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Chemical Profiling of Significant Antioxidant and Phytotoxic Microwave-Extracted Essential Oil from *Araucaria heterophylla* Resin

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Abstract: Due to the various hazards of using synthetic chemical compounds in pharmaceutics, agriculture, and industry, scientists and researchers do their best to explore and assess new green natural compounds from natural resources with potent activity. The essential oil (EO) from the resin collected from *Araucaria heterophylla* Salisb. was extracted by the microwave technique and chemically characterized via GC-MS analysis. Furthermore, the extract EO was assessed for its antioxidant and phytotoxic activities. The EO has 33 compounds, mainly terpenes (98.23%), and the major compounds were α-pinene (62.57%), β-pinene (6.60%), germacrene D (5.88%), and β-caryophyllene (3.56%). The extracted EO showed substantial antioxidant activity, where it showed IC_{50} values of 142.42 and 118.03 mg L^{-1} for DPPH and ABTS, respectively. On the other hand, the EO revealed considerable phytotoxicity against the weed *Chenopodium murale*, where the EO showed IC_{50} values of 304.0, 230.1, and 147.1 mg L^{-1}, for seed germination, seedling shoot growth, and seedling root growth, respectively. Moreover, the EO showed the same pattern of allelopathic inhibition against the weed *Sonchus oleraceus*, where it showed IC_{50} values of 295.7, 224.5, and 106.1 mg L^{-1}, for seed germination, seedling shoot growth, and seedling root growth, respectively. The present study showed that the extraction technique affects the constituents of the EO, particularly the quantitative composition. The EO of *A. heterophylla* resin also revealed considerable antioxidant and phytotoxic activity against weeds. Therefore, it can be considered a promising natural resource that could be integrated into the weed management approach. However, further study is recommended for deep characterization of their authentic compounds and evaluation of their mode of action(s) on a wide spectrum of weeds.

Keywords: Norfolk pine; volatile compounds; free radical scavenging; terpenes; allelopathy

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1. Introduction

The *Araucaria* genus (family Araucariaceae) is a widely distributed coniferous, evergreen and ornamental tree in the world with around 19 species [1,2]. Different plant parts of *Araucaria* species have been documented to be used in the treatment of several traditional diseases such as antiseptic, emollient, ulcers, rheumatism as well as the treatment of contusions, amenorrhea, toothache, and respiratory infection [1]. The essential

oils (EOs) extracted from different organs of *Araucaria* species are well known for their biological and pharmaceutical activities such as anti-inflammation [3,4], anti-gastric ulcer [5], antibacterial, antiviral, antifungal [6], anticancer [7], antipyretic [3], and others [8]. Several phyto-components were isolated and identified from the different extracts of *Araucaria* species such as phenylpropanoids, flavonoids, phenolic compounds, lignans, and terpenoids [9,10]. *Araucaria* plants are very rich in EOs with high terpenoid contents including mono-, sesqui- and diterpenoids [3,7,11,12].

Araucaria heterophylla Salisb. is one of the important traditional plants for the treatment of toothache [1]. Several pharmaceutical potentialities were described for the different extracts of *A. heterophylla* including antitumor, gastroprotection, anti-inflammation, antipyretic, and free radical scavenging [7,9,11]. Several categories of compounds were characterized in the EO of *A. heterophylla* encompassing diterpenes [9], flavananols, phenolic acid, and polysaccharides [10]. The extracted EOs of leaves of *A. heterophylla* around the world were described with a high concentration of terpenes [7,12,13]. Recently, Elshamy and his co-workers described the significant anti-inflammation and antipyretic resin EO with high content of terpenoid compounds, especially monoterpenes [11]. To the best of our knowledge, this is the first time chemometrics have been implemented to investigate the essential oil of *A. heterophylla* extracted with microwave technique. Furthermore, the chemosystematic significance of this plant based upon the chemical composition of this oil was established along with the first description of its antioxidant and allelopathic potentialities.

Continuing the project of chemical and biological characterization of EOs from Egyptian medicinal plants [3], the targets of the current work were (1) providing the chemical profile of the EO extracted with microwave technique (MAE) from *A. heterophylla* resin, (2) evaluation of the free radical scavenging potentialities of the extracted EO via DPPH and ABTS assays, and (3) assessment of the phytotoxic activity of the extracted EO against the weeds *Chenopodium murale* and *Sonchus oleraceus*.

2. Materials and Methods

2.1. Collection of A. heterophyllaresin and EO Microwave-Assisted Extraction (MAE)

The resin of *A. heterophylla* was collected from the cultivated ornamental trees grown in the gardens of Mansoura University, Egypt (31°2′28.67″ N, 31°21′21.82″ E). The plant identification and resin collection were performed by the co-author Prof. Dr. A.M. Abd-ElGawad. A voucher specimen was prepared and deposited in the Herbarium of the Faculty of Science, Mansoura university with the code Mans. 010801005. The resin was dried in air and kept in a glass container till further analysis.

The EO of the *A. heterophylla* resin (120 g) was derived via the MAE technique as our previously documented research [14]. Briefly, the MAE-EO extraction was performed with a focused microwave apparatus (CEM Corporation), model (MARS 240/50, No. 907511, frequency 2450 MHz). The extraction was continued for 60 min at 100 °C in a round flask containing 1 L of water. The EO was separated by diethyl ether and then dried using 0.5 g of anhydrous sodium sulfate. The extraction was repeated three times for three samples and the results EOs were stored in sealed glass vials at 4 °C in a refrigerator till the gas chromatography-mass spectroscopy (GC-MS) and biological activity assays.

2.2. Chemical Characterization of EOs Using GC–MS Analysis

The analysis and components identification of all the three EO samples were carried out via the GC-MS tool under the same previous conditions [3,11]. The identification of the chemical constituents was performed depending upon the (i) (AMDIS) software (Automated Mass spectral Deconvolution and Identification), (ii) spectral collection of the Wiley Library, (iii) The library of NIST database (Gaithersburg, MD, USA; Wiley, Hoboken, NJ, USA).

2.3. Antioxidant Activity

The extracted EO from *A. heterophylla* resin was tested for its antioxidant properties by testing its ability to reduce the free radicals 2,2-diphenyl-1-picrylhydrazyl (DPPH, Sigma-Aldrich, Taufkirchen, Germany) and 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS, Sigma-Aldrich, Germany). For the DPPH assay, the radical was prepared in a concentration of 0.3 mM in methanol. The EO was prepared with a range of concentrations (6.26–200 mg L^{-1}), and the reaction mixture included an equal volume of the extract and the radical [15]. After half an hour of incubation in dark conditions, the absorbance was measured at 517 nm using a spectrophotometer (Spectronic 21D, Milton Roy, East Lyme, New London, CA, USA). On the other side, the scavenging of ABTS radical was performed following the methodology of Re et al. [16]. In brief, the radial was prepared with the same concentrations as previously mentioned for DPPH. A mixture of 2 mL of the radical and 2 mL of the sample was shaken vigorously and incubated for 6 min in dark conditions. The absorbance was measured at 734 nm. Catechol was used as a positive control (standard antioxidant). The inhibition of scavenging was calculated via the following equation:

$$\text{Scavenging activity (\%)} = (A_0 - A_1)/A_0 \times 100.$$

where A_0 is the absorbance of the control and A_1 is the absorbance of the sample

The IC_{50} value was calculated by plotting an exponential curve of concentration and scavenging percentage. The experiment was repeated three times with three replications, and the data were expressed as mean values ± standard deviation.

2.4. Allelopathic Activity

The EO extracted by microwave technique was assessed for its phytotoxicity against the weeds *C. murale* and *S. oleraceus*. The ripened seeds of the weed were collected from the gardens in Mansoura University, Dakahlia, Egypt (31°2′31.17″ N, 31°21′10.07″ E). The seeds were surface-sterilized with sodium hypochlorite (1%) for 1 min three times. For the phytotoxic assay, a series of EO concentrations (100, 200, 300, 400, and 500 mg L^{-1}) were prepared using polysorbate 80 as an emulsifier [17]. In Petri plates (90 mm), a sterilized filter paper was lined and moistened with 5 mL of each concentration as well as polysorbate as a negative control. Twenty seeds were aligned over the filter papers within the plates and the plates were sealed with parafilm and kept in the growth chamber at 25 ± 2 °C with a light cycle of 8 h dark/12 h light. After 10 days of incubation, the germinated seeds were counted, and the length (mm) of the seedling's shoot and root were measured. The inhibition of germination and seedling growth was calculated using the following equation:

$$\text{Inhibition \%} = \frac{(\text{No./length}_{\text{control}} - \text{No./length}_{\text{treatment}})}{\text{No./length}_{\text{control}}}$$

The 50% inhibitive concentration (IC_{50}, mgL^{-1}) was calculated by plotting an exponential curve of concentration and inhibition percentage. The experiment was repeated three times with three biological replicas, and the data were expressed as mean values ± standard deviation.

2.5. Statistical Analysis

The antioxidant and phytotoxicity experiments are repeated three times with three replications, and to test the significance among treatments, the data were subjected to one-way ANOVA, followed by Tukey's HSD. The ANOVA test was carried out using the Costat software program (CoHort Software, Monterey, CA, USA).

3. Results and discussion

3.1. MAE-EO of Araucaria heterophylla Components Characterization

The chemical characterization and biological activities of the EO of resin and leaves of *A. heterophylla* extracted by the hydrodistillation technique have been reported by Elshamy et al., [11] and Elkady and Ayoub [7], respectively. To complement this work, we targeted the EO of the resin via microwave-assisted extraction (MAE). The extracted MA-EO was analyzed via gas chromatography-mass spectroscopy (GC-MS) as presented in Figure 1. The identified components were listed in detail in Table 1 along with their retention times (Rt.), Kovats indices (KI), and relative concentrations. Additionally, Table 2 summarized the relative concentrations of common compounds in the EOs of Egyptian *A. heterophylla* (resin MA-EO) in the current study and those extracted by hydrodistillation (HD-EO) from the resin [11] and leaves [7].

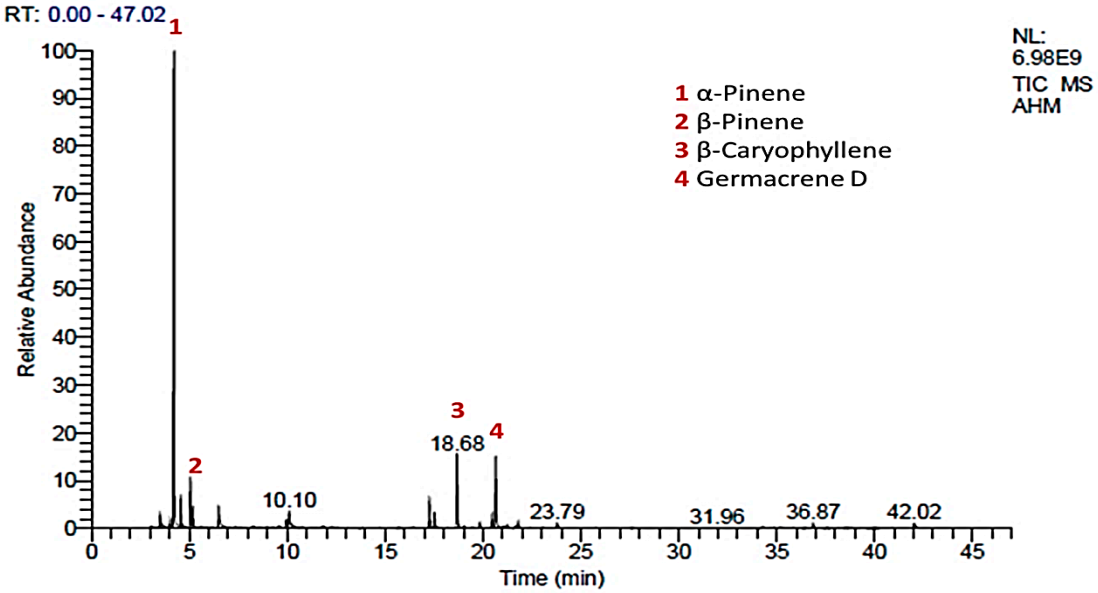

Figure 1. GC-MS analysis chromatogram of MA-EO of Egyptian *Araucaria heterophylla* resin.

Table 1. Chemical compounds of microwave-extracted essential oil (MA-EO) from *Araucaria heterophylla* resin.

No	Rt [a]	Type	Compound Name [b]	KI [c]	KI [d]	Relative Concentration (%)
1	3.52	H	*n*-Nonane	900	901	1.62 ± 0.03
2	4.04	MH	*α*-Thujene	924	926	1.21 ± 0.02
3	4.22	MH	*α*-Pinene	932	933	62.57 ± 0.42
4	4.58	MH	Camphene	946	944	2.51 ± 0.05
5	5.07	MH	*β*-Pinene	974	972	6.60 ± 0.07
6	5.2	MH	Sabinene	975	976	2.58 ± 0.03
7	6.51	MH	D-Limonene	1024	1025	2.31 ± 0.02
8	7.38	MH	*γ*-Terpinene	1054	1054	0.08 ± 0.01
9	7.77	OM	*trans*-Sabinene hydrate	1065	1067	0.01 ± 0.00
10	8.61	OM	*α*-Pinene oxide	1099	1100	0.01 ± 0.00
11	9.39	OM	*α*-Campholenal	1126	1124	0.01 ± 0.00
12	9.58	OM	Chrysanthenone	1127	1129	0.34 ± 0.01
13	9.95	OM	*cis*-Verbenol	1137	1135	0.38 ± 0.01

Table 1. *Cont.*

No	Rt [a]	Type	Compound Name [b]	KI [c]	KI [d]	Relative Concentration (%)
14	10.10	OM	Camphor	1146	1147	1.24 ± 0.03
15	10.22	OM	*trans*-3-Pinanone	1162	1160	0.16 ± 0.01
16	10.65	OM	Pinocarvone	1164	1166	0.01 ± 0.00
17	11.36	OM	Terpinen-4-ol	1177	1175	0.01 ± 0.00
18	11.85	OM	Myrtenal	1195	1197	0.30 ± 0.01
19	12.29	OM	Verbenone	1205	1203	0.06 ± 0.01
20	16.33	SH	α-Cubebene	1351	1354	0.02 ± 0.00
21	17.05	SH	α-Ylangene	1375	1374	0.01 ± 0.00
22	17.27	SH	α-Copaene	1376	1379	2.49 ± 0.06
23	17.53	SH	β-Bourbonene	1387	1386	2.14 ± 0.02
24	18.68	SH	β-Caryophyllene	1427	1430	3.56 ± 0.05
25	19.85	SH	α-Humulene	1452	1450	0.80 ± 0.01
26	20.46	SH	γ-Muurolene	1478	1480	1.11 ± 0.02
27	20.65	SH	Germacrene D	1484	1486	5.88 ± 0.06
28	21.09	SH	γ-Elemene	1436	1435	0.04 ± 0.00
29	21.22	SH	α-Muurolene	1500	1500	0.32 ± 0.01
30	21.68	SH	γ-Cadinene	1513	1511	0.16 ± 0.01
31	21.79	SH	δ-Cadinene	1523	1522	0.54 ± 0.02
32	23.79	OS	Caryophyllene oxide	1583	1584	0.23 ± 0.01
33	42.02	DH	Cembrene	1938	1940	0.54 ± 0.02
			Total identified			99.85
			Hydrocarbons (H)			1.62
			Monoterpenes hydrocarbons (MH)			77.86
			Oxygenated monoterpenes (OM)			2.53
			Sesquiterpenes hydrocarbons (SH)			17.07
			Oxygenated Sesquiterpenes(OS)			0.23
			Diterpene hydrocarbons (DH)			0.54

[a] Rt. Retention time, [b] EO constituents' identification was performed via comparison of the Kovats indices (KI) and mass spectral data with those of NIST Mass Spectral Library (2011) and Wiley Registry of Mass Spectral Data 8th edition and literature, [c] Kovats indices reported by Adams 2017, [d] calculated Kovats indices, relative concentration of MA-EO compounds in current study (±standard deviation of three replications).

Thirty-three compounds were characterized in the EO with a total relative concentration of 99.85%. All these compounds can be categorized into six classes including monoterpenes (oxygenated and hydrocarbons), sesquiterpenes (oxygenated and hydrocarbons), diterpene, and hydrocarbons. A relative concentration of 98.23% from overall EO mass was assigned as terpenoids and this result was in agreement with all extracted EOs from different *Araucaria* species [3,7,11–13]. The current results exhibited that monoterpenes are the fundamental compounds of MA-EO with a relative concentration of 80.39%. These findings showed that the concentration of the monoterpenes in the MA-EO is higher than the HD-EO from resin (66.53%) [11] and less than HD-EO from leaves (83.87%) of the Egyptian ecospecies of *A. heterophylla* [7]. The monoterpenes hydrocarbons (77.86%) were found as the main components with α-pinene (62.57%) as the major compound, along with β-pinene (6.60%), sabinene (2.58%), camphene (2.51%) and D-limonene (2.31%). All these major compounds were also described as majors in HD-EO of resin [11] as well as

the leaves [7] of Egyptian *A. heterophylla* with significant differences in the concentration compared to the present study, especially for α-pinene. The α and β-pinene, sabinene derivatives, and D-limonene were also determined as major monoterpenes hydrocarbons of the EOs extracted from different *Araucaria* species (Table 2) [3,12,13].

Table 2. Main compounds of the EOs of the Egyptian *Araucaria heterophylla* in the current study (MA-EO) and those reported for the EOs that were extracted with hydrodistillation (HD-EO) from resin and leaves.

No	Compound Name [a]	Relative Concentration (%)		
		Resin MA-EO [a]	Resin HD-EO [b]	Leaves HD-EO [c]
1	α-Pinene	62.57	44.88	70.85
2	β-Pinene	6.60	1.79	1.51
3	Sabinene	2.58	4.44	–
4	D-Limonene	2.31	4.13	4.26
5	γ-Terpinene	0.08	0.27	3.00
6	α-Copaene	2.49	4.72	0.20
7	β-Caryophyllene	3.56	7.90	2.93
8	Germacrene D	5.88	10.25	2.99
Total identified		99.85	98.68	95.16
Monoterpenes hydrocarbons (MH)		77.86	61.20	83.01
Sesquiterpenes hydrocarbons (SH)		17.07	30.12	6.69

[a] The relative concentrations of EOs compounds from current study (MA-EO), [b] resin (HD-EO) [11], and [c] leaves (HD-EO) [7].

The oxygenated monoterpenes represented only 2.53% of overall MA-EO mass with eleven identified compounds including camphor (1.24%) as major along with other traces. The oxygenated monoterpenes were also described as a minor class in different *Araucaria* species [3,7,11,13]. Sesquiterpenes were assigned with a relative concentration of 17.30% including sesquiterpene hydrocarbons (17.07%) and traces of oxygenated sesquiterpenes (0.23%). From eleven identified sesquiterpene hydrocarbons, germacrene D (5.88), β-caryophyllene (3.56%), α-copaene (2.49%), and β-bourbonene (2.14%) were determined as major compounds, while only one oxygenated sesquiterpene compound, caryophyllene oxide, was identified in very low concentration (0.23%). All these findings were consistent with the previously documented data of HD-EO of resin [11] and leaves [7] of Egyptian *A. heterophylla* and other *Araucaria* species (Table 2) [3,12,13].

Cembrene was the only characterized diterpene, which is found in trace amounts (0.54%). This is in agreement with the fact of the scarcity of diterpenes in plants' EOs [18,19]. Additionally, the only identified hydrocarbon, *n*-nonane, was assigned as overall hydrocarbon relative concentration (1.62%). All these data confirmed the significant effect of the extraction techniques [20], the plant part, climatic, and environmental conditions, as well as the genetic characteristics of the chemical constituents of EOs [21,22].

3.2. Chemosystematic Significance

The *Araucaria* genus is one of the genera of family Araucariaceae, with approximately 19 accepted plant species (Available online: www.theplantlist.org (accessed on 22 June 2020)). The major components of EO from *A. heterophylla* resin might be guidance for the establishment of the chemosystematic significance of this plant with the other *Araucaria* plants (Table 3). The present and published data revealed the presence of mono- and sesquiterpenes as main constituents both α- and β-isomers of pinene, sabinene, limonene, terpeinene, copaene, caryophyllene, and germacen D as major compounds in EOs derived from different parts of this plant [7,11]. These compounds were found majors in another *Araucaria* plants as *A. cunninghamii* [23], *A. bidwillii* [7,11], *A. araucana* [24], *A. brasiliensis* [25], *A. excels* [26], and others. The pinene isomers and sabinene were documented as abundant

compounds in EOs of *A. excels* [26], *A. cunninghamii* [27], *A. bidwillii* [7,11,28], *A. brasiliensis* [25] and *A. hunsteinii* [13]. By the same, limonene and terpeinene are common and widely distributed components in EOs afforded from the different species of *Araucaria* genus such as *A. araucana* [24], *A. bidwillii* [7,11,28]. Moreover, all the published data concerning the EOs constituents of *Araucaria* plants revealed that presence of copaene, caryophyllene, and germacen D as main constituents such as *A. bidwillii* [29], *A. Montana, A. luxurians, A. muelleri,* and *A. scopulorum* [13]. All these data supported the fact of capability of *Araucaria* plants of biosynthetic production of terpenoids especially the mono- and sesquit- types of terpenes [30]. The previous data along with previous data also went in the same line of the ability of *A. heterophylla* for biosynthetic of the mono- and sesquitterpenes [7,11]. The diterpenes were stated to be rarely described in the EOs derived from many plants with some exceptions in overall the plant kingdom (Essa et al., 2021, Abd-ElGawad et al., 2021, El Gendy et al., 2022, 38). All the documented data of the chemical composition of the EOs derived from different parts of *A. heterophylla* collected from Egypt [7,11], along with present data, supported that diterpenes were present as traces. The EOs of *A. heterophylla* collected from India and Australia were documented to have diterpenes as major components especially with concentrations of 92.5 and 35.6%, respectively [12,13]. This significant variation between the Egyptian, Indian, and Australian *A. heterophylla*, especially in the diterpene contents, could be ascribed directly to the variation of climate, weather humidity, and other environmental conditions [21,22]. The phenomenon of diterpenes' minority in the EOs of the other *Araucaria* plants was not common. The diterpenes abundance was widely described in the EOs of several *Araucaria* species (Table 3) via the preponderance of 16-kaurene, hibaene, beyerene, sclarene, phyllocladene, luxuriadiene, 5,15-rosadiene and others [3,7,13]. From all the above, the chemical components of *A. heterophylla* EOs are completely closed to the documented chemical profiles of the other *Araucaria* ecoplants. Furthermore, this survey showed the significant abilities of *Araucaria* ecoplants for biosynthetical production of different terpene types such as mono-, sesqui-, and di-terpenes. Finally, the *Araucaria* plants were found to be characterised by their ability of enzymatic production of the diterpenes in the EOs byproducts.

3.3. Antioxidant Activity

The extracted EO from the resin of *A. heterophylla* was tested for its antioxidant activity by its ability to scavenge the free radicals 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS). The scavenging activity of both radicals increased with the increment of EO concentration (Table 3). At the highest concentration of the EO (200 mg L^{-1}), the DPPH and ABTS were scavenged by 61.13% and 63.98%, respectively. Based on the IC_{50} values, the EO of *A. heterophylla* extracted with the microwave technique showed IC_{50} values of 142.42 mg L^{-1} and 118.03 mg L^{-1} for DPPH and ABTS, respectively (Table 4).

The substantial antioxidant activity of the *A. heterophylla* EO could be ascribed to the chemical composition especially the main compounds such as α-pinene, β-pinene, β-caryophyllene, and germacrene D. The main compound, α-pinene, has been reported to possess various biological activities including the antioxidant effect [23,24]. Wang, et al. [25] reported that α-pinene is the strongest antioxidant agent among seven tested terpenoids. In this context, several EOs derived from plants were found to have antioxidant potentialities due to the abundance of α- and β-pinene such as *Zanthoxylum armatum* DC [31], *Euphorbia mauritanica* L. [19] and *Pistacia lentiscus* L. [32]. Furthermore, the presence of β-caryophyllene and germacrene Das, a major component in the Eos extracted from plants, were described to be among the agents of increasing antioxidant activities such as *Aquilaria crassna* Pierre [33], *Croton zehntneri* Pax, *Pterodon emarginatus* Vogel, *Schinopsis brasiliensis* Engler [34], and *Vernonia chalybaea* Mart. [35]. In addition to these main components, the other constituents played significant roles via synergetic or singular functions [19].

Table 3. Main components of EOs of some *Araucaria* plants.

Araucaria sp.	Plant Part	Collected from	Main Components (%)	Reference
A. angustifolia	Leaves	Australia	16-Kaurene (60.3), hibaene (29.7%), phyllocladene (20.1%)	[13]
A. bidwillii	Leaves	Australia	Hibaene (76%), 16-kaurene (19.4), phyllocladene (12.5%)	[13]
	Shoots	Egypt	Beyerene (20.81%), α-pinene (16.21%), D-limonene (14.22%)	[3]
	Leaves	Egypt	Beyerene (35.65%), trans-nerolidol (13.66%) α-elemene (6.09%)	[7]
	Oleoresins	Egypt	α-Pinene (63.4%), trans-3-caren-2-ol (4.37%), nonane (5.21%)	[29]
A. columnaris	Leaves	Australia	16-Kaurene (37.3), luxuriadiene (23.3%), hibaene (9.4%)	[13]
A. cunninghamii	Leaves	Australia	16-Kaurene (53.0%), 5,15-rosadiene (60%), hibaene (29.3%),	[13]
	Foliage	India	Beyerene (44.4%), caryophyllene oxide (17.9%), α-pinene (16.2%)	[12]
	Resin	India	E-Caryophyllene (60.8%), caryophyllene oxide (13.4%), E-β-farnesene (4.9%)	[12]
	Leaves	Nigeria	α-Pinene (14.8%), terpinen-4-ol (14.7%), shyobunol (8.9%)	[27]
	softwood	Australia	Hexanal (11.5%), α-copaene (31.1%), β-farnesene (11.3%)	[23]
A. heterophylla	Leaves	Egypt	α-Pinene (70.85%), d-limonene (4.26%) and germacrene D (2.99%)	[7]
	Resin	Egypt	α-Pinene (44.88%), germacrene-D (10.25%), α-copaene (4.72%)	[11]
	oleoresins	Egypt	α-Pinene (57.59%), caryophyllene (5.40%), trans-3-caren-2-ol (4.56%)	[29]
	Leaves	Australia	α-Pinene (52.4%), phyllocladene (32.2%), β- caryophyllene (3.1%)	[13]
	Foliage	India	13-epi-Dolabradiene (42.7%), beyerene (22.2%), rimuene (13.7%)	[12]
	Resin	India	α-Copaene (29.9%), germacrene D (21.4%), γ-gurjunene (9.7%)	[12]
A. hunsteinii	Leaves	Australia	α-Pinene (18.2%), sclarene (10.7%), 16-kaurene (5.7%)	[13]
A. luxurians	Leaves	Australia	Luxuriadienea (65.6%), 5,15-rosadiene (19.6%)	[13]
A. montana	Leaves	Australia	Phyllocladene (61.0%), 16-kaurene (22.8%), α -pinene (3.2%)	[13]
A. muelleri	Leaves	Australia	Sclarene (20.1%), huxuriadienea (18.8%), $C_{20}H_{32}$ (25.1%)	[13]
A. scopulorum	Leaves	Australia	16-Phyllocladanol (41%), luxuriadienea (10.0%), α-copaene (6.0%)	[13]
A. excels	Terminal branchlites	New Zealand	α-Pinene (70%), phyllocladene (19%)	[13]
A. brasiliensis	Leaves	Ecuador	Beyerene (26.08%), kaurene (24.86%), myrcene (11.02%), α-pinene (9.99%)	[25]

Table 4. Antioxidant activity of the essential oil and catechol as standard determined by scavenging of DPPH and ABTS radicals.

Treatment	Conc. (mg L^{-1})	DPPH [a] Scavenging (%)	IC_{50} [b] (mg L^{-1})	ABTS [c] Scavenging (%)	IC_{50} (mg L^{-1})
Essential oil	6.25	61.13 ± 2.36	142.42 ± 5.49	63.98 ± 1.53	118.03 ± 3.97
	12.5	42.10 ± 0.43		50.25 ± 0.94	
	25.0	34.60 ± 0.56		40.27 ± 0.96	
	50.0	23.68 ± 0.21		33.68 ± 1.45	
	100.0	17.53 ± 0.71		25.61 ± 1.55	
	200.0	16.17 ± 0.78		20.55 ± 1.54	
Catechol			19.95 ± 0.73		12.48 ± 0.50

[a] DPPH: 2,2-diphenyl-1-picrylhydrazyl, [b] IC_{50}: concentration required for 50% inhibition, [c] ABTS: 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid.

3.4. Phytotoxic Activity of MAE-EO of *A. heterophylla*

The allelopathic activity of the *A. heterophylla* EO extracted by microwave technique against the weed *C. murale* and *S. oleraceus* is shown in Figures 2 and 3. For *C. murale,* the re-

sults showed that the activity of EO was significantly increased ($p < 0.05$) in a concentration-dependent manner. The seedling growth was inhibited more than germination, and the root was more sensitive to the EO compared to the shoot. At a higher concentration of the EO (500 mg L^{-1}), the seed germination, seedling shoot growth, and seedling root growth of *C. murale* were inhibited by 81.0, 80.5, and 89.4% respectively (Figure 2A). Based on the IC_{50} estimation, the EO showed IC_{50} values of 304.0, 230.1, and 147.1 mg L^{-1}, for seed germination, seedling shoot growth, and seedling root growth, respectively (Figure 2B).

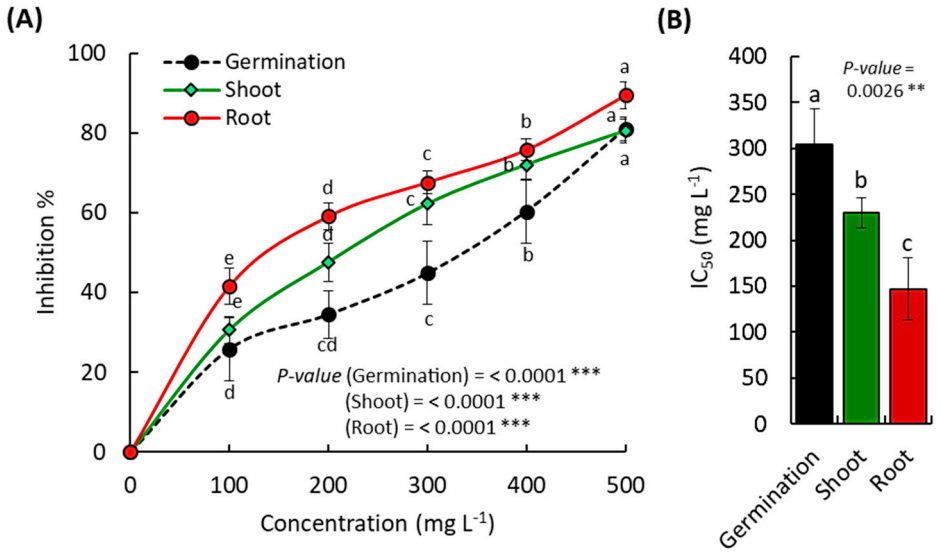

Figure 2. Phytotoxic activity of the EO extracted from the resin of *Araucaria heterophylla* against the germination and seedling growth of the weed *Chenopodium murale*. (**A**) the inhibitory effect with concentration, and (**B**) the IC_{50} value (the concentration of the EO required for 50% inhibition). The bars represent the standard deviation ($n = 3$). ** $p < 0.01$, *** $p < 0.001$.

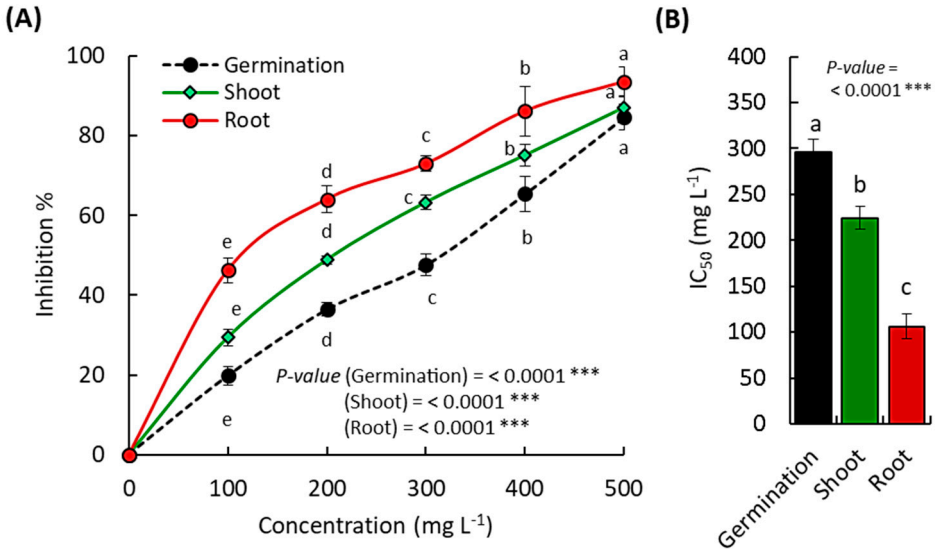

Figure 3. Phytotoxic activity of the EO extracted from the resin of *Araucaria heterophylla* against the germination and seedling growth of the weed *Sonchus oleraceus*. (**A**) the inhibitory effect with concentration, and (**B**) the IC_{50} value (the concentration of the EO required for 50% inhibition). The bars represented the standard deviation ($n = 3$). *** $p < 0.001$.

On the other hand, the allelopathic activity *A. heterophylla* EO against the weed *S. oleraceus* showed more inhibition to the seedling growth than the germination of the seeds (Figure 3). At the lowest concentration (100 mg L^{-1}) of the EO, a high variation was

determined, where the root development was the most inhibited (46.2%), followed by the shoot (29.4%), and finally the seed germination (19.8%), while at the highest concentration of the EO (500 mg L^{-1}), the inhibition of the seed germination, seedling shoot growth, and seedling root growth of *S. oleraceus* was comparable (Figure 3A). Based on the IC_{50} calculations, the root of the *S. oleraceus* seedling was the most inhibited which showed an IC_{50} of 106.1 mg L^{-1}, while seedling shoot growth and seed germination attained the IC_{50} values of 224.5 mg L^{-1} and 295.7 mg L^{-1}, respectively (Figure 3B).

The efficacy of *A. heterophylla* EO on the weed *C. murale* and *S. oleraceus* was lower than those reported for the EO of *Deverra tortuosa* [31], while it is comparable to those extracted from *Bassia muricata* [36]. The identified major compounds *α*- & *β*-pinene have been reported as effective allelopathic monoterpenes in various plants EO such as *Symphyotrichum squamatum* (Spreng.) G.L.Nesom [22], *Schinus terebinthifolius* G. Raddi [37], *Callistemon viminalis* (Sol. ex Gaertn.) Byrnes [38], *Pinus brutia* Ten. [39], *Pinus pinea L.* [40], *Eucalyptus lehmanii* (Schauer) Benth. [41], and *Cotinus coggyria* Scop. [39]. These EOs showed substantial phytotoxic activity against different weeds such as *Bidens pilosa* L. 1753, *Cassia occidentalis* (L.) Link, 1829, *Echinochloa crusgalli* (L.) P.Beauv., *Phalaris minor* Retz., *Sinapis arvensis* L., *Lolium rigidum* Gaud., *Raphanus raphanistrum* L., *Diplotaxis harra* (Forssk.) Boiss., *Trifolium campestre* Schreb., *Phalaris canariensis* L., *Silybum marianum* (L.) Gaertn., and *Portulaca oleracea* L. [42].

The other major compounds, such as germacrene D and *β*-caryophyllene, are identified in the EOs of various plants with considerable phytotoxicity [42–45]. The terpenoid compounds could inhibit the germination and growth of the targeted weeds via their interference with respiration, cell division, membrane permeability, photosynthesis, enzyme activities, nucleic acid formation as well as the production of reactive oxygen species (ROS) that interact with the various biological processes inside the plant cells [46–48].

4. Conclusions

The present results showed that the extraction technique for the EO considerably affects the chemical composition of the compounds. The GC-MS analysis of the EO extracted by microwave technique from *A. heterophylla* resin showed the presence of 33 compounds, mainly terpenes (98.23%). The *α*-pinene, *β*-pinene, germacrene D, and *β*-caryophyllene were the major compounds. The extracted EO revealed substantial antioxidant activity, as well as phytotoxicity against the weed *C. murale* and *S. oleraceus*. The present results showed that the EO of *A. heterophylla* could be used for weed control. Meanwhile, further study is recommended for deep characterization of the effect and mode of action of the major bioactive compounds either alone or in combination, targeting a wide spectrum of weeds.

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References

1. Aslam, M.S.; Choudhary, B.A.; Uzair, M.; Ijaz, A.S. Phytochemical and ethno-pharmacological review of the genus *Araucaria*–review. *Trop. J. Pharm. Res.* **2013**, *12*, 651–659. [CrossRef]
2. Kershaw, P.; Wagstaff, B. The southern conifer family Araucariaceae: History, status, and value for paleoenvironmental reconstruction. *Annu. Rev. Ecol. Syst.* **2001**, *32*, 397–414. [CrossRef]
3. Abdelhameed, M.F.; Asaad, G.F.; Ragab, T.I.; Ahmed, R.F.; El Gendy, A.E.-N.G.; El-Rahman, A.; Sahar, S.; Elgamal, A.M.; Elshamy, A.I. Oral and topical anti-inflammatory and antipyretic potentialities of *Araucaria bidiwillii* shoot essential oil and its nanoemulsion in relation to chemical composition. *Molecules* **2021**, *26*, 5833. [CrossRef]
4. Mota, M.R.; Criddle, D.N.; Alencar, N.M.; Gomes, R.C.; Meireles, A.V.; Santi-Gadelha, T.; Gadelha, C.A.; Oliveira, C.C.; Benevides, R.G.; Cavada, B.S. Modulation of acute inflammation by a chitin-binding lectin from *Araucaria angustifolia* seeds via mast cells. *Naunyn-Schmiedeberg's Arch. Pharmacol.* **2006**, *374*, 1–10. [CrossRef]
5. Schmeda-Hirschmann, G.; Yesilada, E. Traditional medicine and gastroprotective crude drugs. *J. Ethnopharmacol.* **2005**, *100*, 61–66. [CrossRef]
6. Freitas, A.; Almeida, M.; Andrighetti-Fröhner, C.; Cardozo, F.; Barardi, C.; Farias, M.; Simões, C. Antiviral activity-guided fractionation from *Araucaria angustifolia* leaves extract. *J. Ethnopharmacol.* **2009**, *126*, 512–517. [CrossRef]
7. Elkady, W.M.; Ayoub, I.M. Chemical profiling and antiproliferative effect of essential oils of two *Araucaria* species cultivated in Egypt. *Ind. Crops Prod.* **2018**, *118*, 188–195. [CrossRef]
8. Peralta, R.M.; Koehnlein, E.A.; Oliveira, R.F.; Correa, V.G.; Corrêa, R.C.; Bertonha, L.; Bracht, A.; Ferreira, I.C. Biological activities and chemical constituents of *Araucaria angustifolia*: An effort to recover a species threatened by extinction. *Trends Food Sci. Technol.* **2016**, *54*, 85–93. [CrossRef]
9. Abdel-Sattar, E.; Monem, A.R.A.; Ezzat, S.M.; El-Halawany, A.M.; Mouneir, S.M. Chemical and biological investigation of *Araucaria heterophylla* Salisb. Resin. *Z. Für Nat. C* **2009**, *64*, 819–823. [CrossRef]
10. Michael, H.N.; Awad, H.M.; El-Sayed, N.H.; Paré, P.W. Chemical and antioxidant investigations: Norfolk pine needles (*Araucaria excelsa*). *Pharm. Biol.* **2010**, *48*, 534–538. [CrossRef] [PubMed]
11. Elshamy, A.I.; Ammar, N.M.; Hassan, H.A.; Al-Rowaily, S.L.; Ragab, T.I.; El Gendy, A.E.-N.G.; Abd-ElGawad, A.M. Essential oil and its nanoemulsion of *Araucaria heterophylla* resin: Chemical characterization, anti-inflammatory, and antipyretic activities. *Ind. Crops Prod.* **2020**, *148*, 112272. [CrossRef]
12. Verma, R.S.; Padalia, R.C.; Goswami, P.; Verma, S.K.; Chauhan, A.; Darokar, M.P.J.I.C. Chemical composition and antibacterial activity of foliage and resin essential oils of *Araucaria cunninghamii* Aiton ex D. Don and *Araucaria heterophylla* (Salisb.) Franco from India. *Ind. Crops Prod.* **2014**, *61*, 410–416. [CrossRef]
13. Brophy, J.J.; Goldsack, R.J.; Wu, M.Z.; Fookes, C.J.; Forster, P.I. The steam volatile oil of Wollemia nobilis and its comparison with other members of the Araucariaceae (*Agathis* and *Araucaria*). *Biochem. Syst. Ecol.* **2000**, *28*, 563–578. [CrossRef] [PubMed]
14. Elshamy, A.; Abd-ElGawad, A.; Mohamed, T.; El Gendy, A.E.N.; Abd El Aty, A.A.; Saleh, I.; Moustafa, M.F.; Hussien, T.A.; Pare, P.W.; Hegazy, M.E.F. Extraction development for antimicrobial and phytotoxic essential oils from Asteraceae species: *Achillea fragrantissima*, *Artemisia judaica* and *Tanacetum sinaicum*. *Flavour Fragr. J.* **2021**, *36*, 352–364. [CrossRef]
15. Miguel, M.G. Antioxidant activity of medicinal and aromatic plants. *Flavour Fragr. J.* **2010**, *25*, 219–312. [CrossRef]
16. Re, R.; Pellegrini, N.; Proteggente, A.; Pannala, A.; Yang, M.; Rice-Evans, C. Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radic. Biol. Med.* **1999**, *26*, 1231–1237. [CrossRef]
17. Abd El-Gawad, A.M. Chemical constituents, antioxidant and potential allelopathic effect of the essential oil from the aerial parts of *Cullen plicata*. *Ind. Crops Prod.* **2016**, *80*, 36–41. [CrossRef]
18. Abd-ElGawad, A.M.; El-Amier, Y.A.; Bonanomi, G.; Gendy, A.E.-N.G.E.; Elgorban, A.M.; Alamery, S.F.; Elshamy, A.I. Chemical composition of *Kickxia aegyptiaca* essential oil and its potential antioxidant and antimicrobial activities. *Plants* **2022**, *11*, 594. [CrossRef]
19. Essa, A.F.; El-Hawary, S.S.; Abd-El Gawad, A.M.; Kubacy, T.M.; AM El-Khrisy, E.E.D.; Elshamy, A.I.; Younis, I.Y. Prevalence of diterpenes in essential oil of *Euphorbia mauritanica* L.: Detailed chemical profile, antioxidant, cytotoxic and phytotoxic activities. *Chem. Biodivers.* **2021**, *18*, e2100238. [CrossRef]
20. Saleh, I.; Abd-ElGawad, A.; El Gendy, A.E.-N.; Abd El Aty, A.; Mohamed, T.; Kassem, H.; Aldosri, F.; Elshamy, A.; Hegazy, M.-E.F. Phytotoxic and antimicrobial activities of *Teucrium polium* and *Thymus decussatus* essential oils extracted using hydrodistillation and microwave-assisted techniques. *Plants* **2020**, *9*, 716. [CrossRef] [PubMed]
21. Elshamy, A.I.; Abd-ElGawad, A.M.; El-Amier, Y.A.; El Gendy, A.E.N.G.; Al-Rowaily, S.L. Interspecific variation, antioxidant and allelopathic activity of the essential oil from three Launaea species growing naturally in heterogeneous habitats in Egypt. *Flavour Fragr. J.* **2019**, *34*, 316–328. [CrossRef]
22. Abd-ElGawad, A.M.; Elshamy, A.I.; El-Amier, Y.A.; El Gendy, A.E.-N.G.; Al-Barati, S.A.; Dar, B.A.; Al-Rowaily, S.L.; Assaeed, A.M. Chemical composition variations, allelopathic, and antioxidant activities of *Symphyotrichum squamatum* (Spreng.) Nesom essential oils growing in heterogeneous habitats. *Arab. J. Chem.* **2020**, *13*, 4237–4245. [CrossRef]
23. Franich, R.A.; McDonald, A.G.; Steward, D. Essential oil of the wood of *Araucaria cunninghamii* Aiton ex D. Don. *J. Essent. Oil Res.* **1999**, *11*, 38–40. [CrossRef]

24. Briggs, L.; White, G. Constituents of the essential oil of *Araucaria araucana*. *Tetrahedron* **1975**, *31*, 1311–1314. [CrossRef]
25. Jaramillo, D.; Calva, J.; Bec, N.; Larroque, C.; Vidari, G.; Armijos, C. Chemical characterization and biological activity of the essential oil from *Araucaria brasiliensis* collected in Ecuador. *Molecules* **2022**, *27*, 3793. [CrossRef]
26. Briggs, L.H. The essential oil of *Araucaria excelsa* (norfolk island pine). *J. Soc. Chem. Ind.* **1941**, *60*, 222–226. [CrossRef]
27. Olawore, N.O.; Ogunwande, I.A. Analysis of the leaf oil of *Araucaria cunninghamii* Sweet. grown in Nigeria. *J. Essent. Oil Res.* **2005**, *17*, 459–461. [CrossRef]
28. Ali, D.E.; el-Aziz, A.; Marwa, M.; Ibrahim, S.S.A.; Sheta, E.; Abdel-Sattar, E. Gastroprotective and anti-Helicobacter pylori potentials of essential oils from the oleoresins of *Araucaria bidwillii* and *Araucaria heterophylla*. *Inflammopharmacology* **2022**, 1–19, *in press*. [CrossRef]
29. Ali, Z.A.A. Taxonomic study of *Glossostemon bruguieri* Desf.(Malvaceae) in Iraq. *Plant Arch.* **2020**, *20*, 926–929.
30. Frezza, C.; Venditti, A.; De Vita, D.; Toniolo, C.; Franceschin, M.; Ventrone, A.; Tomassini, L.; Foddai, S.; Guiso, M.; Nicoletti, M. Phytochemistry, chemotaxonomy, and biological activities of the Araucariaceae family—A review. *Plants* **2020**, *9*, 888. [CrossRef] [PubMed]
31. Dhami, A.; Singh, A.; Palariya, D.; Kumar, R.; Prakash, O.; Rawat, D.; Pant, A. α-Pinene rich bark essential oils of *Zanthoxylum armatum* DC. from three different altitudes of Uttarakhand, India and their antioxidant, in vitro anti-inflammatory and antibacterial activity. *J. Essent. Oil Bear. Plants* **2019**, *22*, 660–674. [CrossRef]
32. Xanthis, V.; Fitsiou, E.; Voulgaridou, G.-P.; Bogadakis, A.; Chlichlia, K.; Galanis, A.; Pappa, A. Antioxidant and cytoprotective potential of the essential oil *Pistacia lentiscus* var. Chia and its major components myrcene and α-pinene. *Antioxidants* **2021**, *10*, 127. [CrossRef] [PubMed]
33. Dahham, S.S.; Tabana, Y.M.; Iqbal, M.A.; Ahamed, M.B.; Ezzat, M.O.; Majid, A.S.; Majid, A.M. The anticancer, antioxidant and antimicrobial properties of the sesquiterpene β-caryophyllene from the essential oil of *Aquilaria crassna*. *Molecules* **2015**, *20*, 11808–11829. [CrossRef] [PubMed]
34. Donati, M.; Mondin, A.; Chen, Z.; Miranda, F.M.; do Nascimento, B.B., Jr.; Schirato, G.; Pastore, P.; Froldi, G. Radical scavenging and antimicrobial activities of *Croton zehntneri*, *Pterodon emarginatus* and *Schinopsis brasiliensis* essential oils and their major constituents: Estragole, trans-anethole, β-caryophyllene and myrcene. *Nat. Prod. Res.* **2015**, *29*, 939–946. [CrossRef]
35. Nogueira Sobrinho, A.C.; Morais, S.M.d.; Souza, E.B.d.; Albuquerque, M.R.J.R.; Santos, H.S.d.; Cavalcante, C.S.d.P.; Sousa, H.A.d.; Fontenelle, R.O.d.S. Antifungal and antioxidant activities of *Vernonia Chalybaea* Mart. ex DC. essential oil and their major constituent β-caryophyllene. *Braz. Arch. Biol. Technol.* **2020**, *63*, e20190177. [CrossRef]
36. Abd-ElGawad, A.; El Gendy, A.E.-N.; El-Amier, Y.; Gaara, A.; Omer, E.; Al-Rowaily, S.; Assaeed, A.; Al-Rashed, S.; Elshamy, A. Essential oil of *Bassia muricata*: Chemical characterization, antioxidant activity, and allelopathic effect on the weed *Chenopodium murale*. *Saudi J. Biol. Sci.* **2020**, *27*, 1900–1906. [CrossRef]
37. Pinheiro, P.F.; Costa, A.V.; Tomaz, M.A.; Rodrigues, W.N.; Fialho Silva, W.P.; Moreira Valente, V.M. Characterization of the Essential Oil of Mastic Tree from Different Biomes and its Phytotoxic Potential on Cobbler's Pegs. *J. Essent. Oil Bear. Plants* **2016**, *19*, 972–979. [CrossRef]
38. Bali, A.S.; Batish, D.R.; Singh, H.P.; Kaur, S.; Kohli, R.K. Chemical characterization and phytotoxicity of foliar volatiles and essential oil of *Callistemon viminalis*. *J. Essent. Oil Bear. Plants* **2017**, *20*, 535–545. [CrossRef]
39. Ulukanli, Z.; Karabörklü, S.; Bozok, F.; Burhan, A.; Erdogan, S.; Cenet, M.; KARAASLAN, M.G. Chemical composition, antimicrobial, insecticidal, phytotoxic and antioxidant activities of Mediterranean *Pinus brutia* and *Pinus pinea* resin essential oils. *Chin. J. Nat. Med.* **2014**, *12*, 901–910. [CrossRef]
40. Amri, I.; Gargouri, S.; Hamrouni, L.; Hanana, M.; Fezzani, T.; Jamoussi, B. Chemical composition, phytotoxic and antifungal activities of Pinus pinea essential oil. *J. Pest Sci.* **2012**, *85*, 199–207. [CrossRef]
41. Salamci, E.; Kordali, S.; Kotan, R.; Cakir, A.; Kaya, Y. Chemical compositions, antimicrobial and herbicidal effects of essential oils isolated from Turkish *Tanacetum aucheranum* and *Tanacetum chiliophyllum* var. *chiliophyllum*. *Biochem. Syst. Ecol.* **2007**, *35*, 569–581. [CrossRef]
42. Zhu, X.; Han, C.; Gao, T.; Shao, H. Chemical composition, phytotoxic and antimicrobial activities of the essential oil of *Scutellaria strigillosa* Hemsley. *J. Essent. Oil Bear. Plants* **2016**, *19*, 664–670. [CrossRef]
43. Abd-ElGawad, A.M.; El Gendy, A.E.-N.G.; Assaeed, A.M.; Al-Rowaily, S.L.; Alharthi, A.S.; Mohamed, T.A.; Nassar, M.I.; Dewir, Y.H.; Elshamy, A.I. Phytotoxic effects of plant essential oils: A systematic review and structure-activity relationship based on chemometric analyses. *Plants* **2020**, *10*, 36. [CrossRef] [PubMed]
44. Han, C.; Shao, H.; Zhou, S.; Mei, Y.; Cheng, Z.; Huang, L.; Lv, G. Chemical composition and phytotoxicity of essential oil from invasive plant, *Ambrosia artemisiifolia* L. *Ecotoxicol. Environ. Saf.* **2021**, *211*, 111879. [CrossRef] [PubMed]
45. Sarić-Krsmanović, M.; Umiljendić, J.G.; Radivojević, L.; Rajković, M.; Šantrić, L.; Đurović-Pejčev, R.J.C. Chemical composition of *Ambrosia trifida* essential oil and phytotoxic effect on other plants. *Chem. Biodivers.* **2020**, *17*, e1900508. [CrossRef] [PubMed]
46. El-Shora, H.M.; El-Gawad, A.M.A.J.P. Response of *Cicer arietinum* to allelopathic effect of *Portulaca oleracea* root extract. *Phyton Ann. Rei Bot.* **2015**, *55*, 215–232.

47. El-Shora, H.M.; Abd El-Gawad, A.M. Physiological and biochemical responses of *Cucurbita pepo* L. mediated by *Portulaca oleracea* L. allelopathy. *Fresenius Environ. Bull. J.* **2015**, *24*, 386–393.
48. Verdeguer, M.; Sánchez-Moreiras, A.M.; Araniti, F. Phytotoxic effects and mechanism of action of essential oils and terpenoids. *Plants* **2020**, *9*, 1571. [CrossRef]