash was lower than 1% in bark, knots, and cones, slightly higher than 1% in needles and close to 8% in stumps (Celhay et al. 2014; Santos et al. 2021). Gómez-Rey et al. (2021) reported the mineral composition of needles and potassium was the major one, with a content close to 5 g/kg. The content of magnesium was also remarkable, but lower than 2 g/kg, and the average content of calcium was close to 1 g/kg. Phosphorus, sodium and aluminium presented a content between 0.2 and 0.8 g/kg, while the content of manganese, iron and zinc was lower than 0.1 g/kg.

Table 1 Chemical composition of different parts of maritime pine (% of dry matter)

	Bark			Needles	Cones	Knots	Stumps
	Ferreira-Santos et al. (2020)	Fradinho et al. (2002)	Santos et al. (2021)	Santos et al. (2021)	Santos et al. (2021)	Celhay et al. (2014)	Celhay et al. (2014)
Ash/minerals	0.87 ± 0.00	0.8	0.40 ± 0.02	1.17 ± 0.06	0.42 ± 0.03	0.31 ± 0.05	7.92 ± 0.19
Proteins	1.64 ± 0.03	–	–	–	–	0.38 ± 0.02	3.63 ± 0.03
Cellulose	17.39 ± 0.37	48.4[a]	23.2 ± 2.0	29.4 ± 1.6	33.8 ± 0.2	50.86 ± 1.32	57.55 ± 1.42
Hemicellulose	12.31 ± 0.20	48.4[a]	16.1 ± 3.8	16.1 ± 2.2	16.5 ± 3.4	24.58 ± 0.42	9.51 ± 1.25
Lignins	41.65 ± 0.24	33.2	46.2 ± 3.4	36.4 ± 2.1	35.7 ± 2.3	15.44 ± 1.22	15.47 ± 0.08
Lipophilic extractives/fats	2.54 ± 0.26	3.1	1.17 ± 0.09	10.04 ± 0.12	5.14 ± 0.21	16.74 ± 0.17	–
Hydrophilic extractives		3.2	2.09 ± 0.02	2.99 ± 0.18	5.64 ± 0.09	12.94 ± 0.97	8.30 ± 0.33
Ethanol extractives	13.20 ± 0.31	10.3	8.71 ± 0.16	4.56 ± 0.07	2.09 ± 0.11	–	–

[a] Holocellulose (cellulose + hemicellulose)

Copper and boron were minor mineral compounds, and their content was around 2–3 mg/kg.

2.1 Chemical characterization of maritime pine bark in terms of bioactive compounds

2.1.1 *Phenolic compounds*

Maritime pine bark is a rich source of polyphenols, such as flavonoids, phenolic acids, stilbenes, and tannins, which include proanthocyanidins, which in turn include procyanidins. The latter are mixtures of oligomers and polymers consisting of (+)-catechin and/or (−)-epicatechin units linked mainly through C4→C8 and/or C4→C6 bonds. These units can be doubly linked by a C4→C8 bond and an additional ether bond between O7→C2 (D'Andrea 2010). Procyanidins have different degrees of polymerization depending on the number of units, which influence their bioavailability and bioactivity, as well as their industrial potential (Yang et al 2021). After lignins, procyanidins are the most widespread polyphenols in plants, and they can be found in barks, roots, leaves, and fruits, often in high concentrations (D'Andrea 2010).

According to Jerez et al. (2006), the degree of polymerization of procyanidins was 7.0 in aqueous extract, so it contained highly polymerized procyanidins, and the most abundant monomeric units were catechin and epicatechin. The aqueous extract was fractionated and the fraction soluble in both water and ethyl acetate, which is much less polar, contained oligomeric procyanidins with a lower degree of polymerization, 3.0, and taxifolin, catechin and epicatechin as monomeric units. The ethanolic extract was also analysed and the degree of polymerization was 7.6 (Jerez et al. 2007a), slightly higher than the value of the aqueous extract. A fraction soluble in water and ethyl acetate was also obtained from ethanolic extract and the degree of polymerization of procyanidins was 2.3, more than three times lower. According to Jerez et al. (2007a), the higher the polymerization degree, the better antiradical activity against (2,2-diphenyl-1-picrylhydrazyl) DPPH radical, regardless the procyanidin source.

Another fraction which was soluble only in water was obtained from the ethanolic extract. That fraction showed the highest degree of polymerization with an average value of 10.6 (Jerez et al. 2007b). Catechin was the predominant terminal unit in both fractions from the ethanolic extract, while epicatechin was the main extension unit (Jerez et al. 2007a, b). Navarrete et al. (2010) indicated that the extract contained high molecular mass tannins formed by 20–21 flavonoid units, which might have solubility issues and precipitation due to autocondensation.

The content of phenolic compounds of maritime pine bark has been widely studied and the results reported by the different authors were summarised in Table 2. Gascón et al. (2018) reported a procyanidin B1 and B2 content of 5.3 and 42 μg/g of bark, respectively. Procyanidin B1 is a dimer of (+)-catechin and (−)-epicatechin, while procyanidin B2 is a dimer of (−)-epicatechin, in both cases the two units are linked through C4→C8 bonds (Saito et al. 2005). Their chemical structure, together with the most common phenolic compounds in maritime pine bark, were represented in Fig. 3. The two flavonoids are flavan-3-ols, but the major flavonoid was taxifolin, which is a flavanolol, with triple the amount of catechin. Taxifolin was also the main phenolic compound found in maritime pine bark in Mármol et al. (2022) studies being more abundant in aqueous extracts. On the other hand, procyanidin, hydroxybenzoic acid and caffeic acid were present in ethanolic and hydroethanolic (50%) extracts but not detected in aqueous ones (Mármol et al. 2022).

Naringenin, which belongs to the group of flavanones, was also found in different extracts of maritime pine bark with a content similar or higher than catechin. Besides flavonoids, maritime pine bark contains phenolic acids, albeit at lower than flavonoids. Other phenolic compounds which were widely found in maritime pine bark were ellagic acid and resveratrol. The first one showed a content higher than 340 mg/L in aqueous extracts, and even higher than in hydroethanolic extracts (400 mg/L) (Ferreira-Santos et al. 2019), while the content of resveratrol was lower. It should be noted the presence of pinoresinol, which is a lignan that could be found in other parts of the tree, although in very low quantities.

Regarding extraction of phenolic compounds from bark, two parameters that influence the extraction yield are the solvent and the particle size. According to Abilleira et al. (2021), extraction yield of phenolic compounds could be 2.5–3 times higher with ethanol than with water. That is why ethanolic extracts presented a higher antioxidant activity in the ferric

Table 2 Phenolic compounds of maritime pine bark

Compound	Solvent	Unit	Value	References
Total phenolic compounds by type				
Total phenolic compounds	Ethanol	g gallic acid equivalents/L	6.58–17.0	Jerez et al. (2006)
		mg gallic acid equivalents/g bark	63.38	Vieito et al. (2018)
	Ethanol:water (80:20, *v*/*v*)	mg gallic acid equivalents/g extract	379.6–873.2	Abilleira et al. (2014)
		mg gallic acid equivalents/g bark	7.52–39.52	Chupin et al. (2015)
	Ethanol:water (50:50, *v*/*v*)	mg gallic acid equivalents/g bark	73.48	Vieito et al. (2018)
	Ethanol, water	mg gallic acid equivalents/g extract	285.2–660.5	Simões et al. (2021)
	Water	mg gallic acid equivalents/g bark	50.09	Vieito et al. (2018)
	Water (NaOH)	mg gallic acid equivalents/g extract	19.34–96.81	Chupin et al. (2013)
Total condensed tannins	Ethanol:water (80:20, *v*/*v*)	g catechin equivalents/g bark	10.05–48.98	Chupin et al. (2015)
	Water (NaOH)	mg catechin equivalents/g extract	1.77–10.62	Chupin et al. (2013)
	Ethanol, water	mg catechin equivalents/g extract	84.4–125.1	Simões et al. (2021)
Total flavonoids	Ethanol, water	mg catechin equivalents/g extract	64.9–115.0	Simões et al. (2021)
Total proanthocyanidins	Ethanol:water (80:20, *v*/*v*)	mg cyanin chloride equivalents/g extract	217.8–552.4	Abilleira et al. (2014)
	Water (NaOH)	mg cyanidin equivalents/g bark	1.63–11.99	Chupin et al. (2015)
		mg cyanidin equivalents/g extract	1.01–11.73	Chupin et al. (2013)
Phenolic acids				
Caffeic acid	Dichloromethane	mg/kg bark	7	Sousa et al. (2018)
	Ethanol:water (30:70, *v*/*v*)	mg/L	11.5	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	mg/L	10.9–21.4	Ferreira-Santos et al. (2019)
		mg/L	13.8	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	12.0	
	Ethanol:water (90:10, *v*/*v*)	mg/L	12.0	
	Water	mg/L	6.2–6.8	Ferreira-Santos et al. (2019)
		mg/L	4.2	Ferreira-Santos et al. (2020)
	Water, ethyl acetate	g/100 g extract	1.92	Iravani and Zolfaghari (2014)
Chlorogenic acid	Ethanol:water (30:70, *v*/*v*)	mg/L	11.0	Ferreira-Santos et al. (2020)
		mg/L	44.1	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	15.7	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	15.5	
	Ethanol:water (90:10, *v*/*v*)	mg/L	17.2	
	Water	mg/L	5.8	
Cinnamic acid	Ethanol:water (30:70, *v*/*v*)	mg/L	29.5	Ferreira-Santos et al. (2020)
		mg/L	9.5	Ferreira-Santos et al. (2021)

Table 2 (continued)

Compound	Solvent	Unit	Value	References
	Ethanol:water (50:50, *v*/*v*)	mg/L	38.1	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	53.4	
	Ethanol:water (90:10, *v*/*v*)	mg/L	47.4	
	Water	mg/L	5.4	
o-Coumaric acid	Ethanol:water (30:70, *v*/*v*)	mg/L	57.8	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	25.0–63.2	Ferreira-Santos et al. (2019)
	Water	mg/L	29.5–33.5	
p-Coumaric acid	Dichloromethane	mg/kg bark	8	Sousa et al. (2018)
	Ethanol:water (30:70, *v*/*v*)	mg/L	127.7[a]	Ferreira-Santos et al. (2021)
Ferulic acid	Dichloromethane	mg/kg bark	61	Sousa et al. (2018)
	Ethanol:water (30:70, *v*/*v*)	mg/L	23.2	Ferreira-Santos et al. (2020)
		mg/L	48.7	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	26.8–48.3	Ferreira-Santos et al. (2019)
		mg/L	24.5	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	21.2	
	Ethanol:water (90:10, *v*/*v*)	mg/L	21.3	
	Water	mg/L	14.5–15.3	Ferreira-Santos et al. (2019)
		mg/L	9.7	Ferreira-Santos et al. (2020)
	Water, ethyl acetate	g/100 g extract	2.33	Iravani and Zolfaghari (2014)
Gallic acid	Ethanol:water (50:50, *v*/*v*)	mg/L	0.3–4.7	Ferreira-Santos et al. (2019)
	Water (NaOH)	mg/g bark	1.43–5.50	Chupin et al. (2013)
3,4-Dihydroxybenzoic acid	Ethanol:water (30:70, *v*/*v*)	mg/L	35.5	Ferreira-Santos et al. (2020)
		mg/L	93.0	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	9.5–17.3	Ferreira-Santos et al. (2019)
		mg/L	36.0	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	47.4	
	Ethanol:water (90:10, *v*/*v*)	mg/L	64.1	
	Water	mg/L	8.0–11.1	Ferreira-Santos et al. (2019)
		mg/L	29.7	Ferreira-Santos et al. (2020)
Rosmarinic acid	Ethanol:water (30:70, *v*/*v*)	mg/L	46.4	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	37.1–75.4	Ferreira-Santos et al. (2019)
Syringic acid	Dichloromethane	mg/kg bark	1	Sousa et al. (2018)
Vanillic acid	Dichloromethane	mg/kg bark	6	Sousa et al. (2018)
	Ethanol:water (30:70, *v*/*v*)	mg/L	8.0	Ferreira-Santos et al. (2020)
		mg/L	64.5	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	5.8–6.3	Ferreira-Santos et al. (2019)
		mg/L	9.5	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	10.0	
	Ethanol:water (90:10, *v*/*v*)	mg/L	10.5	
	Water	mg/L	3.0	
Flavonoids				
Apigenin	Ethanol:water (30:70, *v*/*v*)	mg/L	1.9	Ferreira-Santos et al. (2020)
		mg/L	3.1	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	15.3–19.6	Ferreira-Santos et al. (2019)
		mg/L	6.2	Ferreira-Santos et al. (2020)

Table 2 (continued)

Compound	Solvent	Unit	Value	References
	Ethanol:water (70:30, *v*/*v*)	mg/L	12.4	
	Ethanol:water (90:10, *v*/*v*)	mg/L	5.1	
Catechin	Dichloromethane	relative abundance %	n.d.–0.2	Simões et al. (2021)
	Ethanol:water (30:70, *v*/*v*)	mg/L	105.0	Ferreira-Santos et al. (2020)
		mg/L	198.2	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	27.8–54.2	Ferreira-Santos et al. (2019)
		mg/L	133.5	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	135.5	
	Ethanol:water (90:10, *v*/*v*)	mg/L	133.0	
	Water (NaOH)	mg/g bark	3.02–5.05	Chupin et al. (2013)
	Water	mg/L	28.3–40.2	Ferreira-Santos et al. (2019)
	Water, ethyl acetate	μg/g bark	102	Gascón et al. (2018)
		g/100 g extract	4.12	Iravani and Zolfaghari (2014)
Epicatechin	Ethanol:water (30:70, *v*/*v*)	mg/L	127.7[a]	Ferreira-Santos et al. (2021)
	Water (NaOH)	mg/g bark	0.84–1.92	Chupin et al. (2013)
Epicatechin gallate	Water (NaOH)	mg/g bark	0.31–0.99	Chupin et al. (2013)
Gallocatechin	Ethanol:water (30:70, *v*/*v*)	mg/L	140.3	Ferreira-Santos et al. (2020)
		mg/L	180.5	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	15.3–19.6	Ferreira-Santos et al. (2019)
	Water	mg/L	7.0–15.0	
		mg/L	149.3	Ferreira-Santos et al. (2020)
Hesperidin	Ethanol:water (30:70, *v*/*v*)	mg/L	125.9	Ferreira-Santos et al. (2021)
Naringenin	Ethanol:water (30:70, *v*/*v*)	mg/L	128.0	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	mg/L	170.5	
	Ethanol:water (70:30, *v*/*v*)	mg/L	249.5	
	Ethanol:water (90:10, *v*/*v*)	mg/L	239.6	
Naringin	Ethanol:water (30:70, *v*/*v*)	mg/L	164.0	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	67.1–208.0	Ferreira-Santos et al. (2019)
	Water	mg/L	89.0–97.8	
Quercetin	Ethanol:water (50:50, *v*/*v*)	mg/L	49.2–105.5	Ferreira-Santos et al. (2019)
		mg/L	10.1	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	8.5	
	Ethanol:water (90:10, *v*/*v*)	mg/L	10.9	
	Water	mg/L	27.6–34.9	Ferreira-Santos et al. (2019)
Taxifolin	Ethanol:water (30:70, *v*/*v*)	mg/L	166.4	Ferreira-Santos et al. (2020)
		mg/L	344.4	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	253.5–470.2	Ferreira-Santos et al. (2019)
		mg/L	422.9	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	463.2	
	Ethanol:water (90:10, *v*/*v*)	mg/L	463.9	
	Water	mg/L	93.5–121.1	Ferreira-Santos et al. (2019)
		mg/L	73.1	Ferreira-Santos et al. (2020)
	Water, ethyl acetate	μg/g bark	128	Gascón et al. (2018)
		g/100 g extract	6.68	Iravani and Zolfaghari (2014)

Table 2 (continued)

Compound	Solvent	Unit	Value	References
Procyanidins				
Procyanidin B1	Water, ethyl acetate	µg/g bark	5.3	Gascón et al. (2018)
Procyanidin B2	Water, ethyl acetate	µg/g bark	42	Gascón et al. (2018)
Others				
Ellagic acid	Ethanol:water (30:70, *v*/*v*)	mg/L	67.2	Ferreira-Santos et al. (2020)
		mg/L	62.1	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50 *v*/*v*)	mg/L	231.1–402.2	Ferreira-Santos et al. (2019)
		mg/L	120.6	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	122.6	
	Ethanol:water (90:10, *v*/*v*)	mg/L	124.4	
	Water	mg/L	123.7–342.2	Ferreira-Santos et al. (2019)
		mg/L	53.6	Ferreira-Santos et al. (2020)
p-Hydroxybenzaldehyde	Dichloromethane	mg/kg bark	4	Sousa et al. (2018)
Pinoresinol	Dichloromethane	relative abundance %	0.7–3.0	Simões et al. (2021)
		mg/kg bark	246	Sousa et al. (2018)
Resveratrol	Ethanol:water (30:70, *v*/*v*)	mg/L	10.9	Ferreira-Santos et al. (2020)
		mg/L	56.8	Ferreira-Santos et al. (2021)
	Ethanol:water (50:50, *v*/*v*)	mg/L	19.5–40.0	Ferreira-Santos et al. (2019)
		mg/L	13.5	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mg/L	18.9	
	Ethanol:water (90:10, *v*/*v*)	mg/L	17.5	
	Water	mg/L	3.8	
Vanillin	Dichloromethane	mg/kg bark	33	Sousa et al. (2018)

tr. traces

[a] Epicatechin + *p*-coumaric acid

reducing antioxidant power (FRAP) assays than aqueous extracts. Besides, the smaller the particle size, the higher the extraction yield. The smallest particle size tested by them was 0.5 mm, and the extraction yields for both ethanol and water were the highest. Chupin et al. (2015) also observed that the extraction yield was higher with a particle size under 0.4 mm, without an impact on the nature of the extracted compounds.

Chupin et al. (2013) also studied the influence of NaOH concentration in phenolic compound extractions and they observed that their content was higher with NaOH 1% than with 5%. Tannin and proanthocyanidin content were also higher with NaOH 1%. Besides, they indicated that the content of these compounds could be different depending on the tree because of the lixiviation of water-soluble compounds caused by rain.

High pressure fractioned extraction methodology was employed by Braga et al. (2008) to obtain different extract fractions having diverse antioxidant capacities, and it was influenced by catechin and epicatechin content, which were higher in ethanolic extracts, as it has been previously stated. Vieito et al. (2018) and Ferreira-Santos et al. (2020) observed that extracts obtained with intermediate ethanol concentrations (50–70%) were those with the highest bioactivities because they contained a higher amount of phenolic compounds, which were correlated with antioxidant activity. It was observed using microwave assisted extraction that the extraction solvent (aqueous, hydroethanolic and ethanolic) strongly influenced the antibacterial and anticancer effectivity of the bark extracts (Mármol et al. 2022).

Jerez et al. (2006) studied the effect of temperature, contact time and liquid–solid ratio on the phenolic compound extraction with ethanol, to maximize industrial process efficiency. The optimum extraction conditions were 50 °C, 90 min and 5:1 liquid–solid ratio, which rendered 17.0 gallic acid equivalents/L,

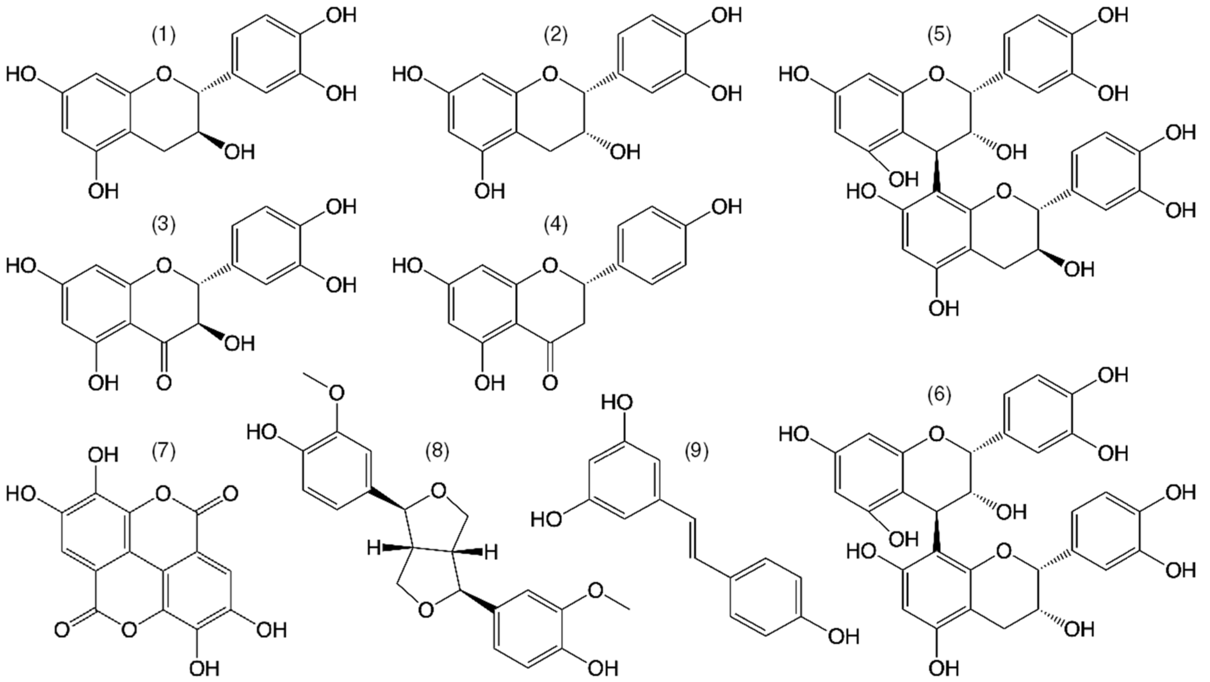

Fig. 3 Chemical structure of different phenolic compounds which are present in maritime pine bark (flavonoids: (+)-catechin (1), (−)-epicatechin (2), taxifolin (3), and naringenin (4); procyanidins: procyanidin B1 (5) and procyanidin B2 (6); other phenolic compounds: ellagic acid (7), pinoresinol (8), and resveratrol (9))

although a high influence of temperature was observed. Testing 25–50 °C showed that the highest temperatures were those with the best yields, which were related to best antiradical activity. However, contact time showed a low influence on phenolic compound yield, so the authors concluded that the matrix structure of pine bark allowed an easier liberation of phenolic compounds than other natural matrices and prolonged extraction times would not be needed.

Chupin et al. (2015) indicated that the microwave assisted extraction is a methodology that allows the obtention of high amounts of condensed tannins. Ferreira-Santos et al. (2019) evaluated the effect of ohmic heating on the extraction of phenolic compounds and they concluded that this methodology caused a significant increase in total phenolic compounds concentration in bark extracts.

2.1.2 Non-phenolic compounds

Besides phenolic compounds, maritime pine bark is a source of terpenoids. The structure of the most outstanding compounds is represented in Fig. 4. Mellouk et al. (2016) carried out the extraction of the essential oil by hydrodistillation with a Clevenger apparatus and through a solvent free microwave extraction, which showed a better yield than the classical method, with values of 3.3 and 2.2 g/100 g, respectively. The optimal irradiation conditions were 92.4 min and 803.5 W. 56 compounds were identified, but only eight presented a relative area higher than 2% in both essential oils, with the following constitution in mono and sesquiterpenes: α-terpineol, β-caryophyllene, β-pinene, cyclofenchene, valencene, α-humulene, α-pinene, and 3-carene, in decreasing order.

Sousa et al. (2018) studied the chemical composition of lipophilic maritime pine bark extract, which was extracted with dichloromethane through a soxhlet apparatus. Diterpenic resin acids represented the majority, with a content of 235.3 mg/100 g of dried bark. Most of them were abietane-type resin acids, but the extract also contained pimarane-type resin acids. Dehydroabietic acid was the major compound, with a content of 95.4 mg/100 g of dried bark, which represented more than 40% of diterpenic resin acids. Several dehydroabietic acid derivatives, included oxidized

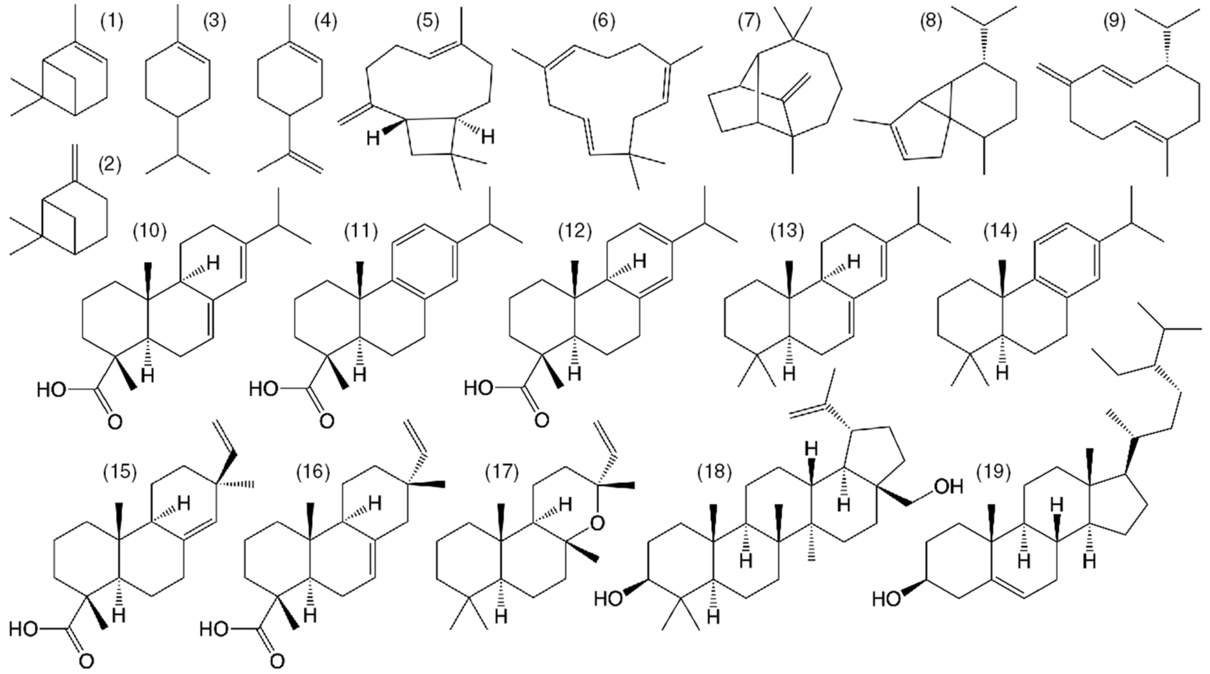

Fig. 4 Chemical structure of several terpenes which are present in different parts of maritime pine (monoterpenes: α-pinene (1), β-pinene (2), α-terpineol (3), and limonene (4); sesquiterpenes: β-caryophyllene (5), α-humulene (6), longifolene (7), α-cubebene (8), and germacrene D (9); diterpenes: abietic acid (10), dehydroabietic acid (11), levopimaric acid (12), abietadiene (13), abietatriene (14), pimaric acid (15), isopimaric acid (16), and manoyl oxide (17); triterpenes: betulin (18) and β-sitosterol (19))

derivatives, were also found, so it was suggested that oxidation/dehydrogenation reactions had taken place. In addition to these compounds, they also found triterpenoids and the major ones were β-sitosterol and betulin, with a content higher than 40 mg/100 g of dried bark. Another compound which was present in the lipophilic maritime pine bark extract was pinoresinol, and its content was 24.6 mg/100 g of dried bark. This compound is a lignan, so it is a phenolic acid derivative and not a terpenoid, as the previous compounds found in the lipophilic extract. Mármol et al. (2022) reported the presence of abietic acid derivate and 15-hydroxydehydroabietic acid in microwave ethanolic and hydroethanolic (50%) extracts but not found in aqueous ones.

Kurtca and Tumen (2020) studied resin acids too, but they focused their work on seasonal variations and related it with fatty acids. Abietic acid was the major resin acid, followed by neoabietic and dehydroabietic acid. Regarding pimarane-type resin acids, their proportion was lower than abietane-type resin acids, and the major one was pimaric acid. Samples obtained in February were those with a higher proportion of resin acids, and it decreased in samples obtained in May and even more in August, but samples collected in November were those with the lowest proportion of resin acids.

Kurtca and Tumen (2020) indicated that the proportion of fatty acids was higher than resin acids only in November, and the proportion of saturated and unsaturated fatty acids was similar. However, in February, the proportion of saturated fatty acids was much lower than unsaturated fatty acids, while in May and August the proportion of unsaturated fatty acids were higher than saturated fatty acids. Still on the subject of fatty acids, available data was summarized in Table 3. Sousa et al. (2018) reported that the content of fatty acids in dried bark was 0.75 g/100 g. So, the lipophilic fraction of maritime pine bark has a higher content of unsaponifiable compounds than saponifiable, which are fatty acids.

Fatty acid profile was mainly saturated, almost 90%, but it has been indicated that there are large variations depending on time of year (Kurtca and Tumen 2020). According to Sousa et al. (2018), major fatty

Table 3 Fatty acid composition of maritime pine bark

	Kurtca and Tumen (2020) (relative abundance %)	Simões et al. (2021) (relative abundance %)	Sousa et al. (2018) (mg/kg)
Caproic acid (6:0)			3
Caprylic acid (8:0)			1
Pelargonic acid (9:0)			1
Myristic acid (14:0)	tr.–0.48		1
Pentadecylic acid (15:0)			1
Palmitic acid (16:0)	3.06–10.47	0.3–3.4	55
Margaric acid (17:0)			4
Stearic acid (18:0)	0.12–0.98	0.4–1.0	23
Oleic acid (18:1*n*-9)	5.10–21.93	2.3–4.0	48
Elaidic acid (18:1*n*-9)			5
Linoleic acid (18:2*n*-6)	2.87–13.60		22
α-Linolenic acid (18:3*n*-3)	0.14–0.59	1.2	
Arachidic acid (20:0)	1.04–3.72	5.6–8.9	67
Behenic acid (22:0)	0.57–9.34	1.4–2.0	251
Tricosylic acid (23:0)	0.26–0.39	0.5–0.9	30
Lignoceric acid (24:0)	0.36–10.30	1.2–2.1	213
Cerotic acid (26:0)	0.11–1.72		20

tr. traces

acids were behenic acid (22:0) and lignoceric acid (24:0), both very-long-chain saturated fatty acids, and they represented 33.5% and 28.4% of total fatty acids, respectively. Next ones were arachidic (20:0) and palmitic (16:0) acids, which represented 8.9% and 7.3%, respectively, so only two fatty acids had a relative abundance higher than 10%. Major unsaturated fatty acid was oleic acid (18:1*n*-9), which represented 6.4% of total fatty acids. These fatty acids were also detected by Kurtca and Tumen (2020), but the proportion was different. Oleic acid was the major one regardless the time of year. According to Simões et al. (2021), major fatty acids were arachidic acid and oleic acid, with outstanding values of behenic and lignoceric acids too.

2.1.3 Bioactive properties

Several compounds previously mentioned, especially phenolic compounds, are well-known because of their biological properties. Chemical composition is affected by environmental factors, such as climate and seasonality (Kurtca and Tumen 2020; Rodríguez-García et al. 2015), so the bioactive properties will also be affected because they depend on chemical composition.

The most studied bioactivity of pine bark is antioxidant and it has been evaluated through ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt), DPPH and FRAP (ferric reducing antioxidant power) assays. Results obtained by different authors are difficult to compare because of the variety of units used to express the results, as it can be seen in Table 4. The most comprehensive study was carried out by Ferreira-Santos et al. (2020), who studied the activity of aqueous and hydroethanolic extracts. According to them, in most cases, hydroethanolic extracts were more active than aqueous extract. They tested different concentrations of ethanol and the extract obtained with ethanol 50% (*v*/*v*) was the most active one, as it showed the lowest IC_{50} values in the ABTS and DPPH assays (59.41 and 49.74 µg/mL, respectively, Table 4) and the highest reducing power (138.5 mmol Fe2 + /g extract).

Besides antioxidant activity, Ferreira-Santos et al. (2020) studied antihyperglycemic and antimicrobial activities. They reported that maritime pine bark extracts had a potent inhibitory activity of digestive enzymes, so they had the potential to reduce glucose absorption and could be used as a food supplement with antidiabetic properties. The antihyperglycemic activity was tested through α-amylase and α-glucosidase inhibition assays. They observed that the extraction with ethanol 70% (*v*/*v*) yielded an

Table 4 Bioactivities of different parts of maritime pine

Bioactivity/part	Solvent	Unit	Value	References
Antioxidant activity				
ABTS assay				
Bark	Ethanol:water (30:70, *v*/*v*)	IC_{50}, µg/mL	89.18	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	µmol trolox equivalents/g bark	394.28–918.49	Ferreira-Santos et al. (2019)
		IC_{50}, µg/mL	59.41	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	IC_{50}, µg/mL	65.57	
	Ethanol:water (90:10, *v*/*v*)	IC_{50}, µg/mL	112.1	
	Water	µmol trolox equivalents/g bark	110.60–155.88	Ferreira-Santos et al. (2019)
		IC_{50}, µg/mL	106.61	Ferreira-Santos et al. (2020)
Needles	Acetone	IC_{50}, µg/mL	163.45	Tümen et al. (2018)
	n-Hexane	IC_{50}, µg/mL	170.92	
	Water (essential oil)	IC_{50}, µg/mL	52–65	Fkiri et al. (2019)
		IC_{50}, µg/mL	107.28	Tümen et al. (2018)
Cones	Acetone	IC_{50}, µg/mL	99.13	
	n-Hexane	IC_{50}, µg/mL	115.82	
	Water (essential oil)	IC_{50}, µg/mL	102.24	
DPPH scavenging activity				
Bark	Ethanol:water (30:70, *v*/*v*)	IC_{50}, µg/mL	73.11	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	µmol trolox equivalents/g bark	165.07–237.27	Ferreira-Santos et al. (2019)
		IC_{50}, µg/mL	49.74	Ferreira-Santos et al. (2020)
		mg ascorbic acid equivalents/g bark	108.74	Vieito et al. (2018)
	Ethanol:water (70:30, *v*/*v*)	IC_{50}, µg/mL	55.04	Ferreira-Santos et al. (2020)
	Ethanol:water (90:10, *v*/*v*)	IC_{50}, µg/mL	100.1	
	Ethanol	inhibition %	32.1–85.6	Jerez et al. (2006)
		mg ascorbic acid equivalents/g bark	95.58	Vieito et al. (2018)
	Water	µmol trolox equivalents/g bark	113.29–199.14	Ferreira-Santos et al. (2019)
		IC_{50}, µg/mL	99.96	Ferreira-Santos et al. (2020)
		mg ascorbic acid equivalents/g bark	82.24	Vieito et al. (2018)
	Ethanol, water	IC_{50}, µg/mL	1.2–1.8	Simões et al. (2021)
Needles	Acetone	IC_{50}, µg/mL	171.12	Tümen et al. (2018)
	n-Hexane	IC_{50}, µg/mL	203.28	
	Water (essential oil)	IC_{50}, µg/mL	228.01	Aloui et al. (2021)
		IC_{50}, mg/mL	12[a]	Fekih et al. (2019)
		IC_{50}, µg/mL	42–56	
		IC_{50}, µg/mL	145.80	Tümen et al. (2018)
Cones	Acetone	IC_{50}, µg/mL	156.23	
	n-Hexane	IC_{50}, µg/mL	192.54	
	Water (essential oil)	IC_{50}, µg/mL	85.82	
Knots	Water	IC_{50}, mg/L	22.1	Celhay et al. (2014)
Stumps	Water	IC_{50}, mg/L	63.6	

Table 4 (continued)

Bioactivity/part	Solvent	Unit	Value	References
FRAP				
Bark	Ethanol:water (30:70, *v*/*v*)	mmol Fe^{2+}/g extract	112.4	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	µmol Fe^{2+}/g bark	1178.78–2158.59	Ferreira-Santos et al. (2019)
		mmol Fe^{2+}/g extract	138.5	Ferreira-Santos et al. (2020)
	Ethanol:water (70:30, *v*/*v*)	mmol Fe^{2+}/g extract	122.9	
	Ethanol:water (80:20, *v*/*v*)	trolox equivalents/g extract	145	Abilleira et al. (2021)
	Ethanol:water (90:10, *v*/*v*)	mmol Fe^{2+}/g extract	101.3	Ferreira-Santos et al. (2020)
	Water	trolox equivalents/g extract	126	Abilleira et al. (2021)
		µmol Fe^{2+}/g bark	473.93–611.70	Ferreira-Santos et al. (2019)
		mmol Fe^{2+}/g extract	101.9	Ferreira-Santos et al. (2020)
	Ethanol, water	mmol TE/g extract	2.8–4.1	Simões et al. (2021)
Needles	Acetone	reducing capacity %	19.74	Tümen et al. (2018)
	n-Hexane	reducing capacity %	16.28	
	Water (essential oil)	reducing capacity %	18.31	
Cones	Acetone	reducing capacity %	30.11	
	n-Hexane	reducing capacity %	25.13	Tümen et al. (2018)
	Water (essential oil)	reducing capacity %	27.92	
Non-site-specific hydroxyl radical scavenging activity				
Needles	Acetone	IC_{50}, µg/mL	192.35	Tümen et al. (2018)
	n-Hexane	IC_{50}, µg/mL	158.26	
	Water (essential oil)	IC_{50}, µg/mL	152.27	
Cones	Acetone	IC_{50}, µg/mL	130.44	
	n-Hexane	IC_{50}, µg/mL	184.26	
	Water (essential oil)	IC_{50}, µg/mL	105.17	
Antihyperglycemic activity				
α-Amylase inhibition assay				
Bark	Ethanol:water (30:70, *v*/*v*)	IC_{50}, µg/mL	536.4	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	IC_{50}, µg/mL	546.3	
	Ethanol:water (70:30, *v*/*v*)	IC_{50}, µg/mL	254.2	
	Ethanol:water (90:10, *v*/*v*)	IC_{50}, µg/mL	300.3	
	Water	IC_{50}, µg/mL	531.5	
α-Glucosidase inhibition assay				
Bark	Ethanol:water (30:70, *v*/*v*)	IC_{50}, µg/mL	132.8	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	IC_{50}, µg/mL	122.7	
	Ethanol:water (70:30, *v*/*v*)	IC_{50}, µg/mL	138.4	
	Ethanol:water (90:10, *v*/*v*)	IC_{50}, µg/mL	162.8	
	Water	IC_{50}, µg/mL	166.2	
Antimicrobial activity				
Acitenobacter baumanii				
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	6[a]	Fekih et al. (2019)

Table 4 (continued)

Bioactivity/part	Solvent	Unit	Value	References
Aeromonas hydrophila				
Needles	Water (essential oil)	zone of inhibition (20 µL/disc), mm	5–6	Fkiri et al. (2019)
Bacillus cereus				
Bark	Ethanol:water (30:70, *v*/*v*)	zone of inhibition (50 mg/mL), mm	10.2	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	zone of inhibition (50 mg/mL), mm	9.9	
	Ethanol:water (70:30, *v*/*v*)	zone of inhibition (50 mg/mL), mm	10.8	
	Ethanol:water (90:10, *v*/*v*)	zone of inhibition (50 mg/mL), mm	10.3	
	Water	zone of inhibition (50 mg/mL), mm	9.6	
	Ethanol	zone of inhibition (65 mg/mL), mm	10.7	Mármol et al. (2022)
	Ethanol:water (50:50, *v*/*v*)	zone of inhibition (65 mg/mL), mm	11.2	
	Water	zone of inhibition (30 mg/mL), mm	8.4	
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	6[a]	Fekih et al. (2019)
		zone of inhibition (20 µL/disc), mm	10–13	Fkiri et al. (2019)
Candida albicans				
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	6-10[a]	Fekih et al. (2019)
Citrobacter freundii				
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	6[a]	Fekih et al. (2019)
Clostridium perfringens				
Bark	Ethanol:water (30:70, *v*/*v*)	zone of inhibition (50 mg/mL), mm	13	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	zone of inhibition (50 mg/mL), mm	13.0	
	Ethanol:water (70:30, *v*/*v*)	zone of inhibition (50 mg/mL), mm	13.0	
	Ethanol:water (90:10, *v*/*v*)	zone of inhibition (50 mg/mL), mm	12.7	
	Water	zone of inhibition (50 mg/mL), mm	12.7	
	Ethanol	zone of inhibition (65 mg/mL), mm	14.4	Mármol et al. (2022)
	Ethanol:water (50:50, *v*/*v*)	zone of inhibition (65 mg/mL), mm	15.6	
	Water	zone of inhibition (30 mg/mL), mm	11.9	
Enterococcus faecalis				
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	12[a]	Fekih et al. (2019)

Table 4 (continued)

Bioactivity/part	Solvent	Unit	Value	References
Escherichia coli				
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	6[a]	Fekih et al. (2019)
		zone of inhibition (20 µL/disc), mm	8–10	Fkiri et al. (2019)
Klebsiella pneumoniae				
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	6[a]	Fekih et al. (2019)
Listeria monocytogenes				
Bark	Ethanol:water (30:70, *v*/*v*)	zone of inhibition (50 mg/mL), mm	7.8	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	zone of inhibition (50 mg/mL), mm	7.9	
	Ethanol:water (70:30, *v*/*v*)	zone of inhibition (50 mg/mL), mm	8.7	
	Ethanol:water (90:10, *v*/*v*)	zone of inhibition (50 mg/mL), mm	8.3	Ferreira-Santos et al. (2020)
	Water	zone of inhibition (50 mg/mL), mm	7.4	
	Ethanol	zone of inhibition (65 mg/mL), mm	8.4	Mármol et al. (2022)
	Ethanol:water (50:50, *v*/*v*)	zone of inhibition (65 mg/mL), mm	8.5	
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	6[a]	Fekih et al. (2019)
		zone of inhibition (20 µL/disc), mm	6–8	Fkiri et al. (2019)
Proteus mirabilis				
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	6[a]	Fekih et al. (2019)
Pseudomonas aeruginosa				
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	7[a]	Fekih et al. (2019)
		zone of inhibition (20 µL/disc), mm	7–9	Fkiri et al. (2019)
Salmonella Typhimurium				
Needles	Water (essential oil)	zone of inhibition (10 µL/disc), mm	6[a]	Fekih et al. (2019)
		zone of inhibition (20 µL/disc), mm	7–8	Fkiri et al. (2019)
Staphylococcus aureus				
Bark	Ethanol:water (30:70, *v*/*v*)	zone of inhibition (50 mg/mL), mm	10.1	Ferreira-Santos et al. (2020)
	Ethanol:water (50:50, *v*/*v*)	zone of inhibition (50 mg/mL), mm	9.7	
	Ethanol:water (70:30, *v*/*v*)	zone of inhibition (50 mg/mL), mm	10.1	
	Ethanol:water (90:10, *v*/*v*)	zone of inhibition (50 mg/mL), mm	10.2	

Table 4 (continued)

Bioactivity/part	Solvent	Unit	Value	References
	Water	zone of inhibition (50 mg/mL), mm	9.4	
	Ethanol	zone of inhibition (65 mg/mL), mm	11.4	Mármol et al. (2022)
	Ethanol:water (50:50, *v*/*v*)	zone of inhibition (65 mg/mL), mm	11.5	
	Water	zone of inhibition (30 mg/mL), mm	9.2	
Needles	Water (essential oil)	zone of inhibition (20 µL/disc), mm	18–20	Fkiri et al. (2019)

ABTS 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt, *DPPH* 2,2-diphenyl-1-picrylhydrazyl, *FRAP* ferric reducing antioxidant power

[a] Needles and other aerial parts (twigs and buds)

extract which showed the best α-amylase inhibitory activity and a good α-glucosidase inhibitory activity (Table 4).

Regarding antimicrobial activity, Ferreira-Santos et al. (2020) tested extracts against several bacteria and fungi, and those at a concentration of 50 mg/mL were more active against Gram-positive bacteria (Table 4), such as *Bacillus cereus*, *Listeria monocytogenes*, *Staphylococcus aureus*, and especially *Clostridium perfringens*. These findings were similar to the results obtained by Mármol et al (2022), Gram-positive bacteria showing to be more susceptible to pine bark extracts than Gram-negative bacteria (Table 4).

Ferreira-Santos et al. (2021) encapsulated bark extract by spray-drying using maltodextrin to understand the influence of encapsulation on the antioxidant and antimicrobial activity and bioaccessibility of phenolic compounds during gastrointestinal digestion (GID). The individual phenolic contents were significantly reduced after in vitro GID, especially in gastric and intestinal phases. The encapsulation increased the bioaccessibility of phenolic compounds when subjected to the digestion conditions of the oral, gastric and intestinal phases by 11%, 15%, and 14%, respectively. After GID, the encapsulated extract showed a smaller reduction in its antioxidant activity when compared to the non-encapsulated extract. They also studied the cellular viability on intestinal Caco-2 cells and the extracts, both non-encapsulated and encapsulated, showed a significant reduction of the viability at concentrations higher than 500 µg/mL. With regard to antioxidant activity in Caco-2 cells, the encapsulated extract presented a reduction of 34% of endogenous intracellular ROS.

A first screening on potential anti-cancer properties was carried out by Ferreira-Santos et al. (2020) in A549 cells (human lung cancer), and they found that only the tumour cells were affected by the extracts as the abnormal cell proliferation was inhibited without interrupting normally functioning cells. Gascón et al. (2018) used Caco-2 cells (human colorectal adenocarcinoma) for testing the antiproliferative effect of bark extracts obtained from several pine species. All of them showed cytotoxic potential and the authors related that effect to disturbances in redox balance, which could change mitochondrial membrane permeabilization, cytochrome *c* release, and caspase-3 activation. The extract obtained from maritime pine bark was the most active, possibly due to the high content of procyanidin B2.

Thaichinda et al. (2020) studied the antiproliferative activity on A375 cells (human malignant melanoma) and the maritime pine bark extract induced apoptosis. It was observed a decrease in the formation of reactive oxygen species (ROS) induced by hydrogen peroxide and an increase in the expression and activity of cleaved caspase-3.

The antiproliferative activity of aqueous, hydroethanolic and ethanolic pine bark extracts was also analysed by Mármol et al. (2022) using the tumour cell lines, Caco-2 (human colorectal adenocarcinoma), MCF-7 (human breast adenocarcinoma) and HepG2 (human hepatocellular carcinoma). Aqueous extracts displayed the highest antiproliferative effect against all the analysed cell models. In terms of effectivity, HepG2 cells showed a better response to both aqueous and hydroethanolic extracts followed by Caco-2 and finally MCF-7 cells, whereas Caco-2 cell line displayed a higher sensitivity to ethanolic extracts than HepG2 and MCF-7 (Mármol et al. 2022).

2.1.4 Pharmacokinetics

Studies about the pharmacokinetics of maritime pine bark extracts are scarce. Grimm et al. (2006b) studied pharmacokinetics of 300 mg single dose and 200 mg multiple dose (five days). In the single dose essay, catechin was detectable after 30 min and over the whole experimental period (14 h), the maximum plasma concentration was observed after 4 h and it subsequently decreased and remained almost constant from 6 to 14 h, because of the metabolic generation of catechin from procyanidins. Caffeic acid showed a similar time course, but plasma concentrations were lower. Ferulic acid reached its maximum plasma concentration at 1 h, it decreased thereafter and remained almost constant and showed a small increase at the end. Pharmacokinetics of taxifolin was different and it was not possible to detected before 2 h. The maximum plasma concentration was observed after 8 h and then it remained constant until 14 h. One of the main metabolites, δ-(3,4-dihydroxyphenyl)-γ-valerolactone, was detected after 6 h and reached the maximum plasma concentration at 10 h. In the multiple dose essay, steady state conditions were reached by catechin, caffeic acid and ferulic acid, but not by taxifolin.

Regarding phase II metabolism, the degree of conjugation with sulphate and glucuronic acid showed significant interindividual variability (Grimm et al. 2006b), but it was possible to detect in urine the presence of ferulic acid and taxifolin, as well as the metabolites δ-(3,4-dihydroxyphenyl)-γ-valerolactone and δ-(3-methoxy-4-hydroxyphenyl)-γ-valerolactone, free and conjugated with glucuronic acid/sulphate (Düweler and Rohdewald 2000; Virgili et al. 2000). According to Düweler and Rohdewald (2000), that could be considered evidence of human metabolism of maritime pine bark procyanidins, and Virgili et al. (2000) identified the excretion of ferulic acid in urine as a marker of maritime pine bark extract consumption.

Kurlbaum and Högger (2011) studied the plasma protein binding of various constituents of the extract by high performance affinity chromatography (HPAC) and ultrafiltration. In both cases, (+)-catechin and taxifolin were the constituents with the highest binding human serum albumin (HSA), from 95 to 100%. The values of binding HSA of ferulic acid were similar and close to 76%. However, the two methodologies gave different results in the case of caffeic acid and procyanidin B1. Caffeic acid showed a binding HSA of 66% and 79% by HPAC and ultrafiltration, respectively, and procyanidin B1showed values of 82% and 35%, respectively. According to the authors, the low binding HSA of procyanidin B1 obtained by ultrafiltration was unexpected, so future studies would let a better understanding of the extract pharmacokinetics.

2.2 Chemical characterization of other parts of maritime pine in terms of bioactive compounds

The chemical composition of the different parts of maritime pine is included in this subsection, which is divided by parts: woody parts (branches, knots, and stumps), needles, cones, and oleoresin. Most important bioactive compounds in these parts are terpenoids and data reported by different authors were summarised in Table 5, while bioactivities were included in Table 4.

2.2.1 Bioactivity of branches, knots and stumps

Gaspar et al. (2020) reported total phenolic content of several branch extracts, reporting that the essential oil contained 1.11 mg of gallic acid equivalents/100 mg of extract, while the aqueous extract presented double the amount, 2.41 mg gallic acid equivalents/100 mg. They also studied the extraction with supercritical CO_2 observing that higher temperatures decreased the content of total phenolic compounds. The maximum content, 3.25 mg gallic acid equivalents/100 mg of extract, was obtained at 35 °C with a density of 600 kg/m^3. Celhay et al. (2014) studied total phenolic compounds of knots and stumps, which contained 1.68% and 0.59% of dry matter, respectively. The hydrophilic extracts of knots and stumps showed a total phenolic content of 132 and 72 mg gallic acid equivalents/g of extract, respectively.

Table 5 Terpenoid composition of different parts of maritime pine (relative area %)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
Monoterpenes		–	–	–	–
Artemiseole	0.18–0.20	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Borneol	1.46–1.54	0.03–0.21	0.25–0.61	0.01–0.03	tr.–0.10
	Mellouk et al. (2016)	Kurtca and Tumen (2020)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	Arrabal et al. (2002)
	10[a]	–	–	–	0.4–0.7
	Sousa et al. (2018)	–	–	–	Arrabal et al. (2005)
Bornyl acetate	–	n.d.–0.5[b]	0.52–0.75	0.11	–
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	n.d.–0.07	0.25	–	–
	–	Fkiri et al. (2019)	Tümen et al. (2018)	–	–
	–	0.28–0.45	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
Camphene	0.31–0.49	n.d.–1.7[b]	1.91–3.16	0.29–0.35	0.63–0.65
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	Arrabal et al. (2002)
	–	n.d.–0.47	1.17	–	0.6–0.7
	–	Fkiri et al. (2019)	Tümen et al. (2018)	–	Arrabal et al. (2005)
	–	0.83–1.34	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.10	–	–	–
	–	Tümen et al. (2018)	–	–	–
6-Camphenol	0.15–0.26	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Campholenic aldehyde	0.14–0.23	0.01–0.12	0.28–0.93	0.02–0.06	–
	Mellouk et al. (2016)	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	n.d.–0.15	0.18	–	–
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	–	–
Camphor	0.17–1.12	n.d.–0.6[b]	0.18–1.01	–	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	–	–
	12	n.d.–0.02	0.10	–	–
	Sousa et al. (2018)	Kurtca and Tumen (2020)	Tümen et al. (2018)	–	–
3-Carene	1.87–2.23	n.d.–15.0[b]	n.d.–4.59	0.01	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	n.d.–0.02	7.32	–	–
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	–	–
	–	0.37	–	–	–
	–	Tümen et al. (2018)	–	–	–
4-Carene	0.42–0.47	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Carvone	–	–	0.05–0.14	–	–
	–	–	Kurtca and Tumen (2020)	–	–
	–	–	0.05	–	–
	–	–	Tümen et al. (2018)	–	–
trans-Carveol	–	–	0.05–0.15	–	–
	–	–	Kurtca and Tumen (2020)	–	–
	–	–	0.12	–	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	–	–	Tümen et al. (2018)	–	–
Cryptone	–	n.d.–0.3^b	–	–	–
	–	Fekih et al. (2019)	–	–	–
Cyclofenchene	3.76–4.36	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
m-Cymene	0.26–0.37	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
o-Cymene	–	0.04–0.14	–	–	–
	–	Fkiri et al. (2019)	–	–	–
p-Cymene	–	n.d.–0.3^b	0.18–0.7	–	–
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	–	–
	–	0.08–0.12	0.48	–	–
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	–	–
	–	0.05	–	–	–
	–	Tümen et al. (2018)	–	–	–
p-Cymenene	0.63–0.99	n.d.–1.3^b	–	0.01–0.02	–
	Mellouk et al. (2016)	Fekih et al. (2019)	–	Mediavilla et al. (2021)	–
p-Cymen-8-ol	–	n.d.–0.3^b	0.14–0.26	–	–
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	–	–
	–	–	0.27	–	–
	–	–	Tümen et al. (2018)	–	–
Eucalyptol	–	n.d.–0.3	n.d.–0.3	0.01–0.02	–
	–	Kurtca and Tumen (2020)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
α-Fenchene	–	0.97	–	0.01	–
	–	Aloui et al. (2021)	–	Mediavilla et al. (2021)	–
α-Fenchol	0.91–1.03	0.03–0.21	0.10–0.33	–	–
	Mellouk et al. (2016)	Kurtca and Tumen (2020)	Kurtca and Tumen (2020)	–	–
	–	–	0.13	–	–
	–	–	Tümen et al. (2018)	–	–
Fencholenic aldehyde	–	–	0.06–0.22	–	–
	–	–	Kurtca and Tumen (2020)	–	–
	–	–	0.05	–	–
	–	–	Tümen et al. (2018)	–	–
cis-Geraniol	–	n.d.–0.03	–	–	–
	–	Fkiri et al. (2019)	–		–
trans-Geraniol	4^a	n.d.–0.08	–	0.01–0.03	–
	Sousa et al. (2018)	Fkiri et al. (2019)	–	Mediavilla et al. (2021)	–
Geranyl acetate	–	n.d.–0.8^b	0.06	0.11–0.13	–
	–	Fekih et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	–
	–	n.d.–1.67	–		–
	–	Kurtca and Tumen (2020)	–		–
	–	0.29	–		–
	–	Tümen et al. (2018)	–		–
Geranyl isovalerate	–	n.d.–0.27	–	0.02	–
	–	Fkiri et al. (2019)	–	Mediavilla et al. (2021)	–
	–	0.11–0.19	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.14	–	–	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	–	Tümen et al. (2018)	–	–	–
Geranyl 2-methylbutirate	–	n.d.–0.4[b]	–	–	–
	–	Fekih et al. (2019)	–	–	–
Homomyrtenol	–	n.d.–0.07	–	–	–
	–	Fkiri et al. (2019)	–	–	–
δ-5,8-Iridadiene	–	n.d.–0.12	–	–	–
	–	Fkiri et al. (2019)	–	–	–
trans-Isolimonene	–	n.d.–0.19	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Isoborneol	1.01–1.27	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Isoterpinolene	–	n.d.–0.01	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Limonene	1.93–2.13	51.89	3.54	n.d.–10.5	1.44–1.78[c]
	Mellouk et al. (2016)	Aloui et al. (2021)	Tümen et al. (2018)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	0.1–7.8[b]	–	3.23–4.35	1.6–1.9[c]
	–	Fekih et al. (2019)	–	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	n.d.–0.03	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Linalool	0.13–0.32	n.d.–1.8[b]	0.10	–	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Tümen et al. (2018)	–	–
	–	0.06–0.08	–	–	–
	–	Fkiri et al. (2019)	–	–	–
	–	0.29–2.17	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.09	–	–	–
	–	Tümen et al. (2018)	–	–	–
Linalyl acetate	–	0.14–0.25	–	0.14–0.16	–
	–	Kurtca and Tumen (2020)	–	Mediavilla et al. (2021)	–
Lyratol	–	n.d.–0.1[b]	–	–	–
	–	Fekih et al. (2019)	–	–	–
p-Mentha-1,5-dien-8-ol	–	0.04–0.16	0.47–0.87	–	–
	–	Kurtca and Tumen (2020)	Kurtca and Tumen (2020)	–	–
	–	–	0.89	–	–
	–	–	Tümen et al. (2018)	–	–
Myrcene	–	n.d.–13.6[b]	1.58–3.92	n.d.–10.9	0.65–0.88
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	n.d.–0.04	0.89	5.97–9.45	1.1–1.2
	–	Fkiri et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	1.77–3.05	–	–	–
	–	Kurtca and Tumen (2020)	–		–
	–	4.14	–		–
	–	Tümen et al. (2018)	–		–
Myrtenal	–	n.d.–7.5[b]	0.59–1.10	0.04–0.05	–
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	n.d.–0.32	–		–
	–	Fkiri et al. (2019)	–		–
	–	0.03–0.16	–		–
	–	Kurtca and Tumen (2020)	–		–
Myrtenol	4[a]	–	1.24	0.03–0.04	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	Sousa et al. (2018)	–	Tümen et al. (2018)	Mediavilla et al. (2021)	–
Neryl acetate	–	n.d.–0.08	–		–
	–	Kurtca and Tumen (2020)	–		–
cis-β-Ocymene	0.12–0.38	n.d.–0.08	–	0.01	–
	Mellouk et al. (2016)	Kurtca and Tumen (2020)	–	Mediavilla et al. (2021)	–
	–	–	–	n.d.–0.978	–
	–	–	–	Gaspar et al. (2020)	–
trans-β-Ocymene	0.45–0.57	n.d.–0.1^{b}	n.d.–0.02	0.25–0.26	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	0.03–0.08	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.06	–	–	–
	–	Tümen et al. (2018)	–	–	–
Perillaldehyde	0.37–0.62	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Perillene	–	–	–	–	–
	–	–	–	Mediavilla et al. (2021)	–
α-Phellandrene	–	n.d.–0.2^{b}	1.98–3.14	0.01–0.02	–
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	Arrabal et al. (2002)
	–	0.07–0.10	–	–	1.9–2.9
	–	Kurtca and Tumen (2020)	–	–	Arrabal et al. (2005)
β-Phellandrene	–	n.d.–2.1^{b}	3.36–4.23	0.77–0.98	1.44–1.68^{c}
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	Arrabal et al. (2002)
	–	0.07–0.18	–	–	1.6–1.9^{c}
	–	Fkiri et al. (2019)	–	–	Arrabal et al. (2005)
	–	1.98–3.15	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.85	–	–	–
	–	Tümen et al. (2018)	–	–	–
α-Phellandren-8-ol	–	n.d.–0.07	–	–	–
	–	Fkiri et al. (2019)	–	–	–
α-Pinene	2.32–2.35	7.02	28.94–37.96	n.d.–8.53	69.92–70.26
	Mellouk et al. (2016)	Aloui et al. (2021)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	18.0–72.7^{b}	32.57	25.50–27.13	70.9–83.1
	–	Fekih et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	0.21–1.99	–	–	–
	–	Fkiri et al. (2019)	–	–	–
	–	18.85–29.83	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	13.53	–	–	–
	–	Tümen et al. (2018)	–	–	–
β-Pinene	5.17–5.46	0.42	10.36–15.13	n.d.–12.2	18.60–18.91
	Mellouk et al. (2016)	Aloui et al. (2021)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	n.d.–33.6^{b}	27.39	18.80–29.44	4.5–13.9
	–	Fekih et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	0.02–0.22	–	–	–
	–	Fkiri et al. (2019)	–	–	–
	–	2.43–4.29	–	–	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	–	Kurtca and Tumen (2020)	–	–	–
	–	9.81	–	–	–
	–	Tümen et al. (2018)	–	–	–
Pinocamphone	–	–	0.13–0.51	0.03–0.1	–
	–	–	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
trans-Pinocarveol	0.87–1.07	0.02–0.11	0.28–0.93	0.04–0.1	–
	Mellouk et al. (2016)	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	0.04–0.12	1.55	–	–
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	–	–
Pinocarvone	0.49–0.72	n.d.–0.3[b]	0.14–0.51	0.02–0.03	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	6[a]	n.d.–0.04	0.33	–	–
	Sousa et al. (2018)	Fkiri et al. (2019)	Tümen et al. (2018)	–	–
	–	n.d.–0.04	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
Piperitone	–	0.01–0.03	–	0.02	–
	–	Fkiri et al. (2019)	–	Mediavilla et al. (2021)	–
	–	n.d.–0.04	–	–	–
	–	Tümen et al. (2018)	–	–	–
Sabinene	–	1.25	–	0.03–0.05	–
	–	Aloui et al. (2021)	–	Mediavilla et al. (2021)	–
	–	n.d.–0.3[b]	–	–	–
Terpin	16[a]	Fekih et al. (2019)	–	–	–
	Sousa et al. (2018)	–	–	–	–
	–	–	–	–	–
α-Terpinene	–	n.d.–0.83	0.05–0.11	0.01–0.02	–
	–	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	0.07–0.15	0.06	–	–
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	–	–
γ-Terpinene	–	n.d.–0.2[b]	0.08	0.02–0.03	–
	–	Fekih et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	–
	–	0.02	–	–	–
	–	Tümen et al. (2018)	–	–	–
α-Terpineol	8.35–19.54	n.d.–2.1[b]	2.71–4.00	n.d.–1.24	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
	13[a]	0.18–0.32	1.20	0.1–0.27	–
	Sousa et al. (2018)	Fkiri et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	–
	–	0.31	–	–	–
	–	Tümen et al. (2018)	–	–	–
cis-β-Terpineol	0.39–0.46	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
trans-β-Terpineol	0.13–0.26	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
4-Terpineol	0.71–2.19	n.d.–0.5[b]	0.27–0.48	–	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	–	–
	–	0.03–0.12	0.21	–	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	–	Fkiri et al. (2019)	Tümen et al. (2018)	–	–
	–	0.03–0.15	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.03	–	–	–
	–	Tümen et al. (2018)	–		
Terpinolene	0.13–0.23	n.d.–1.7[b]	0.71	n.d.–0.334	0.67–0.68
	Mellouk et al. (2016)	Fekih et al. (2019)	Tümen et al. (2018)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	0.25–0.55	–	0.35–0.91	0.2–0.5
	–	Fkiri et al. (2019)	–	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	0.19	–	–	–
	–	Tümen et al. (2018)	–	–	–
Thuja-2,4(10)-diene	–	n.d.–0.3[b]	–	–	–
	–	Fekih et al. (2019)	–	–	–
α-Thujene	0.21–0.33	n.d.–0.1[b]	n.d.–0.05	0.01	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	n.d.–0.02	0.10	–	–
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	–	–
Tricyclene	–	n.d.–0.1[b]	0.15–0.19	0.04	–
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	0.1–0.16	0.11	–	–
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	–	–
Thymol methyl ether	–	1.1	0.11–0.18	0.05–0.11	–
	–	Aloui et al. (2021)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	n.d.–0.1[b]	–	–	–
	–	Fekih et al. (2019)	–	–	–
	–	0.07–0.09	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
trans-Verbanol	–	–	0.03	–	–
	–	–	Tümen et al. (2018)	–	–
Verbanone	–	–	n.d.–0.08	–	–
	–	–	Kurtca and Tumen (2020)	–	–
	–	–	0.36	–	–
	–	–	Tümen et al. (2018)	–	–
Verbenene	–	n.d.–0.05	0.27–0.87	0.02–0.04	–
	–	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	n.d.–0.07	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
cis-Verbenol	–	n.d.–0.2[b]	0.13	–	–
	–	Fekih et al. (2019)	Tümen et al. (2018)	–	–
trans-Verbenol	–	n.d.–0.02	n.d.–0.14	–	–
	–	Kurtca and Tumen (2020)	Kurtca and Tumen (2020)	–	–
Verbenone	–	n.d.–0.6[b]	0.38–0.86	–	–
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	–	–
	–	n.d.–0.07	0.41	–	–
	–	Fkiri et al. (2019)	Tümen et al. (2018)	–	–
	–	n.d.–0.04	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
Sesquiterpenes	–	–	–	–	–
Alloaromadendrene oxide	–	n.d.–0.05	–	–	–
	–	Fkiri et al. (2019)	–	–	–
α-Amorphene	–	1.51	0.75–1.33	0.49–1.3	–
	–	Aloui et al. (2021)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	1.39–10.72	0.03	–	–
	–	Fkiri et al. (2019)	Tümen et al. (2018)	–	–
	–	6.91	–	–	–
	–	Tümen et al. (2018)	–	–	–
γ-Amorphene	–	–	–	0.15–0.37	–
	–	–	–	Mediavilla et al. (2021)	–
Aromadendrene	–	0.14–0.17	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Aromadendrene oxide	0.24–0.36	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Aristol-9-en-3-ol	–	n.d.–0.2	–	–	–
	–	Fkiri et al. (2019)	–	–	–
α-Bisabolene	–	n.d.–0.4^{b}	–	0.02–0.1	–
	–	Fekih et al. (2019)	–	Mediavilla et al. (2021)	–
	–	n.d.–1.8	–	–	–
	–	Fkiri et al. (2019)	–	–	–
	–	0.26–0.46	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
β-Bisabolene	–	–	n.d.–0.32	–	–
	–	–	Kurtca and Tumen (2020)	–	–
β-Bourbonene	–	n.d.–0.5	0.12–0.26	–	–
	–	Fkiri et al. (2019)	Kurtca and Tumen (2020)	–	–
	–	n.d.–0.53	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
Cadalene	–	0.12	–	–	–
	–	Aloui et al. (2021)	–	–	–
Cadina-1,4-diene	–	n.d.–0.66	0.05–0.08	0.05–0.08	–
	–	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	0.09–0.34	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.10	–	–	–
	–	Tümen et al. (2018)	–	–	–
Cadina-1(6),4-diene	–	–	–	0.04–0.1	–
	–	–	–	Mediavilla et al. (2021)	–
Cadina-3,5-diene	–	–	–	n.d.–0.265	–
	–	–	–	Gaspar et al. (2020)	–
α-Cadinene	0.24–0.37	n.d.–0.99	n.d.–0.09	n.d.–0.515	–
	Mellouk et al. (2016)	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
	–	0.16–0.33	–	0.05–0.1	–
	–	Kurtca and Tumen (2020)	–	Mediavilla et al. (2021)	–
	–	0.05	–	–	–
	–	Tümen et al. (2018)	–	–	–
γ-Cadinene	–	0.1–5.0^{b}	0.50–0.91	0.129–3.26	0.85–0.87
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	1.32–2.10	0.14	0.32–0.7	n.d.–0.5
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	Mediavilla et al. (2021)	Arrabal et al. (2005)

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	–	0.49	–	–	–
	–	Tümen et al. (2018)	–	–	–
δ-Cadinene	0.61–1.06	n.d.–8.43	1.11–2.03	0.896–7.11	–
	Mellouk et al. (2016)	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
	–	3.17–5.48	–	0.94–2.09	–
	–	Kurtca and Tumen (2020)	–	Mediavilla et al. (2021)	–
	–	1.52	–	–	–
	–	Tümen et al. (2018)	–	–	–
α-Cadinol	–	0.62–1.44	n.d.–0.27	n.d.–1.6	–
	–	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
	–	0.11–0.76	–	0.04	–
	–	Kurtca and Tumen (2020)	–	Mediavilla et al. (2021)	–
	–	0.35	–	–	–
	–	Tümen et al. (2018)	–	–	–
α-Calacorene	–	0.47–1.66	n.d.–0.04	n.d.–0.368	–
	–	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
β-Calacorene	–	–	–	n.d.–0.136	–
	–	–	–	Gaspar et al. (2020)	–
Calamenene	–	n.d.–1.9[b]	–	n.d.–0.0950	–
	–	Fekih et al. (2019)	–	Gaspar et al. (2020)	–
	–	n.d.–0.1	–	0.02–0.03	–
	–	Fkiri et al. (2019)	–	Mediavilla et al. (2021)	–
Calarene epoxide	0.14–0.18	–	–		–
	Mellouk et al. (2016)	–	–		–
Caryolan-8-ol	–	–	–	n.d.–0.243	–
	–	–	–	Gaspar et al. (2020)	–
Caryophylla-3,8(13)-dien-5-β-ol	–	n.d.–0.52	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Caryophylla-2(12),6(13)-dien-5-one	–	0.02–0.07	–	–	–
	–	Fkiri et al. (2019)	–	–	–
cis-β-Caryophyllene	–	0.08–0.19	n.d.–0.09	–	–
	–	Kurtca and Tumen (2020)	Kurtca and Tumen (2020)	–	–
trans-β-Caryophyllene	4.92–7.63	8.2	0.38–0.86	0.207–13.7	3.15
	Mellouk et al. (2016)	Aloui et al. (2021)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	0.3–25.1[b]	1.49	8.31–12.06	2.1–5.5
	–	Fekih et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	10.74–14.66	–	–	–
	–	Fkiri et al. (2019)	–	–	–
	–	8.26–12.14	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	15.46	–	–	–
	–	Tümen et al. (2018)	–	–	–
Caryophyllene oxide	1.42–1.51	n.d.–1.3[b]	n.d.–0.02	n.d.–0.411	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
	7[a]	0.09–2.24	0.04	0.25–0.26	–
	Sousa et al. (2018)	Fkiri et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	–	0.10–0.18	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.47	–	–	–
	–	Tümen et al. (2018)	–	–	–
Caryophyllenyl alcohol	1.09–1.19	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Cedreanol	–	n.d.–0.02	–	–	–
	–	Fkiri et al. (2019)	–	–	–
α-Cedrenal	–	n.d.–0.38	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Clovene	–	–	–	n.d.–1.07	–
	–	–	–	Gaspar et al. (2020)	–
α-Copaene	–	n.d.–3.8[b]	0.53–0.71	n.d.–0.785	0.09–0.14
	–	Fekih et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	0.09–0.36	0.19	0.35–0.6	n.d.–0.1
	–	Fkiri et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	1.2–1.77	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.61	–	–	–
	–	Tümen et al. (2018)	–	–	–
β-Copaene	–	1.83	n.d.–0.14	0.369–8.14	–
	–	Aloui et al. (2021)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
α-Costol	–	n.d.–0.29		0.06–0.16	–
	–	Fkiri et al. (2019)	–	Mediavilla et al. (2021)	–
γ-Costol	–	n.d.–0.36	–	–	–
	–	Fkiri et al. (2019)	–	–	–
α-Cubebene	–	n.d.–0.4[b]	–	0.0434–0.247	0.11–0.13
	–	Fekih et al. (2019)	–	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	2.23–3.40	–	0.12–0.24	0.1–0.4
	–	Fkiri et al. (2019)	–	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	0.28–0.43	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
β-Cubebene	–	0.64–1.30	–	n.d.–0.214	–
	–	Fkiri et al. (2019)	–	Gaspar et al. (2020)	–
	–	0.18–0.27	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
Cubenol	0.75–0.81	–	–	0.04–0.05	–
	Mellouk et al. (2016)	–	–	Mediavilla et al. (2021)	–
Cycloisosativene	–	–	0.15–0.16	–	–
	–	–	Kurtca and Tumen (2020)	–	–
Cyclosativene	–	n.d.–0.02	0.08	–	–
	–	Fkiri et al. (2019)	Tümen et al. (2018)	–	–
Dehydroaromadendrene	–	n.d.–0.25	–	–	–
	–	Fkiri et al. (2019)	–	–	–
9,10-Dehydro-isolongifolene	–	n.d.–0.07	–	–	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	–	Fkiri et al. (2019)	–	–	–
8,9-Dehydro-neoisolongifolene	–	n.d.–0.03	–	–	–
	–	Fkiri et al. (2019)	—	–	–
1-Deoxycapsidiol	–	n.d.–0.11	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Diepicedrene-1-oxide	–	n.d.–0.06	–	–	–
	–	Fkiri et al. (2019)	–	–	–
1,10-Diepicubenol	–	–	–	n.d.–0.264	–
	–	–	–	Gaspar et al. (2020)	–
α-Elemene	–	n.d.–0.42	n.d.–0.20	0.02–0.03	–
	–	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
β-Elemene	–	0.05	–	–	–
	–	Tümen et al. (2018)	–	–	–
δ-Elemene	–	0.16–0.24	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
δ-Elemol	–	–	n.d.–0.08	–	–
	–	–	Kurtca and Tumen (2020)	–	–
Epizonarene	–	–	–	n.d.–0.675	–
	–	–	–	Gaspar et al. (2020)	–
Eudesma-4(14),7(11)-diene	–	n.d–0.15	–	–	–
	–	Fkiri et al. (2019)	–	–	–
β-Eudesmol	0.84–0.99	n.d.–0.28	0.03–0.18	–	–
	Mellouk et al. (2016)	Fkiri et al. (2019)	Kurtca and Tumen (2020)	–	–
	–	n.d.–0.04	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
Farnesal	–	n.d.–0.12	–	–	–
	–	Fkiri et al. (2019)	–	–	–
β-Farnesene	–	0.30–0.40	0.25–0.45	n.d.–0.297	–
	–	Kurtca and Tumen (2020)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
		0.17	0.07	0.1–0.14	–
	–	Tümen et al. (2018)	Tümen et al. (2018)	Mediavilla et al. (2021)	–
Farnesol	–	n.d.–0.73	–	n.d.–0.232	–
	–	Fkiri et al. (2019)	–	Gaspar et al. (2020)	–
	–	0.21	–	0.01–0.05	–
	–	Tümen et al. (2018)	–	Mediavilla et al. (2021)	–
Farnesyl acetate	–	0.64	–	0.05	–
	–	Aloui et al. (2021)	–	Mediavilla et al. (2021)	–
	–	n.d.–0.5[b]	–	–	–
	–	Fekih et al. (2019)	–	–	–
	–	0.06–0.43	–	–	–
	–	Fkiri et al. (2019)	–	–	–
	–	0.88	–	–	–
	–	Tümen et al. (2018)	–	–	–
Fonenol	–	n.d.–0.29	–	n.d.–0.656	–
	–	Fkiri et al. (2019)	–	Gaspar et al. (2020)	–
β-Funebrene	–	–	–	0.09–0.23	–
	–	–	–	Mediavilla et al. (2021)	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
Germacrene	–	n.d.–4.7^b	–	–	–
	–	Fekih et al. (2019)	–	–	–
Germacrene B	–	n.d.–0.11	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Germacrene D	–	1.86–4.63	3.22–9.66	4.05–10.37	–
	–	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	20.36–25.63	0.01	–	–
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	–	–
	–	0.40	–	–	–
	–	Tümen et al. (2018)	–	–	–
Globulol	–	n.d.–0.45	–	–	–
	–	Fkiri et al. (2019)	–	–	–
α-Guaiene	–	n.d.–0.05	–	–	–
	–	Fkiri et al. (2019)	–	–	–
	–	n.d.–0.03	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
Guiaol	–	n.d.–0.5^b	–	0.09–0.19	–
	–	Fekih et al. (2019)	–	Mediavilla et al. (2021)	–
	–	n.d.–1.62	–	–	–
	–	Fkiri et al. (2019)	–	–	–
	–	0.24–0.59	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.56	–	–	–
	–	Tümen et al. (2018)	–	–	–
α-Gurjunene	–	n.d.–0.21	–	–	–
	–	Fkiri et al. (2019)	–	–	–
γ-Gurjunene	–	n.d.–0.11	–	–	–
	–	Fkiri et al. (2019)	–	–	–
γ-Gurjunenepoxide-(2)	0.18–0.37	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
α-Himachalene	0.20–0.50	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
α-Humulene	2.19–3.34	tr.–30.7^b	0.07–0.13	0.0565–2.65	0.39–0.42
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	3.53–4.45	0.28	1.2–1.79	0.3–0.9
	–	Fkiri et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	1.82–2.22	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	2.70	–	–	–
	–	Tümen et al. (2018)	–	–	–
Humelene epoxide II	–	n.d.–0.4^b	–	–	–
	–	Fekih et al. (2019)	–	–	–
Humulol	0.42–0.47	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Isoaromadendrene epoxide	0.43–0.49	0.04–0.11	–	–	–
	Mellouk et al. (2016)	Fkiri et al. (2019)	–	–	–
Isogermacrene D	–	–	–	n.d.–0.195	–
	–	–	–	Gaspar et al. (2020)	–
Isoledene	–	n.d.–0.04	–	–	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	–	Fkiri et al. (2019)	–	–	–
Isolongifolol	4[a]	–	–	–	–
	Sousa et al. (2018)	–	–	–	–
Isospathulenol	–	n.d.–0.03	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Lepidozenal	–	n.d.–0.04	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Longiborneol	0.63–0.82	–	n.d.–1.09	n.d.–0.287	–
	Mellouk et al. (2016)	–	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
Longicamphenylone	0.16–0.19	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Longicyclene	–	–	0.79–0.99	–	–
	–	–	Kurtca and Tumen (2020)	–	–
	–	–	0.42	–	–
	–	–	Tümen et al. (2018)	–	–
Longifolene	21[a]	1.53	11.22–12.82	n.d.–1.86	2.38–3.02
	Sousa et al. (2018)	Aloui et al. (2021)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	n.d.–3.4[b]	9.45	1.70–2.11	2.2.–5.3
	–	Fekih et al. (2019)	Tümen et al. (2018)	Mediavilla et al. (2021)	Arrabal et al. (2005)
	–	n.d.–0.03	–	–	–
	–	Fkiri et al. (2019)	–	–	–
	–	0.16–0.27	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.64	–	–	–
	–	Tümen et al. (2018)	–	–	–
α-Longipinene	–	1.16	1.71–2.44	n.d.–0.273	–
	–	Aloui et al. (2021)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
	–	0.15	1.20	0.14–0.18	–
	–	Tümen et al. (2018)	Tümen et al. (2018)	Mediavilla et al. (2021)	–
Muurola-3,5-diene	–	–	–	0.04–0.09	–
	–	–	–	Mediavilla et al. (2021)	–
Muurola-4(14),5-diene	–	–	–	n.d.–0.302	–
	–	–	–	Gaspar et al. (2020)	–
α-Muurolene	0.16–0.17	n.d.–0.4[b]	0.38–0.63	n.d.–2.42	–
	Mellouk et al. (2016)	Fekih et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
	–	1.19–1.92	0.07	0.3–0.63	–
	–	Kurtca and Tumen (2020)	Tümen et al. (2018)	Mediavilla et al. (2021)	–
	–	0.07	–	–	–
	–	Tümen et al. (2018)	–	–	–
γ-Muurolene	–	–	–	n.d.–0.168	–
	–	–	–	Gaspar et al. (2020)	–
τ-Muurolol	–	n.d.–1.52	0.03–0.16	n.d.–2.18	–
	–	Fkiri et al. (2019)	Kurtca and Tumen (2020)	Gaspar et al. (2020)	–
	–	0.10–0.63	–	n.d.–0.03	–
	–	Kurtca and Tumen (2020)	–	–	–
Nerolidol	–	n.d.–0.7[b]	–	n.d.–0.228	–
	–	Fekih et al. (2019)	–	Gaspar et al. (2020)	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
γ-Patchoulene	–	n.d.–0.12	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Salvial-4(14)-en-1-one	–	n.d.–0.51	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Sativene	–	–	0.52–0.64	0.04–0.05	–
	–	–	Kurtca and Tumen (2020)	Mediavilla et al. (2021)	–
	–	–	0.26	–	–
	–	–	Tümen et al. (2018)	–	–
α-Selinene	–	n.d.–0.18	–	0.02–0.05	–
	–	Fkiri et al. (2019)	–	Mediavilla et al. (2021)	–
β-Selinene	–	0.16–0.32	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Spathulenol	–	0.36	–	–	–
	–	Aloui et al. (2021)	–	–	–
Valencene	2.70–2.76	n.d.–0.05	0.24–0.43	–	–
	Mellouk et al. (2016)	Fkiri et al. (2019)	Kurtca and Tumen (2020)	–	–
	–	0.88–1.36	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
Vilgarol B	–	n.d.–1.99	–	–	–
	–	Fkiri et al. (2019)	–	–	–
α-Ylangene	–	0.33–0.66	–	n.d.–0.233	–
	–	Fkiri et al. (2019)	–	Gaspar et al. (2020)	–
	–	0.17–0.25	–	0.06–0.15	–
	–	Kurtca and Tumen (2020)	–	Mediavilla et al. (2021)	–
	–	0.04	–	–	–
	–	Tümen et al. (2018)	–	–	–
Diterpenes	–	–	–	–	–
Abienol	–	–	–	–	0.36–0.69
	–	–	–	–	Arrabal et al. (2002)
	–	–	–	–	0.3–1.3
	–	–	–	–	Arrabal et al. (2005)
Abietadiene	–	2.5	–	0.579–36.3	–
	–	Aloui et al. (2021)	–	Gaspar et al. (2020)	–
	–	1.51–4–10	–	0.85–4.34	–
	–	Kurtca and Tumen (2020)	–	Mediavilla et al. (2021)	–
	–	10.81	–	–	–
	–	Tümen et al. (2018)	–	–	–
Abieta-8,12-diene	–	n.d.–3.4[b]	–	0.35–1.33	–
	–	Fekih et al. (2019)	–	Mediavilla et al. (2021)	–
Abieta-8(14),12-diene	–	–	–	n.d.–1.50	–
	–	–	–	Gaspar et al. (2020)	–
Abieta-8(14),13(15)-diene	–	n.d.–2.3[b]	–	n.d.–3.07	–
	–	Fekih et al. (2019)	–	Gaspar et al. (2020)	–
Abietal	–	–	–	n.d.–3.46	–
	–	–	–	Gaspar et al. (2020)	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
Abietane	–	n.d.–8.61	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Abietatriene	–	0.92	–	n.d.–4.39	–
	–	Aloui et al. (2021)	–	Gaspar et al. (2020)	–
	–	n.d.–4.97	–	0.06–0.87	–
	–	Fkiri et al. (2019)	–	Mediavilla et al. (2021)	–
	–	0.35–0.62	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	8.36	–	–	–
	–	Tümen et al. (2018)	–	–	–
7,13,15-Abietatrienoic acid	–	–	–	–	0.68–0.72
	–	–	–	–	Arrabal et al. (2002)
	–	–	–	–	0.9–1.7
	–	–	–	–	Arrabal et al. (2005)
Abieta-8,11,13-trien-7-one	–	n.d.–0.11	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Abietic acid	0.61–23.53	–	–	n.d.–4.12	13.36–13.67
	Kurtca and Tumen (2020)	–	–	Gaspar et al. (2020)	Arrabal et al. (2002)
	9.1–14.14	–	–	–	12.8–14.7
	Simões et al. (2021)	–	–	–	Arrabal et al. (2005)
	62[a]	–	–	–	14.0–16.1
	Sousa et al. (2018)	–	–	–	Ottavioli et al. (2019)
Abietol	–	–	–	n.d.–3.86	–
	–	–	–	Gaspar et al. (2020)	–
Agathadiol	–	n.d.–0.14	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	0.29	–	–	–
	–	Tümen et al. (2018)	–	–	–
Biformene	0.68–1.34	n.d.–0.01	–	–	–
	Mellouk et al. (2016)	Fkiri et al. (2019)	–	–	–
Cembrene	–	12.22	–	–	–
	–	Aloui et al. (2021)	–	–	–
	–	n.d.–0.02	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Cupressene	–	0.98–3.43	–	–	–
	–	Kurtca and Tumen (2020)	–	–	–
	–	5.21	–	–	–
	–	Tümen et al. (2018)	–	–	–
Dehydroabietal	–	–	–	n.d.–1.26	–
	–	–	–	Gaspar et al. (2020)	–
Dehydroabietic acid	2.23–6.61	n.d.–0.2	–	n.d.–3.17	3.01–3.60
	Kurtca and Tumen (2020)	Fkiri et al. (2019)	–	Gaspar et al. (2020)	Arrabal et al. (2002)
	6.9–11.4	–	–	–	3.5–6.6
	Simões et al. (2021)	–	–	–	Arrabal et al. (2005)
	954[a]	–	–	–	10.1–23.5

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	Sousa et al. (2018)	–	–	–	Ottavioli et al. (2019)
Dehydroabietol	–	–	–	n.d.–1.09	–
	–	–	–	Gaspar et al. (2020)	–
Epimanoyl oxide	–	1.74	–	–	–
	–	Aloui et al. (2021)	–	–	–
	–	0.17–0.29	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Ferruginol	–	n.d.–0.08	–	–	–
	–	Fkiri et al. (2019)	–	–	–
7-Hydroxydehydroabietic acid	2.3–3.7	–	–	–	–
	Simões et al. (2021)	–	–	–	–
	297^{a}	–	–	–	–
	Sousa et al. (2018)	–	–	–	–
15-Hydroxydehydroabietic acid	1.5–2.5	–	–	–	0.2–1.2
	Simões et al. (2021)	–	–	–	Ottavioli et al. (2019)
	269^{a}	–	–	–	–
	Sousa et al. (2018)	–	–	–	–
15-Hydroxy-7-oxodehydroabietic acid	75^{a}	–	–	–	–
	Sousa et al. (2018)	–	–	–	–
Di(dehydroabietic acid)	1.5–3.9	–	–	–	–
	Simões et al. (2021)	–	–	–	–
	18^{a}	–	–	–	–
	Sousa et al. (2018)	–	–	–	–
7,15-Dihydroxydehydroabietic acid	100^{a}	–	–	–	–
	Sousa et al. (2018)	–	–	–	–
		–	–	–	–
Isoabienol	–	–	–	–	0.94–1.07
	–	–	–	–	Arrabal et al. (2002)
	–	–	–	–	0.1–0.9
	–	–	–	–	Arrabal et al. (2005)
Isopimara-7,15-diene	–	n.d.–0.05	–	–	
	–	Fkiri et al. (2019)	–	–	
Isopimaral	–	–	–	–	0.82–0.85
	–	–	–	–	Arrabal et al. (2002)
	–	–	–	–	0.1–0.5
	–	–	–	–	Arrabal et al. (2005)
Isopimaric acid	0.39–1.66	–	–	–	7.86–8.48
	Kurtca and Tumen (2020)	–	–	–	Arrabal et al. (2002)
	1.63–2.15	–	–	–	4.0–11.00
	Simões et al. (2021)	–	–	–	Arrabal et al. (2005)
	128^{a}	–	–	–	6.1–6.9
	Sousa et al. (2018)	–	–	–	Ottavioli et al. (2019)
11,13-Labdien-8-ol	–	–	–	–	0.34–0.36
	–	–	–	–	Arrabal et al. (2002)
	–	–	–	–	n.d.–0.2
	–	–	–	–	Arrabal et al. (2005)

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
13(16),14-Labdien-8-ol	–	–	–	n.d.–0.724	–
	–	–	–	Gaspar et al. (2020)	–
Levopimaric acid	0.96–2.70	–	–	n.d.–2.99	42.03–42.30[e]
	Kurtca and Tumen (2020)	–	–	Gaspar et al. (2020)	Arrabal et al. (2002)
	–	–	–	–	41.2–45.3[e]
	–	–	–	–	Arrabal et al. (2005)
	–	–	–	–	8.1–21.2
	–	–	–	–	Ottavioli et al. (2019)
Manool	–	n.d.–0.01	–	n.d.–7.19	–
	–	Fkiri et al. (2019)	–	Gaspar et al. (2020)	–
Manoyl oxide	1.28–1.95	3.45	–	–	–
	Mellouk et al. (2016)	Aloui et al. (2021)	–	–	–
Methyl abietate	–	0.03–0.04	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Neoabietadiene	–	0.19–0.61	–	n.d.–0.76	–
	–	Kurtca and Tumen (2020)	–	Mediavilla et al. (2021)	–
	–	0.87	–	–	–
	–	Tümen et al. (2018)	–	–	–
Neoabietic acid	tr.–13.39	–	–	–	16.99–17.72
	Kurtca and Tumen (2020)	–	–	–	Arrabal et al. (2002)
	–	–	–	–	16.1–17.2
	–	–	–	–	Arrabal et al. (2005)
	–	–	–	–	5.5–10.5
	–	–	–	–	Ottavioli et al. (2019)
Neoabietol	–	–	–	n.d.–1.03	–
	–	–	–	Gaspar et al. (2020)	–
Neophytadiene	–	0.07–0.1	–	n.d.–0.434	–
	–	Fkiri et al. (2019)	–	Gaspar et al. (2020)	–
7-Oxoabieta-8,11,13-triene	–	n.d.–0.22	–	–	–
	–	Fkiri et al. (2019)	–	–	–
7-Oxodehydroabietic acid	179[a]	–	–	–	–
	Sousa et al. (2018)	–	–	–	–
Palustric acid	–	–	–	–	42.03–42.30[e]
	–	–	–	–	Arrabal et al. (2002)
	–	–	–	–	41.2–45.3[e]
	–	–	–	–	Arrabal et al. (2005)
	–	–	–	–	8.5–9.5
	–	–	–	–	Ottavioli et al. (2019)
Pimara-8(9),15-diene	–	n.d.–0.58	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Pimara-8(14),15-diene	–	n.d.–0.03	–	n.d.–0.0957	–
	–	Fkiri et al. (2019)	–	Gaspar et al. (2020)	–
Pimaric acid	1.12–2.87	–	–	–	6.63–7.14
	Kurtca and Tumen (2020)	–	–	–	Arrabal et al. (2002)
	6.1–10.2	–	–	–	6.6–7.5

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
	Simões et al. (2021)	–	–	–	Arrabal et al. (2005)
	217^{a}	–	–	–	9.3–10.8
	Sousa et al. (2018)	–	–	–	Ottavioli et al. (2019)
Pimarinal	–	–	–	–	0.48–0.61
	–	–	–	–	Arrabal et al. (2002)
	–	–	–	–	0.1–0.4
	–	–	–	–	Arrabal et al. (2005)
Phytol	–	1.23	–	–	–
	–	Aloui et al. (2021)	–	–	–
	–	n.d.–0.04	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Pumiloxide	–	n.d.–0.12	–	–	–
	–	Fkiri et al. (2019)	–	–	–
Rimuene	–	0.78–2.44	–	n.d.–7.58	–
	–	Kurtca and Tumen (2020)	–	Gaspar et al. (2020)	–
	–	9.13	–	0.35–1.63	–
	–	Tümen et al. (2018)	–	Mediavilla et al. (2021)	
Sandaracopimaric acid	0.39–1.66	–	–	–	1.61–1.74
	Kurtca and Tumen (2020)	–	–	–	Arrabal et al. (2002)
	128^{a}	–	–	–	1.3–1.5
	Sousa et al. (2018)	–	–	–	Arrabal et al. (2005)
	–	–	–	–	1.2–1.3
	–	–	–	–	Ottavioli et al. (2019)
Sandaracopimarinal	–	–	–	n.d.–0.672	–
	–	–	–	Gaspar et al. (2020)	–
Sandaracopimarinol	–	–	–	n.d.–0.665	–
	–	–	–	Gaspar et al. (2020)	–
Sclarene	0.36–0.77	n.d.–8.25	–		–
	Mellouk et al. (2016)	Fkiri et al. (2019)	–	–	–
Sclareol	–	0.06	–	–	–
	–	Tümen et al. (2018)	–	–	–
Verticiol	0.33–0.77	–	–	–	–
	Mellouk et al. (2016)	–	–	–	–
Triterpenes	–	–	–	–	–
Betulin	465^{a}	–	–	–	–
	Sousa et al. (2018)	–	–	–	–
Campesterol	33^{a}	–	–	–	–
	Sousa et al. (2018)	–	–	–	–
β-Sitosterol	0.31–6.69	–	–	–	–
	Kurtca and Tumen (2020)	–	–	–	–
	0.4–0.8	–	–	–	–
	Simões et al. (2021)	–	–	–	–
	434^{a}	–	–	–	–
	Sousa et al. (2018)	–	–	–	–

Table 5 (continued)

	Bark	Needles	Cones	Branches/twigs	Oleoresin
Stigmast-5-ene	n.d.–0.1	–	–	–	–
	Simões et al. (2021)	–	–	–	–
Stigmast-4-en-3-one[d]	120[a]	–	–	–	–
	Sousa et al. (2018)	–	–	–	–

n.d. not detected, *tr.* traces

[a] Result expressed as mg/kg of dried bark

[b] Needles and other aerial parts (twigs and buds)

[c] Limonene + α-phellandrene

[d] Stigmast-4-en-3-one + 2,3-dihydroxypropyl tetracosanoate

[e] Levopimaric acid + palustric acid

Gabaston et al. (2020) identified several phenolic compounds in maritime pine knots, many of them lignans, such as isolariciresinol, nortrachelogenin, matairesinol, lariciresinol, secoisolariciresinol, and derivatives. In addition to lignans, the knots contained several stilbenes, which were resveratrol, pinosylvin, pinostilbene, pterostilbene, and derivatives, and flavonoids, mainly taxifolin, pinocembrin, aromadendrin, and derivatives.

Volatile compounds of branches were studied by Gaspar et al. (2020) and Mediavilla et al. (2021). According to Gaspar et al. (2020), monoterpenes were those naturally emitted by maritime pine branches, especially β-pinene, which represented 12.2% of relative abundance (Table 5). Limonene and β-myrcene were major compounds too, with more than 10%, while α-pinene represented 8.5%. The extract obtained by hydrodistillation was rich in sesquiterpenes and diterpenes. The only sesquiterpene with a relative abundance higher than 10% was β-caryophyllene, with 13.7%. β-Copaene and δ-cadinene represented 8.14% and 7.11%, respectively. Regarding diterpenes, abietadiene was the major one with 20.2%. Mediavilla et al. (2021) reported higher relative abundances for α-pinene and β-pinene, which were higher than 20% in most cases, and even close to 30%. β-Myrcene maximum relative abundance was close to 10%, but limonene showed lower values. β-Caryophyllene was a major sesquiterpene and the maximum relative abundance was 12.06%, close to the value reported by Gaspar et al. (2020). However, β-copaene and δ-cadinene were minor sesquiterpenes, according to Mediavilla et al. (2021), and they reported a high relative abundance of germacrene D, which had a maximum value of 10.37%. Diterpenes showed lower relative abundances and abietadiene presented a maximum value of 4.34%. Celhay et al. (2014) studied antioxidant activity of knots and stumps through DPPH assay and aqueous extracts of knots were more active, with an IC_{50} of 22.1 mg/L.

2.2.2 *Needles*

Aloui et al. (2021) studied the essential oil obtained from needles by steam distillation, identifying 20 compounds, but only six presented a relative abundance higher than 2% (Table 5). Major compounds were monoterpenes, especially limonene, which represented more than half of essential oil, 51.9%, and α-pinene about 7.0%. Cembrene, manoyl oxide and abietadiene, all of them diterpenes, represented 12.2, 3.5 and 2.2%, respectively. Regarding sesquiterpenes, the major one was β-caryophyllene, which presented a relative abundance of 8.2%.

These results do not seem consistent with the previous data of Fkiri et al. (2019), who found more than 100 compounds in the needle essential oil. They analysed the essential oil, obtained by hydrodistillation, from two different varieties and most of the compounds were only present in one of them. Major compounds were sesquiterpenes and β-caryophyllene presented the highest relative abundance, from 10.7 to 14.7%. α-Humulene and α-cubenene were the two other compounds with a relative abundance higher than 2% in the two varieties, while α-amorphene and germacrene D exceeded 2% only in one of them, but it was close to it in the other one. Limonene was detected in one of the varieties and its content was very low, while it represented more than half of essential oil according to Aloui et al. (2021). α-Pinene was the other major compound reported by Aloui et al. (2021), detected in the two varieties analysed by Fkiri et al. (2019), but in lower quantities. Kurtca and Tumen (2020) reported a high relative abundance of α-pinene, from 18.85 to 29.83%, and it was the major compound in needle essential oil. Tümen et al. (2018) indicated that relative abundance of α-pinene was 13.53% and the major monoterpene, followed by β-pinene, with a relative abundance of 9.81% (Table 3).

Fekih et al. (2019) studied the essential oil obtained by hydrodistillation from aerial parts, which included needles, twigs and buds. Their results could not be compared directly because the plant material contained more than the needles, still, there were interesting similarities and differences to discuss. Limonene, with a maximum value of 7.8%, showed a higher relative abundance than in the case of Fkiri et al. (2019), but it did not reach the value reported by Aloui et al. (2021). Even so, the monoterpenes were the major compounds because the relative abundance of α-pinene was very high, from 18.0 to 72.7%, and β-pinene showed higher results as well, with a maximum value of 33.6%.

As previously stated, one of the major sesquiterpene compounds was β-caryophyllene, and the relative abundance reported by Fkiri et al. (2019) was the highest and reached a maximum value of 25.1%. The presence of α-humulene, α-cubebene and a germacrene derivative was reported by Fkiri et al. (2019) too, and the relative abundance of the first one, which was 30.7%, stood out because it was much higher than data reported by Fekih et al. (2019). According to Kurtca and Tumen (2020), the major sesquiterpene was germacrene D, with a maximum relative abundance of 25.63%, more than twice maximum value of β-caryophyllene, which were 12.14%. However, Tümen et al. (2018) reported a much higher relative abundance of β-caryophyllene, 15.46%, than germacrene D, 0.40%. Regarding diterpenoids, several abietane derivatives were reported by all the authors, but compounds and relative abundances were differed depending on the study. Abietadiene and abietatriene, as well as manoyl oxide, were those reported by a higher number of authors. The relative abundance of abietadiene indicated by Tümen et al. (2018) was the highest one, 10.81%.

Maritime pine needles are covered by cuticular waxes and Nikolić et al. (2020) studied their composition. Nonacosal-10-ol was the major compound and represented more than three quarters of wax composition. They also studied the *n*-alkanes proportion and long chain alkanes (n-$C_{25\text{-}35}$) represented more than 80% of total *n*-alkanes. The most dominant was n-C_{29}, which represented a quarter of total *n*-alkanes.

Antioxidant activity of needle essential oil was studied by several authors, but Tümen et al. (2018) studied extracts too, and according to their results, which are included in Table 4, the essential oil was more effective than the extracts in all assays with the lowest IC_{50} values (107.28–152.27 µg/mL), except in the case of FRAP because acetonic extract showed the highest reducing capacity (19.74%). DPPH scavenging activity was the most frequent methodology for testing antioxidant activity of needle essential oil and IC_{50} values ranged from 42 µg/mL (Fkiri et al. 2019) to 12 mg/mL (Fekih et al. 2019), so there was a several orders of magnitude difference between them.

Aloui et al. (2021) tested the antibacterial activity of needle essential oil against *Bacillus subtilis*, *Listeria monocytogenes*, *Salmonella enterica* and *Escherichia coli* and they considered that it showed a strong growth inhibition in all cases. The study of Fkiri et al. (2019) included seven bacteria and the best results were observed against *Bacillus cereus* and *Staphylococcus aureus* (Table 4). Fekih et al. (2019) tested nine bacteria and the highest inhibitory activity was detected against *Enterococcus faecalis*. Besides, they observed antifungal activity against several *Candida albicans* strains.

2.2.3 *Cones*

Tümen et al. (2018) and Kurtca and Tumen (2020) studied essential oil from cones too, and they found that monoterpenes were major compounds, especially α-pinene and β-pinene, which presented a maximum relative abundance of 37.96% and 27.39%, respectively (Table 5). Regarding sesquiterpenes, β-caryophyllene's relative abundance was much lower than in needles, and longifolene (or junipene) was the major one, with a maximum relative abundance of 12.82%. According to Kurtca and Tumen (2020), germacrene D was also present in cone essential oil and its relative abundance ranged from 3.22 to 9.66%, but Tümen et al. (2018) reported a much lower value, 0.01%. The authors did not detect any diterpene in cone essential oil.

Antioxidant activity of cone essential oil and acetonic and *n*-hexanic extracts has also been studied by Tümen et al. (2018). The essential oil was more active than extracts in non-site-specific hydroxyl and DPPH radical scavenging activity assays (IC_{50} 105.17 and 85.82 µg/mL, respectively, Table 4), while acetonic extract was the most effective in the ABTS and FRAP assays (IC_{50} 99.13 µg/mL and 30.11% reducing capacity, respectively, Table 4). The acetonic extract was more active than n-hexanic extract in all the methods tested.

2.2.4 *Oleoresin*

Oleoresins are semi-solid extracts composed of resin and essential fatty oils. The oleoresin of maritime pine is especially rich in resin acids, mainly abietic acid and pimaric acid derivatives, which are diterpenoids with implication in plant defence, especially against insects (López-Goldar et al. 2020). Ottavioli et al. (2019) studied Corsican maritime pines and they established a classification in two groups, the first one stood out due to the presence of dehydroabietic acid, with an average relative abundance of 23.5%, while levopimaric acid was highlighted in the second group, with an average relative abundance of 21.2% (Table 5). These compounds showed a lower relative abundance in the other groups, but the values (10.8% and 8.1%) were higher than other resin acids. Abietic acid was similar in the two groups, with average values of 16.1% and 14.0%. Its major derivatives, in addition to dehydroabietic and levopimaric acids, were neoabietic acid, which showed a relative abundance higher than 10% in one the groups, and palustric acid, with a relative abundance close to 9%. Pimaric acid was close to 10% in both groups, while isopimaric acid was lower than 7% and sandaracopimaric acid close to 1%. Ottavioli et al. (2019) also reported the presence of the lignan pinoresinol in maritime pine oleroresin.

The previous studies of Arrabal et al. (2002, 2005) indicated that diterpenes were major compounds of oleoresin of Iberian maritime pines, but they reported the presence of monoterpenes and sesquiterpenes too. Abietane-type resin acids showed the highest relative abundances, especially the sum of levopimaric and palustric acids, which represented more than 40%. Abietic acid relative abundance was similar in the three studies (Arrabal et al. 2002, 2005; Ottavioli et al. 2019), but dehydroabietic acid showed a lower relative abundance in the studies of Arrabal et al. (2002, 2005), close to 3% in most cases. On the contrary, neoabietic acid reached higher relative abundance percentages (16–17%) in their studies. The profile of pimarane-type resin acids was similar, although there were differences in values, with pimaric and isopimaric acids as the main ones, followed by sandaracopimaric acid (Arrabal et al. 2002, 2005; Ottavioli et al. 2019).

3 Industrial applications of bark and other parts of maritime pine

Maritime pine is especially exploited for its wood, as stated above, and one of the main by-products of the wood industry is bark, which represents up to 20% of the pine's trunk (Vieito et al. 2019). Bark is discarded in the first stages of transformation, as well as the branches and needles, while woodchips and sawdust are by-products which are generated in other transformation stages (Abilleira et al. 2021; Zhou 2003). Branches are considered a pruning residue too (Gaspar et al. 2020). Needles and cones were widely used in small rural farms to light the fire in traditional kitchens and as agricultural mulches. However, nowadays they are mostly left in the forest, and contribute towards dissemination of forest fires due to being extremely flammable (Santos et al. 2021). In this section, several industrial applications of the different parts of maritime pine were covered. It is worthy of mention that some of these applications are not exclusive to maritime pine (Neis et al. 2019), although this review does not contain information on other species.

3.1 Applications of bark in pharma-food industries

Pine bark was traditionally used in Europe against scurvy, kidney, and bladder symptoms (Drehsen 1999) as well as other ailments. Recently, it is monographed in the United States Pharmacopeia (USP) as a dietary supplement (Kurlbaum and Högger 2011). Nowadays, it has become somewhat interesting for pharma-food industries, namely by patenting it as a source of procyanidins under the trade name of Pycnogenol® (Horphag Research, Ltd. UK, Geneva, Switzerland) and its quality is specified in the USP. The term pycnogenol is confusing due it being used as a synonym of proanthocyanidins from different plants, not only maritime pine. Some grape seed extracts were labelled in the USA as containing pycnogenols because they had proanthocyanidins, but they were considerably different (D'Andrea 2010). Oligopin® is another formulation based on maritime pine bark (Dziedziński et al. 2021), as well as Flavangenol®, which consist of aqueous extracts of maritime pine bark and (Mármol et al. 2019).

Systemic toxicity and mutagenicity of maritime pine bark extract was evaluated by Segal et al. (2018), having carried out a bacterial reverse mutation assay and an in vitro mammalian chromosome aberration assay with human lymphocytes, and the results indicated that the extract was not genotoxic in both bacterial and human cell assays. Toxicity was evaluated in an acute oral limit test and a 90-day repeated oral dose toxicity study with Sprague Dawley rats. The extracts were not acutely toxic by oral administration up to 2 g/kg, and that the oral administration of 1 g/kg/day for 90 days was well tolerated and no adverse effects were observed.

3.1.1 Therapeutic applications

Therapeutic applications of pycnogenol are very widespread, but D'Andrea (2010) considered that none of them had strong evidence and only two of them presented good scientific evidence, against asthma and chronic venous insufficiency. Other therapeutic uses, more than 20, were considered unclear. Dziedziński et al. (2021) referred that the pharmacological activity declared by the manufacturer for Pycnogenol® were antimicrobial activity, treatment of asthma, attention deficit hyperactivity disorder (ADHD), chronic venous insufficiency, diabetes, erectile disorders and osteoarthritis. Oligopin® manufacturer declared that its pharmacological activity is cardiovascular and vein health, antioxidant, treatment of male disorders and ADHD.

Notwithstanding the foregoing, there are several studies about the positive health effects of the extract of maritime pine bark and the commercial products. David et al. (2019) indicated that dietary supplementation with this extract was related to attenuated oxidative and inflammatory mediators and impaired tumour development due to the chemoprotective activity of the procyanidins. Ďuračková et al. (2003) reported positive effects of supplementation with extract of maritime pine bark to patients with erectile dysfunction. Enseleit et al. (2012) studied the effect on endothelial function in patients with stable coronary artery disease and an improvement was observed. The extract had a great effect upon nitric oxide availability in untreated and dysfunctional cells, and plasma nitrite concentrations increased 8 h post-consumption in healthy volunteers (Jones et al. 2020). However, according to Uhlenhut and Högger (2012), one of the main metabolites of maritime pine bark extract, δ-(3,4-dihydroxyphenyl)-γ-valerolactone, inhibited nitrite production because it had the capacity to reduce the expression of nitric oxide synthase. Valls et al. (2016) reported an improvement on lipid cardiovascular profile in stage-1 hypertensive patients after supplementation with maritime pine bark extract. The concentration of oxidized-low density lipoprotein and the systolic pressure decreased, while the concentration of high-density lipoprotein-cholesterol increased.

A study carried out by Feng et al. (2011) suggested the potential of the procyanidin-rich extract from bark as a new anti-human immunodeficiency virus type-1 (HIV-1) agent, as it inhibited not only HIV-1 binding to host cells, but also its replication in vitro after entry in susceptible cells. Malekahmadi et al. (2020) suggested that maritime pine bark extract could improve clinical and nutritional status in traumatic brain injury patients. According to Furumura et al. (2012), supplementation with maritime pine bark extract showed a significant decrease in clinical grading of skin photoaging scores, which meant a clinically significant improvement in photodamaged skin. Paarmann et al. (2019) suggested that maritime pine bark extract could be potentially used in the prevention of mild cognitive impairment of Alzheimer's disease, in early stages, but clinical evaluation should be carried out.

Panahande et al. (2019) tested the effectiveness of maritime pine bark extract on bone remodelling in postmenopausal osteopenic women, and a positive effect on bone markers was observed. Rašković et al. (2019) evaluated the hepatoprotective potential of maritime pine bark extract, specifically the protective effect on acetaminophen-induced acute liver injury in rats. The hepatoprotective effect was due to the free radical scavenging properties of the extract to inhibit the production of acetaminophen reactive metabolites.

Schäfer et al. (2005) observed that human plasma obtained from people who had consumed maritime pine bark extract inhibited Cyclooxygenase 1 (COX-1) and COX-2 enzyme activity. They concluded that the bioavailability of the active compounds should be high because the effect was observed only 30 min after the ingestion of the extract.

Shin et al. (2016) evaluated the potential of maritime pine bark extract to inhibit chronic obstructive pulmonary disease (COPD), but some clinical trials did not show beneficial effects of maritime pine bark extracts, particularly the case for polycystic ovary syndrome (PCOS). According to Qorbani et al. (2020), supplementation with maritime pine bark extract did not seem to improve hormonal and metabolic parameters in women with PCOS.

The potential use of maritime pine bark extract in prophylaxis and therapy of several disorders related to a lack of balance or an excessive matrix metalloproteinases (MMP) activity was studied by Grimm et al. (2003). MMP are Zn-dependent proteolytic enzymes that can be activated by ROS and contribute to the inflammatory network and proteolytic tissue damage in pathophysiological conditions. In vivo metabolites of maritime pine bark extract showed antioxidant activity and inhibitory activity on MMP. Two major metabolites of the extract, which were products of (+)-catechin metabolism, were δ-(3,4-dihydroxyphenyl)-γ-valerolactone and δ-(3-methoxy-4-hydroxyphenyl)-γ-valerolactone. Both showed a big inhibitory activity toward MMP-1 (collagenase 1), MMP-2 (gelatinase A), and MMP-9 (gelatinase B). However, only the former showed a good antioxidant activity because the latter was less active in the FRAP assay and did not display superoxide scavenging activity. Still, δ-(3,4-dihydroxyphenyl)-γ-valerolactone was more active than its metabolic precursor, (+)-catechin. Later, Grimm et al. (2006a) provided evidence of anti-inflammatory activity of maritime pine bark extract by inhibition of proinflammatory gene expression. After oral administration of 200 mg of the extract for five days, plasma obtained from volunteers showed a significant inhibition of ex vivo metallopeptidase 9 (MMP-9) enzyme release from monocytes as well as an inhibition of NF-κB activation. Thaichinda et al. (2020) also observed a reduction of MMP-9 release, which was associated to the antiproliferative activity of the maritime pine bark extract on malignant melanoma.

Besides the oral administration, topical use of maritime pine bark extract has also been studied. Pagano et al. (2021) developed a bio-adhesive film which was based on xanthan gum and alginate and that contained glycerol as plasticizing agent. The film was loaded with the maritime pine bark extract, and it released within 24 h by a sustained mechanism. It was considered that the film could be used in wound treatment because it was capable to absorb a simulated wound fluid, nearly 65% of its own weight, it was adaptable to different surfaces, and it showed mechanical resistance. Wound treatment is not exclusive of bark because Tümen et al. (2018) studied the effects of cones and needles on wound healing, and they observed that cone essential oil was also promising.

3.1.2 *Food enrichment*

Maritime pine bark extracts have been used for food enrichment. Yesil-Celiktas et al. (2010) added maritime pine bark extract to orange juice to develop a beverage which could provide a daily intake of the extract and fulfill the expectations of consumers. The fortified juice showed higher total phenolic compounds, ascorbic acid content, and radical scavenging activity compared to the control. The shelf-life was established in six months due to reduction of scavenging activity beyond that date, as well as color degradation. Frontela-Saseta et al. (2011) added the extracts to fruit juices to increase the phenolic content. Fruit juices without extract showed a significant decrease in total phenolic compounds after the in vitro gastrointestinal digestion (GID), while an increase in the antioxidant potential of enriched fruit juices was observed after the digestion process. A similar trend was observed in the antiproliferative activity of fruit juices with and without extracts after in vitro GID. The authors concluded that to obtain a stable phenolic-enriched-fruit juice with better antioxidant properties, the use of maritime pine bark extracts should be studied in depth.

Subsequently, Frontela-Saseta et al. (2013) studied the effect of fresh and digested juices with and without extracts in an in vitro model of intestinal inflammation with Caco-2 cells. It was concluded that in vitro GID reduced the anti-inflammatory effect of fruit juices regardless of the presence of extracts. However, the production of inflammatory mediators, mainly IL-8 and NO, by Caco-2 cells after the inflammatory stimuli did not result in a decrease of transepithelial electrical resistance, so the maritime pine extracts seemed to protect the permeability of intestinal cells. Besides, the extracts were effective in reducing the secretion of the mentioned inflammatory mediators, but they did not show a significative effect on radical oxygen species (ROS) production.

The influence of fruit juices with maritime pine bark extracts on gut microbiota was tested before and after in vitro GID. Fresh fruit juices enriched with the extract showed the highest inhibitory activity on pathogenic bacterial growth, mainly *Escherichia coli* and *Enterococcus faecalis*. The presence of the extract slightly increased the growth of *Lactobacillus casei rhamnosus* and *L. gasseri*, as well as *Bifidobacterium longum* and *B. breve*. GID process reduced in approximately 10% the antibacterial activity of juices against most pathogenic bacteria. So, the addition of maritime pine bark extract to fruit juices could maintain the probiotic population and decrease the pathogenic bacteria, therefore, it may be a potential modulator of intestinal microflora (López-Nicolás et al. 2014).

Most of the studies with maritime pine bark extracts were based on their bioactive properties beneficial for human health and only a few studies focused on its ability for preserving foods. Its addition in meat reduced growth of *Staphylococcus aureus*, numbers of *Escherichia coli* (O157:H7), and *Salmonella* Typhimurium and retarded the growth of *Listeria monocytogenes* and *Aeromonas hydrophila* (Hameş-Kocabaş et al. 2008; Ahn et al. 2007). Another studied carried out in food of animal origin was that of Ahn et al. (2002), who studied the addition of maritime pine bark extract to ground beef and it retarded the formation of thiobarbituric acid reactive substances (TBARS) and hexanal during the refrigerated storage and reduced the development of warmed-over flavour (WOF) in the cooked meat. Iglesias et al. (2010) studied the efficacy of maritime pine bark extract for inhibiting lipid oxidation in bulk fish oil and fish oil-in-water emulsions. They used non-galloylated fractions with different polymerization degrees, and it was observed that the lowest polymerized fractions were the most active in bulk fish oils, whereas proanthocyanidins with an intermediate polymerization degree showed the highest efficiency in the emulsions. The results obtained in both studies provided useful information to design natural antioxidant additives with application in foods of animal origin.

Ruggeri et al. (2008) studied the addition of maritime pine bark extract to yogurt, and they concluded that it was a valuable ingredient to enrich it in phenolic compounds. It was not observed any modification of the nutritional composition (pH, titratable acidity, macronutrients, and folates) and the growth of microorganisms (*Lactobacillus delbrueckii* ssp. *bulgaricus* and *Streptococcus thermophilus*). Besides, the phenolic content was not affected during storage.

3.2 Adsorbent applications of bark

Another application of maritime pine bark is the use as adsorbent for the removal of metals and metalloids from liquid effluents. Vázquez et al. (1994) tested the adsorption of Zn(II), Cu(II) and Pb(II) from wastewater with the bark pre-treated with formaldehyde in acidic medium with good results. The same pre-treated formaldehyde bark was also used for Cd(II) and Hg(II) adsorption, and the adsorption capacity was similar to the three previous metals. According to Vázquez et al. (2002), the mechanism was based on ion exchange with the hydroxyl protons of ring B of the procyanidin.

Cutillas-Barreiro et al. (2014, 2016) studied the adsorption of several heavy metals and the adsorption percentage was higher than 70% for all of them, being Pb(II) the metal with the highest value, 99%. Cu(II), Cd(II), Zn(II) adsorption percentages were close to 80%, while Ni(II) adsorption percentage was 75%. The retention of Pb(II) and Cu(II) in the maritime pine bark was mostly irreversible. Besides, Pb(II) and Cu(II) could displace the others from their adsorption sites and reduced their removal in multielement conditions. Cu(II) could be partially displaced by Pb(II), but Pb(II) could not be displaced by Cu(II). So, maritime pine bark could be very effective for Pb(II) and Cu(II) from water.

Arim et al. (2018a, b, c, 2019) studied the uptake of Cr(III) ions with maritime pine bark from aqueous solutions, not only for environmental protection, but its high interest of removal at the industrial level because of economic reasons. The adsorption capacity of maritime pine bark towards Cr(III) ions is significantly influenced by the particle size and initial pH solution, while the adsorbed amount of Cr(III) ions is strongly dependent on the pore volume distribution of the adsorbent (Arim et al. 2018b). The superficial properties of bark are suitable to promote modifications by physical or chemical treatments, which results in an increased adsorption capacity (Ahmaruzzaman 2011). One of the most effective treatments is the xanthation treatment of hydroxyls groups, which consists in an alkaline wash of bark with NaOH and the addition of CS_2 (Arim et al. 2019), because sulphur-bearing groups, such as xanthates, have a higher affinity for heavy metals (Pillai et al. 2013). The xanthate bark showed a Cr(III) removal efficiency of 95% in aqueous solutions, much better than the 16% of non-treated maritime pine bark (Arim et al. 2019).

Bacelo et al. (2018) developed a tannin-adsorbent for Sb uptake; for this, tannins were extracted from the bark in aqueous alkaline solution with NaOH, and converted into biosorbents, which are insoluble matrices, by polymerization with NaOH as solvent/catalyst and formaldehyde as reactant. The adsorption of Sb(III) took place extensively in the pH range from 2 to 8, with optimum removals found at pH close to the neutrality (pH 6–8), while the uptake of Sb(V) was only efficient from strong acidic waters (pH 2–4). Bacelo et al. (2020) modified this tannin-adsorbent by Fe(III) loading for As uptake. An oxidation with HNO_3 as step prior to contact with the Fe(III) solution was carried out and the resultant adsorbent was efficient for As(V) adsorption, especially at pH 3. The adsorption of As(III) was negligible because its conversion to As(V) was blocked because the reduction of Fe(III) to Fe(II) was coupled with the oxidation of the OH groups of the tannin-adsorbent.

Recently, Torrinha et al. (2021) studied the potential of maritime pine bark to uptake Au(III) from hydrochloric acid and aqua regia solutions, which were simulated hydrometallurgical liquors. Bark was previously treated with NaOH and the adsorbent presented high selectivity towards Au(III). That adsorbent could be used to recover this precious metal from waste electrical and electronic equipment. However, the elution in acidic thiourea solution was limited, 19%. So, future research will be needed to improve the gold elution from the exhausted adsorbents.

Besides metals and metalloids, maritime pine bark can be used for phenolic compounds adsorption. Vázquez et al. (2006, 2007) tested the adsorption of phenol from aqueous solutions with the formaldehyde pretreated bark that was previously used for cation adsorption (Vázquez et al. 1994, 2002). In the case of phenol, the time necessary to reach the breakthrough point decreased with an increase in the flow rate, which also implied a better utilization of the adsorbent because the equivalent length of unused material was lower (Vázquez et al. 2006). The highest phenol removal was achieved with a high solid/liquid ratio and a low pH. However, it was only efficient for low phenol concentrations (Vázquez et al. 2007).

Litefti et al. (2019) studied the potential of maritime pine bark as a low-cost adsorbent for the removal of Congo red dye, which contains several phenolic rings, from wastewaters. Congo red adsorption was a spontaneous and exothermic process which was strongly dependent on pH, and natural pH of 6 provided the highest adsorption rate. Adsorbent dosage and temperature influenced the adsorption rate too. The adsorption followed the pseudo-second-order kinetic model and Freundlich isotherm provided the most accurate fit to the data, which showed a heterogeneous and multi-layer adsorption with simultaneous intra-particle and external diffusion. The study was conducted with water-treated bark and high adsorption percentages were achieved, but too much time was needed to reach equilibrium compared to other adsorbents. So, alternative pre-treatments must be tested in order to improve the adsorption efficiency.

Bark tannins can be used as organic coagulants for microalgae harvesting, which is a technique that can control cyanobacterial harmful blooms. Álvarez et al. (2021) studied the efficiency of different flocculants obtained from tannin-rich barks, and they concluded that coagulation-flocculation using tannins from *P. pinaster* was the most suitable harvest method. The main advantages were the high harvesting efficiency, the reduction of environmental and energy impacts, and the improvement of the process economics.

3.3 Applications of bark in biomaterial industries

Pine bark can also be used for biomaterial production, mainly tannin-based resins and foams. These biomaterials are a natural alternative for petroleum-based polymers (García et al. 2014; Feng et al. 2013).

One the most common ways for tannin-based resin preparation is to mix tannin with hardeners, such as paraformaldehyde, and then to adjust the pH of the mixture to around 10 because alkaline conditions are necessary for the decomposition of the hardeners into formaldehyde (Feng et al. 2013). Vázquez et al. (1992, 1993, 1996) specifically studied maritime pine bark tannins and they observed that their copolymerization with high-methylol resoles yielded a resin which was superior to commercial phenol–formaldehyde resin for the manufacture of weather and boil proof plywood boards. Besides, phenol–formaldehyde resole fortified with maritime pine bark tannins was successfully used in bonding eucalyptus veneer to plywood, with shorter press time and higher veneer moisture content tolerance. Phenol–formaldehyde resin with up to 50% of phenol substituted by tannins met the correspond standards for plywood adhesives and with 60% it was found to cure at a lower temperature. López-Suevos and Riedl (2003) also observed a lower resin curing temperature, 75–85 °C, when tannins were added to phenol–urea–formaldehyde resins.

García et al. (2014) worked with tannin-based resins which were prepared from bark condensed tannins and different aldehydes. In that case, phenolic resins were novolacs and not resoles, as they were synthesised by acid-catalysed polycondensation and were not methylol-bearing structures (Pizzi and Ibeh 2014).

Navarrete et al. (2013) developed a tannin-based adhesive for wood panels from maritime pine bark. Several hardeners were tested, but paraformaldehyde showed good results and the adhesive obtained could fulfil the quality standards. Ndiwe et al. (2019) obtained bio-adhesives without aldehydes from maritime pine tannins and bio-hardeners, which were exudates from two African gum arabic trees (*Vachellia nilotica* (L.) P.J.H.Hurter & Mabb. and *Senegalia senegal* (L.) Britton). The bio-adhesive was used for particleboard manufacture and the panels met the requirements of European legislation.

The first generation of tannin-based foams were obtained from prorobinetinidin/profisetinidin tannins, but procyanidin condensed tannins have been used for this purpose more recently. Procyanidin tannin-based foams are good insulation materials because of their low thermal conductivity, self-extinguishing property, and high fire resistance (Lacoste et al. 2014a). Lacoste et al. (2013a, b) worked with radiata pine (*Pinus radiata* D.Don) bark as source of procyanidins with good results, and then started working with maritime pine bark (Lacoste et al. 2014a, b, 2015). The foams they synthetised from maritime pine bark were tannin/furanic foams which were obtained using glyoxal as hardener. The reactivity of formaldehyde was higher, but it has been classified as carcinogenic, so glyoxal, which has been classified as non-toxic and non-volatile, was chosen. In addition, 1-methoxy-2propanol, polyethoxylatedcastor oil, and polyethylene glycol 400 were used as surfactants and plasticizers, which were very important in the foam formulation because of the high reactivity of maritime pine bark tannins (Lacoste et al. 2014a).

Thermal conductivity of tannin-based foams was highly dependent of temperature and humidity, but they could be included among the best organic insulation foams (Lacoste et al. 2014b). Besides thermal conductivity, tannin-based foams obtained from maritime pine bark have shown to give good sound absorption and acoustic insulation characteristics, especially at frequencies equal and higher than 1000 Hz. At lower frequencies, 250–500 Hz, the insulation was lower, but respectable (Lacoste et al. 2015).

Hydroxypropyl tannin derivatives are useful for tannin-based foam industry too, and their synthesis from maritime pine bark tannins was described by García et al. (2013). The authors used propylene oxide in a NaOH aqueous solution at pH 12 for their synthesis, and hydroxypropylated tannins from maritime pine bark showed an outstanding potential to be used as macromeric building-blocks. In addition, the hydroxypropylated tannin reaction products showed different thermal and solubility (in organic solvents) properties depending on the degree of substitution. Besides, tannins can be used as precursors for polyurethane foam production because they are natural polyols which contain both aliphatic and aromatic hydroxyl groups (Feng et al. 2013), as polyurethane chemistry is based on the combination of isocyanates with polyols. García et al. (2015) described the synthesis of novel thermosetting polyphenol-based polyurethane films from hydroxypropylated tannins, which were the source of polyols, and diisocyanates. Different hydroxypropylated tannins, which were produced by different degrees of substitution (García et al. 2013), influenced the elasticity of polyurethane films (García et al. 2015).

3.4 Industrial applications of other parts of the tree

Maritime pine needles and cones have been used for activated carbon production. The plant material was pyrolyzed under argon flow and the obtained biochar was activated with a chemical activation agent.

Yumak (2021) observed that better results were obtained with cones and KOH as activation agent. Cone derived activated carbon showed higher BET (Brunauer–Emmett–Teller) surface area, mesopore volume/micropore volume ratio, and specific capacitance. According to the author, electrodes based on that type of activated carbon could have supercapacitor applications because of their high electrochemical stability and their repeatable cycle behaviour. Wood chips were used for biochar production by pyrolysis too. Aguirre et al. (2021) studied its application on corn production, and they observed an improvement in the Mediterranean climate. Corn production could increase even 84% because of the enhancement of sulphate, magnesium, and saturation percentage in soil, as well as the increase of nitrate retention after planting. However, further research is needed in order to improve its economic profitability.

Cones have been used for particleboard production with good results. According to Santos et al. (2021), the incorporation of cones showed a positive influence on the internal bond strength of the particleboards. Besides, the particleboards produced with maritime pine-cones had a higher water resistance than conventional wood-based panels. They concluded that it was possible to replace up to 20% of wood particles on particleboards and comply the industrial specifications.

Oleoresin is considered a renewable non-timber product which gains relevance in the European resin industry. Its extraction is a complementary forestry activity to timber production which contributes to the social and economic development of rural areas. Besides, this activity helps to preserve forest ecosystems (Vázquez-González et al. 2021).

Resin is considered the most important non-wood product. It is obtained by tapping and it undergoes steam distillation to obtain turpentine and rosin. Turpentine represents 15–53% of resin and contains volatile compounds, while rosin remains in the still as a non-volatile residue (Abad Viñas et al. 2016; Ottavioli et al. 2019; Rubini et al. 2021). Rosin has many industrial applications, and it is used to obtain of varnishes, printing inks, and paintings, as well as glues and adhesives (Ottavioli et al. 2019). Varnishes with maritime pine rosin have been used since sixteenth century, especially by violin makers. Those varnishes used to contain linseed oil and new formulations inspired by the antique violin coating were studied recently (Frances et al. 2020). They studied the influence of heat treatment of rosin and they concluded that softening point and glass transition increased with temperature, while brightness and solvent resistance decreased with temperature. Regarding chemical composition, heat treatment caused the apparition of dehydrogenated and oxidised forms of abietane-type acids.

As it has been previously said, another industrial application of maritime pine resin is the production of printing inks. According to Karademir et al. (2020), it is an alternative to alkyd resins in the production of printing ink. They added the resin into vegetable and mineral oil-based solvents in pure form with alkyd resin in different proportions, and they reported a positive effect in high print gloss, high light fastness, good set-off, and rub resistance of ink. Hybrid uses including maritime pine resin will enable production of varnish and viscoelastic ink with high rheology stability. Lastly, Donoso et al. (2021) indicated that turpentine has appropriate properties to become a drop-in bio-jet-fuel. However, it has a major drawback which is its high sooting tendency, which can be mitigated by partial hydrogenation, which saturates the double bounds of pinenes and avoids the formation of *m*-xylene during the combustion process. They reported that hydrogenated turpentine could be blended up to 50% with Jet A-1 aviation fuel, so it could be a sustainable alternative to fossil fuels in aviation.

4 Perspectives and conclusions

Future perspectives of maritime pine non-wood parts are promising, especially bark. Secondary metabolism of this species is quite active and different compounds are synthesized, the main one being phenolic compounds and terpenes. Phenolic compounds are mainly located in bark, which is rich is condensed tannins derived from flavan-3-ols, such as catechin and epicatechin. These compounds stand out because of their bioactive potential, especially antioxidant and antimicrobial activities. Besides, maritime pine bark contains terpenes, group to which resin acids belong. Resin acids have a diterpenic structure and are abietic and pimaric acid derivatives. In addition to bark, they are present in other parts, especially resin. Needles and cones are rich in terpenes too, but monoterpenes and sesquiterpenes are the majority. These compounds showed antioxidant and antimicrobial potential too.

Non-woody parts have a diverse range of industrial applications, especially bark. This part of the tree is commonly used as a dietary supplement because of the phenolic compounds of its extract, which has shown good scientific evidence in the treatment of asthma and chronic venous insufficiency. Bark extract has been used for food enrichment too, in food of animal and plant origin, especially fruit juices, as a functional ingredient. In addition to pharma-food industries, maritime pine bark has applications as bioadsorbent for the removal of different substances from liquid effluents, which could allow for decontamination of both inorganic and organic compounds, especially metals and metalloids. Bark has industrial applications in biomaterial industry too. Pine bark can also be used for biomaterial production, mainly tannin-based resins and foams, which are a natural alternative for petroleum-based polymers. Industrial potential of resin stands out too because it is raw material in the production of turpentine and rosin, which are widely used by several chemical industries.

In conclusion, maritime pine is part of the Iberian landscape and plays an important role in their environment, industry, and economy. Maritime pine is more than a source of wood, but several parts of the tree, bark being prominent among them, are discarded and became industrial by-products. Besides, other parts of the tree are left in the forest and have a negative impact on the environment because of risks of fire. So, the development, consolidation, and implementation of industrial applications of maritime pine by-products and apparently little useful parts of the tree can enable full use of the plant material and reduce the amount of industrial waste, which implies better use of forest resources with an improvement of the long-term sustainability of industrial activities, accordingly to the principles of circular economy.

Acknowledgements The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support through national funds FCT/MCTES to the CIMO (UIDB/00690/2020) and to the CISAS (UIDB/05937/2020). S. Heleno and M. Carocho thank FCT for their individual employment program—contract (CEEC-IND/00831/2018, CEECIND/03040/2017), Diana Barros PhD grant (SFRH/BD/146720/2019) and L. Barros also thanks to the national funding by FCT through the institutional scientific employment program—contract for her contract. This work was financed by the European Regional Development Fund (ERDF) through the Regional Operation Program North 2020, within the scope of the R&D Enterprise Copromotion project PICAR – Funcionalização de produtos cárneos curados com extratos de córtex de pinheiro-bravo do Minho (*Pinus pinaster* subsp. atlantica) (PICAR – Functionalization of meat products with maritime pine cortex extracts (NORTE-01-0247-FEDER-069584). José Ignacio also thanks his contract under the project PICAR.

Declarations

Conflict of interest The authors state no conflict of interest concerning this manuscript.

References

Abad Viñas R, Caudullo G, Oliveira S, de Rigo D (2016) *Pinus pinaster* in Europe: distribution, habitat, usage and threats. In: San-Miguel-Ayanz J, de Rigo D, Caudullo G, Houston Durrant T, Mauri A (eds) European atlas of forest tree species. Publications Office of the European Union, Luxembourg, pp 128–129

Abilleira F, Varela P, Cancela Á, Álvarez X, Sánchez Á, Valero E (2021) Tannins extraction from *Pinus pinaster* and *Acacia dealbata* bark with applications in the industry. Ind Crops Prod 164:113394. https://doi.org/10.1016/j.indcrop.2021.113394

Aguiar FC, Rodrigues C, Pina JP, Soares P (2021) Regeneration of riparian and maritime pine forests after a large wildfire on the largest public forest of Portugal. Forests 12:477. https://doi.org/10.3390/f12040477

Aguirre JL, Martín MT, González S, Peinado M (2021) Effects and economic sustainability of biochar application on corn production in a Mediterranean climate. Molecules 26:3313. https://doi.org/10.3390/molecules26113313

Ahmaruzzaman M (2011) Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. Adv Colloid Interface Sci 166:36–59. https://doi.org/10.1016/j.cis.2011.04.005

Ahn J, Grün IU, Fernando LN (2002) Antioxidant properties of natural plant extracts containing polyphenolic compounds in cooked ground beef. Food Chem Toxicol 67:1364–1369. https://doi.org/10.1111/j.1365-2621.2002.tb10290.x

Ahn J, Grün IU, Mustapha A (2007) Effects of plant extracts on microbial growth, color change, and lipid oxidation in cooked beef. Food Microbiol 24:7–14. https://doi.org/10.1016/j.fm.2006.04.006

Aloui F, Baraket M, Jedidi S, Hosni K, Bouchnak R, Salhi O, Jdaidi N, Selmi H, Ghazghazi H, Khadhri A, Abbes C (2021) Chemical composition, anti-radical and antibacterial activities of essential oils from needles of *Pinus halepensis* Mill., *P. pinaster* Aiton., and *P. pinea* L. J Essent Oil-Bear Plants 24:453–460. https://doi.org/10.1080/0972060X.2021.1943541

Álvarez X, Jiménez A, Cancela Á, Valero E, Sánchez A (2021) Harvesting freshwater algae with tannins from the bark of forest species: comparison of methods and pelletization of the biomass obtained. Chemosphere 268:129313. https://doi.org/10.1016/j.chemosphere.2020.129313

Arim AL, Cecílio DFM, Quina MJ, Gando-Ferreira LM (2018a) Development and characterization of biosorbent with enhanced capacity for uptaking Cr(III) from aqueous solutions. Can J Chem Eng 96:855–864. https://doi.org/10.1002/cjce.23029

Arim AL, Quina MJ, Gando-Ferreira LM (2018b) Insights into the sorption mechanisms of Cr(III) by chemically modified pine bark. Chem Eng Technol 41:1378–1389. https://doi.org/10.1002/ceat.201800034

Arim AL, Neves K, Quina MJ, Gando-Ferreira LM (2018c) Experimental and mathematical modelling of Cr(III) sorption in fixed-bed column using modified pine bark. J Clean Prod 183:272–281. https://doi.org/10.1016/j.jclepro.2018.02.094

Arim AL, Quina MJ, Gando-Ferreira LM (2019) Uptake of trivalent chromium from aqueous solutions by xanthate pine bark: Characterization, batch and column studies. Process Saf Environ Prot 121:374–386. https://doi.org/10.1016/j.psep.2018.11.001

Arrabal C, Cortijo M, Fernández de Simón B, García Vallejo MC, Cadahía E (2002) *Pinus pinaster* oleoresin in plus trees. Holzforschung 56:261–266. https://doi.org/10.1515/HF.2002.043

Arrabal C, Cortijo M, Fernández de Simón B, García Vallejo MC, Cadahía E (2005) Differentiation among five Spanish *Pinus pinaster* provenances based on its oleoresin terpenic composition. Biochem Syst Ecol 33:1007–1016. https://doi.org/10.1016/j.bse.2005.03.003

Arrillaga I, Morcillo M, Zanón I, Lario F, Segura J, Sales E (2019) New approaches to optimize somatic embryogenesis in maritime pine. Front Plant Sci 10:138. https://doi.org/10.3389/fpls.2019.00138

Bacelo H, Vieira BRC, Santos SCR, Boaventura RAR, Botelho CMS (2018) Recovery and valorization of tannins from a forest waste as an adsorbent for antimony uptake. J Clean Prod 198:1324–1335. https://doi.org/10.1016/j.jclepro.2018.07.086

Bacelo H, Santos SCR, Botelho CMS (2020) Removal of arsenic from water by an iron-loaded resin prepared from *Pinus pinaster* bark tannins. EuroMediterr J Environ Integr 5:47. https://doi.org/10.1007/s41207-020-00190-y

Braga MEM, Santos RMS, Seabra IJ, Facanali R, Marques MOM, de Sousa HC (2008) Fractioned SFE of antioxidants from maritime pine bark. J Supercrit Fluids 47:37–48. https://doi.org/10.1016/j.supflu.2008.05.005

Calviño-Cancela M, Neumann M, López de Silanés ME (2020) Contrasting patterns of lichen abundance and diversity in *Eucalyptus globulus* and *Pinus pinaster* plantations with tree age. For Ecol Manag 462:117994. https://doi.org/10.1016/j.foreco.2020.117994

Celhay C, Mathieu CE, Candy L, Vilarem G, Rigal L (2014) Aqueous extraction of polyphenols and antiradicals from wood by-products by a twin-screw extractor: feasibility study. C R Chimie 17:204–211. https://doi.org/10.1016/j.crci.2014.01.008

Chupin L, Motillon C, Charrier-El Bouhtoury F, Pizzi A, Charrier B (2013) Characterisation of maritime pine (*Pinus pinaster*) bark tannins extracted under different conditions by spectroscopic methods, FTIR and HPLC. Ind Crop Prod 49:897–903. https://doi.org/10.1016/j.indcrop.2013.06.045

Chupin L, Maunu SL, Reynaud S, Pizzi A, Charrier B, Charrier-El Bouhtoury F (2015) Microwave assisted extraction of maritime pine (*Pinus pinaster*) bark: impact of particle size and characterization. Ind Crop Prod 65:142–149. https://doi.org/10.1016/j.indcrop.2014.11.052

Correia AV, Oliveira AC, Fabião A (2007) Biologia e ecologia do pinheiro-bravo. In: Silva JS (ed) Pinhais e eucaliptais, a floresta cultivada. Edições Publico, Lisboa, pp 17–35

Cutillas-Barreiro L, Ansias-Manso L, Fernández-Calviño D, Arias-Estévez M, Nóvoa-Muñoz JC, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Núñez-Delgado A (2014) Pine bark as bio-adsorbent for Cd, Cu, Ni, Pb and Zn: batch-type and stirred flow chamber experiments. J Environ Manag 144:258–264. https://doi.org/10.1016/j.jenvman.2014.06.008

Cutillas-Barreiro L, Paradelo R, Igrexas-Soto A, Núñez-Delgado A, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Garrote G, Nóvoa-Muñoz JC, Arias-Estévez M (2016) Valorization of biosorbent obtained from a forestry waste: competitive adsorption, desorption and transport of Cd, Cu, Ni, Pb and Zn. Ecotoxicol Environ Saf 131:118–126. https://doi.org/10.1016/j.ecoenv.2016.05.007

D'Andrea G (2010) Pycnogenol: a blend of procyanidins with multifaceted therapeutic applications? Fitoterapia 81:724–736. https://doi.org/10.1016/j.fitote.2010.06.011

David IMB, Fernandes FS, Ferreira JBSS, Lüdtke DD, Martins DF, Bobinski F, da Silva TBGC, Buffon LD, Kopper MBR, da Silva GS, Zeferino RC, Pedrosa RC, Kviecinski MR (2019) Dietary supplementation with procyanidin-rich *Pinus pinaster* extract is associated with attenuated Ehrlich tumor development in mice. Nut Res 62:41–50. https://doi.org/10.1016/j.nutres.2018.11.005

de las Heras J, Moy D, Vega J, Daskalakou E, Vallejo VR, Grigoriadis N, Tsitsoni T, Baeza J, Valdecantos A, Fernández C, Espelta J, Fernandes P (2012) Post-fire management of serotinous pine forests. In: Moreira F, Arianoutsou M, Corona P, de las Heras J (eds) Post-fire management and restoration of southern European forests. Springer, Dordrecht, pp 121–150. https://doi.org/10.1007/978-94-007-2208-8_6

Deutz P (2020) Circular economy. In: Kobayashi A (ed) Encyclopedia of human geography, 2nd edn. Elsevier, Amsterdam, pp 193–201. https://doi.org/10.1016/B978-0-08-102295-5.10630-4

Donoso D, Ballesteros R, Bolonio D, García-Martínez MJ, Lapuerta M, Canoira L (2021) Hydrogenated turpentine: a biobased component for jet fuel. Energy Fuels 35:1465–1475. https://doi.org/10.1021/acs.energyfuels.0c03379

Drehsen G (1999) From ancient pine bark uses to Pycnogenol. In: Packer L, Hiramatsu M, Yoshikawa T (eds) Antioxidant food supplements in human health. Academic Press, San Diego, pp 311–322

Ďuračková Z, Trebatický B, Novotný V, Žitňanová Breza R (2003) Lipid metabolism and erectile function improvement by Pycnogenol®, extract from the bark of *Pinus pinaster* in patients suffering from erectile dysfunction—a pilot study. Nutr Res 23:1189–1198. https://doi.org/10.1016/S0271-5317(03)00126-X

Düweler KG, Rohdewald P (2000) Urinary metabolites of French maritime pine bark extract in humans. Pharmazie 55:364–368

Dziedziński M, Kobus-Cisowska J, Stachowiak B (2021) *Pinus* species as prospective reserves of bioactive compounds with potential use in functional food-current state of knowledge. Plants 10:1306. https://doi.org/10.3390/plants10071306

Eckenwalder JE (2009) Conifers of the world: the complete reference. Timber Press, Portland

Enseleit F, Sudano I, Périat D, Winnik S, Wolfrum M, Flammer AJ, Fröhlich GM, Kaiser P, Hirt A, Haile SR, Krasniqi N, Matter MC, Uhlenhut K, Högger P, Neidhart M, Lüscher TF, Ruschitzka F, Noll G (2012) Effects of Pycnogenol on endothelial function in patients with stable coronary artery disease: a double-blind, randomized, placebo-controlled, cross-over study. Eur Heart J 33:1589–1597. https://doi.org/10.1093/eurheartj/ehr482

Fekih N, Allali H, Merghache S, Bouchentouf S, Costa J (2019) *In vitro* assessment of two species of the genus *Pinus* growing in Algeria for their antimicrobial and antioxidant activity. Agric Conspec Sci 84:103–114

Feng WF, Tanaka R, Inagaki Y, Saitoh Y, Chang MO, Amet T, Yamamoto N, Yamaoka S, Yoshinaka Y (2011) Pycnogenol®, a procyanidin-rich extract from French maritime pine, inhibits intracellular replication of HIV-1 as well as its binding to host cells. Jpn J Infect Dis 61:279–285

Feng S, Cheng S, Yuan Z, Leitch M, Xu C (2013) Valorization of bark for chemicals and materials: a review. Renew Sustain Energy Rev 26:560–578. https://doi.org/10.1016/j.rser.2013.06.024

Fernández-Guisuraga JM, Suárez-Seoane S, Fernandes PM, Fernández-García V, Fernández-Manso A, Quintano C, Calvo L (2022) Pre-fire aboveground biomass, estimated from LiDAR, spectral and field inventory data, as a major driver of burn severity in maritime pine (*Pinus pinaster*) ecosystems. For Ecosyst 9:100022. https://doi.org/10.1016/j.fecs.2022.100022

Ferreira-Santos P, Genisheva Z, Pereira RN, Teixeira JA, Rocha CMR (2019) Moderate electric fields as a potential tool for sustainable recovery of phenolic compounds from *Pinus pinaster* Bark. ACS Sustain Chem Eng 7:8816–8826. https://doi.org/10.1021/acssuschemeng.9b00780

Ferreira-Santos P, Genisheva Z, Botelho C, Santos J, Ramos C, Teixeira JA, Rocha CMR (2020) Unravelling the biological potential of *Pinus pinaster* Bark extracts. Antioxidants 9:334. https://doi.org/10.3390/antiox9040334

Ferreira-Santos P, Ibarz R, Fernandes JM, Pinheiro AC, Botelho C, Rocha CMR, Teixeira JA, Martín-Belloso O (2021) Encapsulated pine bark polyphenolic extract during gastrointestinal digestion: bioaccessibility. Bioact Oxidative Stress Prev Foods 10:328. https://doi.org/10.3390/foods10020328

Fkiri S, Ghazghazi H, Rigane G, Ben Salem R, Mezni F, Khaldi A, Khouja L, Nasr Z (2019) Chemical compositions and biological activities essential oil from the needles of north African *Pinus pinaster* var. Rev Roum Chim 64:511–517. https://doi.org/10.33224/rrch.2019.64.6.07

Fradinho DM, Neto CP, Evtuguin D, Jorge FC, Irle MA, Gil MH, de Jesus JP (2002) Chemical characterisation of bark and of alkaline bark extracts from maritime pine grown in Portugal. Ind Crop Prod 16:23–32. https://doi.org/10.1016/S0926-6690(02)00004-3

Frances M, Gardere Y, Rubini M, Duret E, Leroyer L, Cabaret T, Bikoro Bi Athomo A, Charrier B (2020) Effect of heat treatment on *Pinus pinaster* rosin: a study of physico chemical changes and influence on the quality of rosin linseed oil varnish. Ind Crops Prod 155:112789. https://doi.org/10.1016/j.indcrop.2020.112789

Franco-Manchón I, Salo K, Oria-de-Rueda JA, Bonet JA, Martín-Pinto P (2019) Are wildfires a threat to fungi in European *Pinus* forests? A case study of boreal and Mediterranean forests. Forests 10:309. https://doi.org/10.3390/f10040309

Frontela-Saseta C, López-Nicolás R, González-Bermúdez CA, Peso-Echarri P, Ros-Berruezo G, Martínez-Graciá C, Canali R, Virgili F (2011) Evaluation of antioxidant activity and antiproliferative effect of fruit juices enriched with Pycnogenol® in colon carcinoma cells. The effect of in vitro gastrointestinal digestion. Phytother Res 25:1870–1875. https://doi.org/10.1002/ptr.3625

Frontela-Saseta C, López-Nicolás R, González-Bermúdez CA, Martínez-Graciá C, Ros-Berruezo G (2013) Anti-inflammatory properties of fruit juices enriched with pine bark extract in an *in vitro* model of inflamed human intestinal epithelium: the effect of gastrointestinal digestion. Food Chem Toxicol 53:94–99. https://doi.org/10.1016/j.fct.2012.11.024

Furumura M, Sato N, Kusaba N, Takagaki K, Nakayama J (2012) Oral administration of French maritime pine bark extract (Flavangenol®) improves clinical symptoms in photoaged facial skin. Clin Interv Aging 7:275–286. https://doi.org/10.2147/CIA.S33165

Gabaston J, Leborgne C, Waffo-Teguo P, Pedrot E, Richard T, Mérillon JM, Valls Fonayet J (2020) Separation and isolation of major polyphenols from maritime pine (*Pinus pinaster*) knots by twostep centrifugal partition chromatography monitored by LC-MS and NMR. J Sep Sci 43:1080–1088. https://doi.org/10.1002/jssc.201901066

García DE, Glasser WG, Pizzi A, Osorio-Madrazo A, Laboire MP (2013) Hydroxypropyl tannin derivatives from *Pinus pinaster* (Ait.) bark. Ind Crops Prod 49:730–739. https://doi.org/10.1016/j.indcrop.2013.06.019

García DE, Glasser WG, Pizzi A, Lacoste C, Laboire MP (2014) Polyphenolic resins prepared with maritime pine bark tannin and bulky-aldehydes. Ind Crops Prod 62:84–93. https://doi.org/10.1016/j.indcrop.2014.08.010

García DE, Glasser WG, Pizzi A, Paczkowski S, Laboire MP (2015) Hydroxypropyl tannin from *Pinus pinaster* bark as polyol source in urethane chemistry. Eur Polym J 67:152–165. https://doi.org/10.1016/j.eurpolymj.2015.03.039

Gascón S, Jiménez-Moreno N, Jiménez S, Quero J, Rodríguez-Yoldi MJ, Ancín-Azpilicueta C (2018) Nutraceutical composition of three pine bark extracts and their antiproliferative effect on Caco-2 cells. J Funct Foods 48:420–429. https://doi.org/10.1016/j.jff.2018.07.040

Gaspar MC, de Sousa HC, Seabra IJ, Braga MEM (2020) Environmentally-safe scCO2 *P. pinaster* branches extracts: composition and properties. J CO2 Util 37:74–84. https://doi.org/10.1016/j.jcou.2019.11.027

Gómez-Rey MX, Couto-Vázquez A, González-Prieto SJ (2021) Age and thinning effects on elemental composition of *Pinus pinaster* and *Pinus radiata* needles. iForest 14:299–306. https://doi.org/10.3832/ifor3575-014

Grimm T, Chovanová Z, Muchová J, Sumegová K, Liptáková A, Ďuračková Z, Höoger P (2006a) Inhibition of NF-κB activation and MMP-9 secretion by plasma of human volunteers after ingestion of maritime pine bark extract (Pycnogenol). J Inflamm 3:1. https://doi.org/10.1186/1476-9255-3-1

Grimm T, Schäfer A, Högger P (2003) Antioxidant activity and inhibition of matrix metalloproteinases by metabolites of maritime pine bark extract (Pycnogenol). Free Radic Biol Med 36:811–822. https://doi.org/10.1016/j.freeradbiomed.2003.12.017

Grimm T, Skrabala R, Chovanová Z, Muchová J, Sumegová K, Liptáková A, Ďuračková Z, Högger P (2006b) Single and multiple dose pharmacokinetics of maritime pine bark extract (Pycnogenol) after oral administration to healthy volunteers. BMC Clin Pharmacol 6:4. https://doi.org/10.1186/1472-6904-6-4

Hameş-Kocabaş EE, Yeşil-Çeliktaş Ö, İşleten M, Vardar-Sukan F (2008) Antimicrobial activities of pine bark extract and assessment of potential application in cooked red meat. GIDA 33:123–127

Herrero C, Berraondo I, Bravo F, Pando V, Ordóñez C, Olaizola J, Martín-Pinto P, Oria de Rueda JA (2019) Predicting mushroom productivity from long-term field-data series in Mediterranean *Pinus pinaster* Ait. forests in the context of climate change. Forests 10:206. https://doi.org/10.3390/f10030206

Iglesias J, Pazos M, Lois S, Medina I (2010) Contribution of galloylation and polymerization to the antioxidant activity of polyphenols in fish lipid systems. J Agric Food Chem 58:7423–7431. https://doi.org/10.1021/jf100832z

Iravani S, Zolfaghari B (2014) Phytochemical analysis of *Pinus eldarica* bark. Res Pharm Sci 9:243–250

Jerez M, Pinelo M, Sineiro J, Núñez MJ (2006) Influence of extraction conditions on phenolic yields from pine bark: assessment of procyanidins polymerization degree by thiolysis. Food Chem 94:406–414. https://doi.org/10.1016/j.foodchem.2004.11.036

Jerez M, Selga A, Sineiro J, Torres JL, Núñez MJ (2007a) A comparison between bark extracts from *Pinus pinaster* and *Pinus radiata*: antioxidant activity and procyanidin composition. Food Chem 100:439–444. https://doi.org/10.1016/j.foodchem.2005.09.064

Jerez M, Touriño S, Sineiro J, Torres JL, Núñez MJ (2007b) Procyanidins from pine bark: relationships between structure, composition and antiradical activity. Food Chem 104:518–527. https://doi.org/10.1016/j.foodchem.2006.11.071

Jones HS, Papageorgiou M, Gordon A, Ehtesham JZ, Wells LK, Greetham S, Doyle B, Hayes N, Rigby A, Atkin SL, Courts FL, Sathyapalan T (2020) Physiologically relevant screening of polyphenol-rich commercial preparations for bioactivity in vascular endothelial cells and application to healthy volunteers: a viable workflow and a cautionary tale. Biochem Pharmacol 173:113754. https://doi.org/10.1016/j.bcp.2019.113754

Karademir A, Aydemir C, Yenidogan S, Kandırmaz EA, Kıter RG (2020) The use of natural (*Pinus pinaster*) resin in the production of printing ink and the printability effect. Color Res Appl 45:1170–1178. https://doi.org/10.1002/col.22534

Kurlbaum M, Högger P (2011) Plasma protein binding of polyphenols from maritime pine bark extract (USP). J Pharm Biomed Anal 54:127–132. https://doi.org/10.1016/j.jpba.2010.07.038

Kurtca M, Tumen I (2020) Investigation into seasonal variations of chemical compounds of maritime pine (*Pinus pinaster* Ait.) grown in Turkey. Fresenius Environ Bull 29:8156–8167

Lacoste C, Basso MC, Pizzi A, Laborie MP, Celzard A, Fierro V (2013a) Pine tannin-based rigid foams: mechanical and thermal properties. Ind Crops Prod 43:245–250. https://doi.org/10.1016/j.indcrop.2012.07.039

Lacoste C, Basso MC, Pizzi A, Laborie MP, Garcia D, Celzard A (2013b) Bioresourced pine tannin/furanic foams with glyoxal and glutaraldehyde. Ind Crops Prod 45:401–405. https://doi.org/10.1016/j.indcrop.2012.12.032

Lacoste C, Pizzi A, Basso MC, Laborie MP, Celzard A (2014a) *Pinus pinaster* tannin/furanic foams: part I. Formul Ind Crops Prod 52:450–456. https://doi.org/10.1016/j.indcrop.2013.10.044

Lacoste C, Pizzi A, Laborie MP, Celzard A (2014b) *Pinus pinaster* tannin/furanic foams: part II. Phys Prop Ind Crops Prod 61:531–536. https://doi.org/10.1016/j.indcrop.2014.04.034

Lacoste C, Basso MC, Pizzi A, Celzard A, Ella Ebang E, Gallon N, Charrier B (2015) Pine (*P. pinaster*) and quebracho (*S. lorentzii*) tannin-based foams as green acoustic absorbers. Ind Crops Prod 67:70–73. https://doi.org/10.1016/j.indcrop.2014.12.018

Layton RJ, Horta Arduin R, Yazdeen H, Pommier R, Sonnemann G (2021) Material flow analysis to evaluate supply chain evolution and management: an example focused on maritime pine in the Landes de Gascogne forest, France. Sustainability 13:4378. https://doi.org/10.3390/su13084378

Litefti K, Freire MS, Stitou M, González-Álvarez J (2019) Adsorption of an anionic dye (Congo red) from aqueous solutions by pine bark. Sci Rep 9:16530. https://doi.org/10.1038/s41598-019-53046-z

López-Goldar X, Lundborg L, Borg-Karlson AK, Zas R, Sampedro L (2020) Resin acids as inducible chemical defences of pine seedlings against chewing insects. PLoS ONE 15:e0232692. https://doi.org/10.1371/journal.pone.0232692

López-Nicolás R, González-Bermúdez CA, Ros-Berruezo G, Frontela-Saseta C (2014) Influence of in vitro gastrointestinal digestion of fruit juices enriched with pine bark extract on intestinal microflora. Food Chem 157:14–19. https://doi.org/10.1016/j.foodchem.2014.01.126

López-Suevos F, Riedl B (2003) Effects of *Pinus pinaster* bark extracts content on the cure properties of tannin-modified adhesives and on bonding of exterior grade MDF. J Adhes Sci Technol 17:1507–1523. https://doi.org/10.1163/156856103769207374

Malekahmadi M, Moghaddam OM, Islam SMS, Tanha K, Nematy M, Pahlavani N, Firouzi S, Zali MR, Norouzy A (2020) Evaluation of the effects of pycnogenol (French maritime pine bark extract) supplementation on inflammatory biomarkers and nutritional and clinical status in traumatic brain injury patients in an intensive care unit: a randomized clinical trial protocol. Trials 21:162. https://doi.org/10.1186/s13063-019-4008-x

Mármol I, Quero J, Jiménez-Moreno N, Rodríguez-Yoldi MJ, Ancín-Azpilicueta C (2019) A systematic review of the potential uses of pine bark in food industry and health care. Trends Food Sci Technol 88:558–566. https://doi.org/10.1016/j.tifs.2018.07.007

Mármol I, Vieito C, Andreu V, Levert A, Amiot A, Bertrand C, Rodríguez-Yoldi MJ, Santos J, Vaz-Velho M (2022) Influence of extraction solvent on the biological properties of maritime pine bark (*Pinus pinaster*). Int J Food Stud. https://doi.org/10.7455/ijfs/11.1.2022.a5

Mediavilla I, Guillamón E, Ruiz A, Esteban LS (2021) Essential oils from residual foliage of forest tree and shrub species: yield and antioxidant capacity. Molecules 26:3257. https://doi.org/10.3390/molecules26113257

Mellouk H, Meullemiestre A, Maache-Rezzoug Z, Bejjani B, Dani A, Rezzoug SA (2016) Valorization of industrial wastes from French maritime pine bark by solvent free microwave extraction of volatiles. J Clean Prod 112:4398–4405. https://doi.org/10.1016/j.jclepro.2015.06.129

Molina JR, Ortega M, Rodríguez y Silva M (2021) Useful life of prescribed fires in a southern Mediterranean basin: an application to *Pinus pinaster* stands in the Sierra Morena range. Forests 12:486. https://doi.org/10.3390/f12040486

Navarrete P, Pizzi A, Pasch H, Rode K, Delmotte L (2010) MALDI-TOF and ^{13}C NMR characterization of maritime pine industrial tannin extract. Ind Crop Prod 32:105–110. https://doi.org/10.1016/j.indcrop.2010.03.010

Navarrete P, Pizzi A, Pasch H, Rode K, Delmotte L (2013) Characterization of two maritime pine tannins as wood adhesives. J Adhes Sci Technol 27:2462–2479. https://doi.org/10.1080/01694243.2013.787515

Ndiwe B, Pizzi A, Danwe R, Tibi B, Konai N, Amirou S (2019) Particleboard bonded with bio-hardeners of tannin adhesives. Eur J Wood Prod 77:1221–1223. https://doi.org/10.1007/s00107-019-01460-5

Neis FA, de Costa F, de Araújo AT, Fett JP, Fett-Neto AG (2019) Multiple industrial uses of non-wood pine products. Ind Crop Prod 130:248–258. https://doi.org/10.1016/j.indcrop.2018.12.088

Nikolić B, Todosijević M, Đorđević I, Stanković J, Mitić ZS, Tešević V, Marin PD (2020) Nonacosan-10-ol and n-alkanes in leaves of *Pinus pinaster*. Nat Prod Commun 15:1–4. https://doi.org/10.1177/1934578X20926073

Nunes LJR, Meireles CIR, Gomes CJP, Ribeiro NMCA (2019) Historical development of the Portuguese forest: the introduction of invasive species. Forests 10:974. https://doi.org/10.3390/f10110974

Nystedt B, Street NR, Wetterbom A et al (2013) The Norway spruce genome sequence and conifer genome evolution. Nature 497:579–584. https://doi.org/10.1038/nature12211

Ottavioli J, Paoli M, Casanova J, Tomi F, Bighelli A (2019) Identification and quantitative determination of resin acids from Corsican *Pinus pinaster* Aiton oleoresin using ^{13}C-NMR spectroscopy. Chem Biodivers 16:e1800482. https://doi.org/10.1002/cbdv.201800482

Paarmann K, Prakash SR, Krohn M, Möhle L, Brackhan M, Brüning T, Eiriz I, Pahnke J (2019) French maritime pine bark treatment decelerates plaque development and improves spatial memory in Alzheimer's disease mice. Phytomedicine 57:39–48. https://doi.org/10.1016/j.phymed.2018.11.033

Pagano C, Puglia D, Luzi F, Di Michele A, Scuota S, Primavilla S, Ceccarini MR, Beccari T, Iborra CAS, Ramella D, Ricci M, Perioli L (2021) Development and characterization of xanthan gum and alginate based bioadhesive film for Pycnogenol topical use in wound treatment. Pharmaceutics 13:324. https://doi.org/10.3390/pharmaceutics13030324

Panahande SB, Maghbooli Z, Hossein-Nezhad A, Qorbani M, Moeini-Nodeh S, Haghi-Aminjan H, Hosseini S (2019) Effects of French maritime pine bark extract (Oligopin®) supplementation on bone remodeling markers in postmenopausal osteopenic women: a randomized clinical trial. Phytother Res 33:1233–1240. https://doi.org/10.1002/ptr.6320

Pillai SS, Deepa B, Abraham E, Girija N, Geetha P, Jacob L, Koshy M (2013) Biosorption of Cd(II) from aqueous solution using xanthated nano banana cellulose: equilibrium and kinetic studies. Ecotoxicol Environ Saf 98:352–360. https://doi.org/10.1016/j.ecoenv.2013.09.003

Pizzi A, Ibeh CC (2014) Phenol-formaldehydes. In: Dodiuk H, Goodman SH (eds) Handbook of thermoset plastics. Elsevier, Cambridge, pp 13–44

Qorbani M, Sanginabadi M, Mohajeri-Tehrani MR, Karimi S, Gerami H, Mahdavi-Gorabi A, Shirzad N, Samadi M, Baygi F, Hosseini S, Mansour A (2020) The effect of Oligopin supplementation on hormonal and metabolic profiles in the polycystic ovary syndrome: a randomized controlled trial. Front Endocrinol 11:590392. https://doi.org/10.3389/fendo.2020.590392

Rašković A, Bukumirović N, Kusturica MP, Milić N, Čabarkapa V, Borišev I, Čapo I, Miljković D, Stilinović N, Mikov M (2019) Hepatoprotective and antioxidant potential of Pycnogenol® in acetaminophen-induced hepatotoxicity in rats. Phytother Res 33:631–639. https://doi.org/10.1002/ptr.6251

Ratola N, Lacorte S, Barceló D, Alves A (2009) Microwave-assisted extraction and ultrasonic extraction to determine polycyclic aromatic hydrocarbons in needles and bark of *Pinus pinaster* Ait. and *Pinus pinea* L. by GC-MS. Talanta 77:1120–1128. https://doi.org/10.1016/j.talanta.2008.08.010

Rodríguez-García A, Martín JA, López R, Mutke S, Pinillos F, Gil L (2015) Influence of climate variables on resin yield and secretory structures in tapped *Pinus pinaster* Ait. in central Spain. Agric for Meteorol 202:83–93. https://doi.org/10.1016/j.agrformet.2014.11.023

Rubini M, Feuillerat L, Cabaret T, Leroyer L, Leneveu L, Charrier B (2021) Comparison of the performances of handheld and benchtop near infrared spectrometers: application on the quantification of chemical components in maritime pine (*Pinus Pinaster*) resin. Talanta 221:121454. https://doi.org/10.1016/j.talanta.2020.121454

Ruggeri S, Straniero R, Pacifico S, Aguzzi A, Virgili F (2008) French marine bark extract Pycnogenol as a possible enrichment ingredient for yogurt. J Dairy Sci 91:4484–4491. https://doi.org/10.3168/jds.2008-1250

Saito A, Mizushina Y, Ikawa H, Yoshida H, Doi Y, Tanaka A, Nakajima N (2005) Systematic synthesis of galloyl-substituted procyanidin B1 andB2, and their ability of DPPH radical scavenging activityand inhibitory activity of DNA polymerases. Bioinorg Med Chem 13:2759–2771. https://doi.org/10.1016/j.bmc.2005.02.023

Santos J, Pereira J, Ferreira N, Paiva N, Ferra J, Magalhães FD, Martins JM, Dulyanska Y, Carvalho LH (2021) Valorisation of non-timber by-products from maritime pine (*Pinus pinaster*, Ait) for particleboard production. Ind Crops Prod 168:113581. https://doi.org/10.1016/j.indcrop.2021.113581

Schäfer A, Chovanová Z, Muchová J, Sumegová K, Liptáková A, Ďuračková Z, Högger P (2005) Inhibition of COX-1 and COX-2 activity by plasma of human volunteers after ingestion of French maritime pine bark extract (Pycnogenol). Biomed Pharmacother 60:5–9. https://doi.org/10.1016/j.biopha.2005.08.006

Segal L, Penman MG, Piriou Y (2018) Evaluation of the systemic toxicity and mutagenicity of OLIGOPIN®, procyanidolic oligomers (OPC) extracted from French Maritime Pine Bark extract. Toxicol Rep 5:531–541. https://doi.org/10.1016/j.toxrep.2018.03.013

Shin NR, Ryu HW, Ko JW, Park JW, Kwon OK, Oh SR, Kim JC, Shin IS, Ahn KS (2016) A standardized bark extract of *Pinus pinaster* Aiton (Pycnogenol®) attenuated chronic obstructive pulmonary disease via Erk-sp1 signaling pathway. J Ethnopharmacol 194:412–420. https://doi.org/10.1016/j.jep.2016.10.029

Simões R, Pimentel C, Ferreira-Dias S, Miranda I, Pereira H (2021) Phytochemical characterization of phloem in maritime pine and stone pine in three sites in Portugal. Heliyon 7:e06718. https://doi.org/10.1016/j.heliyon.2021.e06718

Sousa JLC, Ramos PAB, Freire CSR, Silva AMS, Silvestre AJD (2018) Chemical composition of lipophilic bark extracts from *Pinus pinaster* and *Pinus pinea* cultivated in Portugal. Appl Sci 8:2575. https://doi.org/10.3390/app8122575

Thaichinda S, Tancharoen S, Kanekura T, Higashi Y, Dararat P, Kikuchi K, Nararatwanchai T (2020) *Pinus maritima* extract induces apoptosis in human malignant melanoma cells via ROS/caspase-3 signaling. Nat Prod Commun 15:1–10. https://doi.org/10.1177/1934578X20926889

Torrinha MBQLF, Bacelo HAM, Santos SCR, Boaventura RAR, Botelho CMS (2021) Uptake and recovery of gold from simulated hydrometallurgical liquors by adsorption on pine bark tannin resin. Water 12:3456. https://doi.org/10.3390/w12123456

Tümen İ, Akkol EK, Taştan H, Süntar I, Kurtca M (2018) Research on the antioxidant, wound healing, and anti-inflammatory activities and the phytochemical composition of maritime pine (*Pinus pinaster* Ait). J Ethnopharmacol 211:235–246. https://doi.org/10.1016/j.jep.2017.09.009

Uhlenhut K, Högger P (2012) Facilitated cellula ruptake and suppression of inducible nitric oxide synthase by a metabolite of maritime pine bark extract (Pycnogenol). Free Radical Biol Med 53:305–313. https://doi.org/10.1016/j.freeradbiomed.2012.04.013

Valls RM, Llauradó E, Fernández-Castillejo S, Puiggrós F, Solà R, Arola L, Pedret A (2016) Effects of low molecular weight procyanidin rich extract from french maritime pine bark on cardiovascular disease risk factors in stage-1 hypertensive subjects: randomized, double-blind, crossover, placebo-controlled intervention trial. Phytomedicine 23:1451–1461. https://doi.org/10.1016/j.phymed.2016.08.007

Vázquez G, Antorrena G, Francisco JL, González J (1992) Properties of phenolic-tannin adhesives from *Pinus pinaster* bark extracts as related to bond quality in eucalyptus plywoods. Holz Als Roh-Und Werkstoff 50:253–256. https://doi.org/10.1007/BF02650319

Vázquez G, Antorrena G, Francisco JL, Arias MC, González J (1993) Exterior plywood resins formulated from *Pinus pinaster* bark extracts. Holz Als Roh-Und Werkstoff 51:221–224. https://doi.org/10.1007/BF02628284

Vázquez G, Antorrena G, González J, Doval MD (1994) Adsorption of heavy metal ions by chemically modified *Pinus pinaster* bark. Bioresour Technol 48:251–255. https://doi.org/10.1016/0960-8524(94)90154-6

Vázquez G, Antorrena G, González J, Álvarez JC (1996) Tannin based adhesives for bonding high moisture Eucalyptus veneers: influence of tannin extraction and press conditions. Holz Als Roh-Und Werkstoff 54:93–97. https://doi.org/10.1007/s001070050144

Vázquez G, González-Álvarez J, Freire S, López-Moreno M, Antorrena G (2002) Removal of cadmium and mercury ions from aqueous solution by sorption on treated *Pinus pinaster* bark: kinetics and isotherms. Bioresour Technol 82:247–251. https://doi.org/10.1016/S0960-8524(01)00186-9

Vázquez G, Alonso R, Freire S, González-Álvarez J, Antorrena G (2006) Uptake of phenol from aqueous solutions by adsorption in a *Pinus pinaste*r bark packed bed. J Hazard Mater 133:61–67. https://doi.org/10.1016/j.jhazmat.2004.12.041

Vázquez G, González-Álvarez J, García AI, Freire MS, Antorrena G (2007) Adsorption of phenol on formaldehyde-pretreated *Pinus pinaster* bark: equilibrium and kinetics. Bioresour Technol 98:1535–1540. https://doi.org/10.1016/j.biortech.2006.06.024

Vázquez-González C, López-Goldar X, Alía R, Bustingorri G, Lario FJ, Lema M, de la Mata R, Sampedro L, Touza R, Zas R (2021) Genetic variation in resin yield and covariation with tree growth in maritime pine. For Ecol Manag 482:118843. https://doi.org/10.1016/j.foreco.2020.118843

Vergarechea M, del Río M, Gordo J, Martín R, Cubero D, Calama R (2019) Spatio-temporal variation of natural regeneration in *Pinus pinea* and *Pinus pinaster* Mediterranean forests in Spain. Eur J for Res 138:313–326. https://doi.org/10.1007/s10342-019-01172-8

Vieito C, Fernandes É, Vaz Velho M, Pires P (2018) The effect of different solvents on extraction yield, total phenolic content and antioxidant activity of extracts from pine bark (*Pinus pinaster* subsp. *atlantica*). Chem Eng Trans 64:127–132. https://doi.org/10.3303/CET1864022

Vieito C, Pires P, Vaz Velho M (2019) *Pinus pinaster* bark composition and applications: a review. In: Gaspar PD, da Silva PD (eds) Novel technologies and systems for food preservation. IGI Global, Pennsylvania, pp 174–189. https://doi.org/10.4018/978-1-5225-7894-9.ch008

Virgili F, Pagana G, Bourne L, Rimbach G, Natella F, Rice-Evans C, Packer L (2000) Ferulic acid excretion as a marker of consumption of a French maritime pine (*Pinus maritima*) bark extract. Free Radic Biol Med 28:1249–1256. https://doi.org/10.1016/S0891-5849(00)00244-6

Yang H, Tuo X, Wang L, Tundis R, Portillo MP, Simal-Gandara J, Yu Y, Zou L, Xiao J, Deng J (2021) Bioactive procyanidins from dietary sources: the relationship between bioactivity and polymerization degree. Trends Food Sci Technol 111:114–127. https://doi.org/10.1016/j.tifs.2021.02.063

Yesil-Celitkas O, Isleten M, Vardar-Sukan F, Oyku-Cetin E (2010) *In vitro* release kinetics of pine bark extract enriched orange juice and the shelf stability. Br Food J 112:1063–1076. https://doi.org/10.1108/00070701011080203

Yumak T (2021) Surface characteristics and electrochemical properties of activated carbon obtained from different parts of *Pinus pinaster*. Colloids Surf A 625:126982. https://doi.org/10.1016/j.colsurfa.2021.126982

Zhou H (2003) Reducing, reusing, and recycling solid wastes from wood fiber processing. In: Burton PJ, Messier C, Smith DW, Adamowicz WL (eds) Towards sustainable management of the boreal forest. NRC Research Press, Ottawa, pp 759–798

Zimin AV, Stevens KA, Crepeau MW, Puiu D, Wegrzyn JL, Yorke JA, Langley GH, Neale DB, Salzberg SL (2017) An improved assembly of the loblolly pine mega-genome using long-read single-molecule sequencing. GigaScience 6:1–4. https://doi.org/10.1093/gigascience/gix072