

Ailanthus altissima as a Source of Natural Pesticides

Subjects: Biodiversity Conservation

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The extensive use of pesticides may negatively affect human health. Additionally, it is one of the main reasons for the decline of pollinators and is thus a hazard for most crops and biodiversity as a whole. Good candidates for the replacement of pesticides with ones less toxic to humans and pollinators are natural products (bioactive compounds extracted from plants), even though it should be kept in mind that some of them can be toxic too. *Ailanthus altissima* (Mill.), swingle, known also as tree of heaven, (Simaroubaceae) is one of the most aggressive alien invasive plants. It demonstrates a high tolerance to various habitat conditions and a potent propagation ability. This plant has a prominent ability to suppress the seed development of local vegetation.

Keywords: biopesticides ; essential oils ; quassinoids ; invasive plants' management

1. Ethnobotanical Data about *Ailanthus altissima* (Mill.) Swingle

Ethnobotanical information is usually focused on the medicinal properties of plants. Therefore, information regarding the pesticide potentials of plants is valuable but scarce. For invasive plant species, ethnobotanical records are collected in their native ranges of distribution. The local human populations in these regions have established traditions in the application of such plants. The bark of *Ailanthus altissima* (臭椿 chou chun) was initially recorded in Xin Xiu Ben Cao, a renowned traditional Chinese medicine monograph ^[1]. The information within this book relates that besides the many others therapeutic effects of *A. altissima*, the bark of the plant was used as an insecticide ^[1]. *A. altissima* plant materials were often used in ancient China against insect predators of stored grains ^[2]. The traditional use of *A. altissima* in Chinese medicine represents the starting point for scientific research seeking evidence of such pharmacological activities, and in this particular case, its potential pesticidal effects.

2. Chemical Constituents of *Ailanthus altissima* and Extraction Methods

A. altissima contains various secondary metabolites such as alkaloids, terpenoids, flavonoids, essential oil, etc., with a wide range of pharmacological effects such as anti-cancer, anti-inflammatory, anti-protozoal, etc. ^{[1][3][4][5][6][7][8][9][10][11][12][13][14][15]}. For instance, extracts of *A. altissima* stems containing ailanthone possess antiplasmodial activity against *Plasmodium falciparum* P. berghei ^{[16][17]}. An interesting new discovery is the antifungal effect of the alkaloid canthin-6-one isolated from *A. altissima* against *Fusarium oxysporum* f. sp. *cucumerinum* ^[18].

Here the researchers focus on the quassinoids and essential oils as potential biopesticides since there is an indication that these groups of compounds have such effects ^{[19][20][21][22][23][24][25][26][27][28]}.

3. Essential Oil of *Ailanthus altissima*: Composition and Extraction Overview

The qualitative and quantitative compositions of *A. altissima* essential oil vary considerably. This variability depends on the plant populations/ecological factors, the extractable parts, the ontogenesis stage, and the drying process. The main components are α -curcumene, α -gurjunene, γ -cadinene, α -humulene, β -caryophyllene, caryophyllene oxide, germacrene D, etc. ^{[5][29][30][31]}.

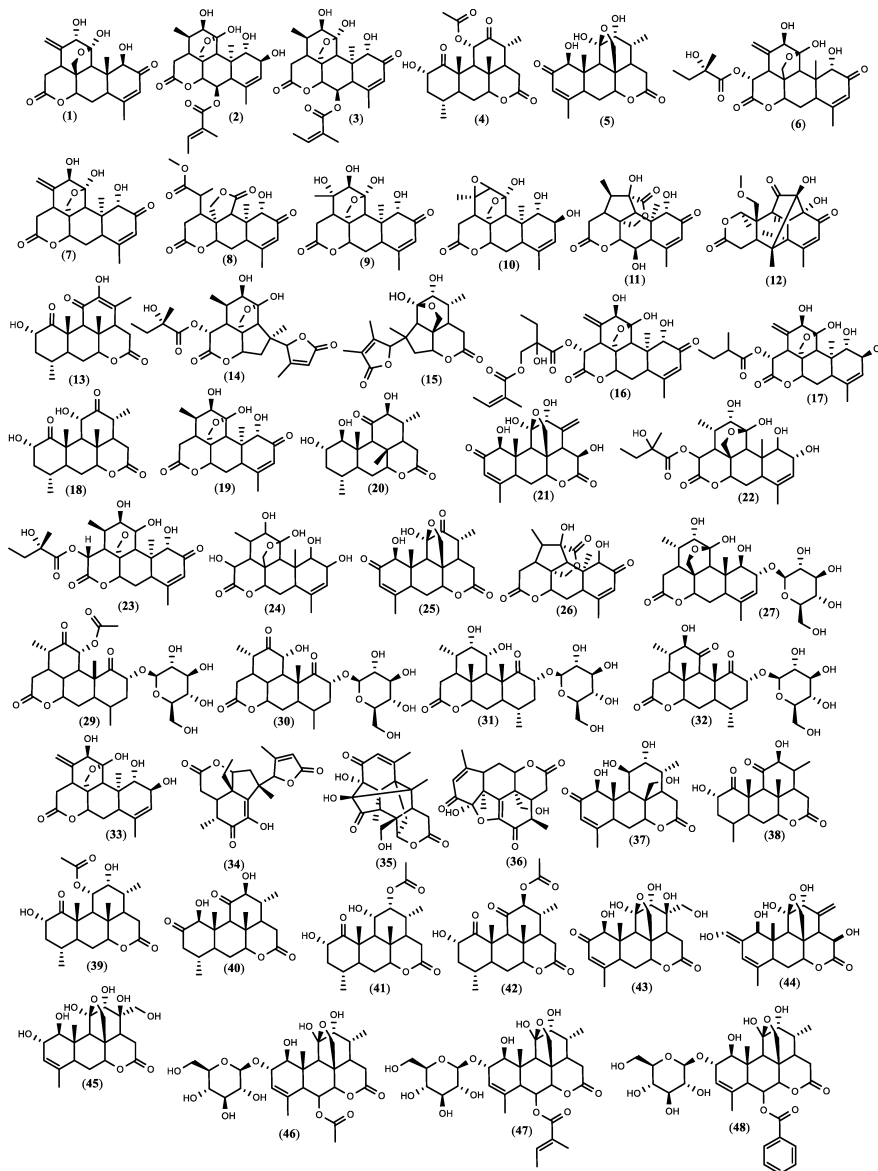
The extraction methods are summarized here. The collection of the materials for *A. altissima* essential oil extraction may take place in the summer in Tunisia ^{[29][30]} or in September in Croatia ^[5]. The extraction of essential oil is a technological challenge as the researchers' own experience revealed (unpublished data). Basically, the essential oil of different plant parts (roots, stems, leaves/young and old plants, flowers, and ripe fruits, all cut into small pieces) is extracted by hydrodistillation for 3–4 h using a Clevenger-type apparatus ^{[5][30]} or a simple laboratory Quick-fit apparatus ^[29]. The identification of the components is performed by GC-FID and GC/MS analyses.

Additionally, the essential oil of *A. altissima* bark was extracted by the Soxhlet method with anhydrous diethyl ether until the distilled liquid became colorless. The solvent was evaporated under a vacuum in a rotary evaporator and the fumigant activity was tested against four major stored grain insects [32].

4. Quassinoids Extraction, Fractionation, and Isolation Overview

Quassinoids are all-chair cyclic and highly oxygenated derivatives of squalene. Biogenetically, they can be regarded as the degraded triterpenoids, which are isolated exclusively as bitter principles from plants of the Simaroubaceae family [33].

A. altissima is rich in quassinoids (**Figure 1**) and the process of the identification of new quassinoids is still progressing [12]. The concentration of ailanthone, one of the main quassinoids, may range from 6.44 $\mu\text{g/mL}$ to 825 $\mu\text{g/mL}$, depending on the source locality in China [34].



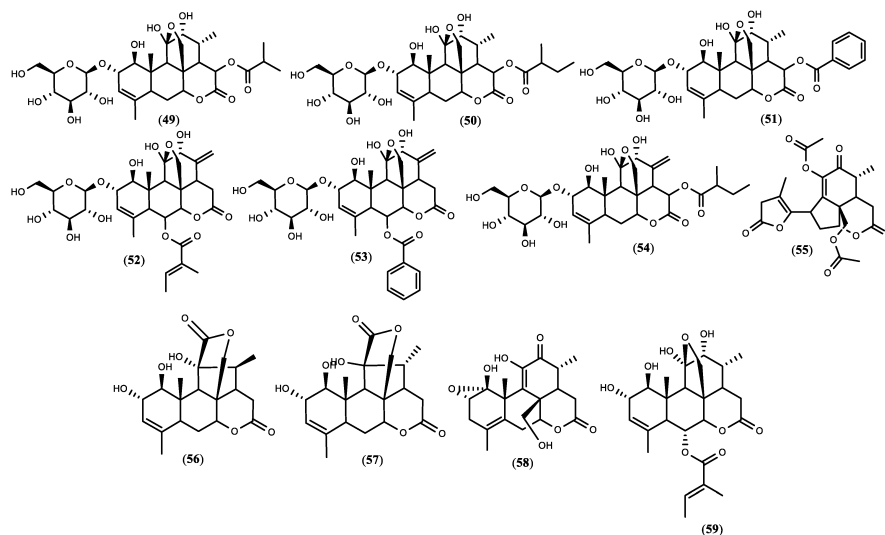


Figure 1. The structure of

quassinoids isolated from *A. altissima*.

5. Biopesticide Potential of *Ailanthus altissima* and Tests' Design

5.1. Phytotoxicity Assay of *Ailanthus altissima*

Essential Oil Phytotoxicity

The essential oils of *A. altissima* negatively affect the seed germination and early-stage development of the seedlings of the target species. The effect is dose-dependent and is greater in the light than in the dark. In addition, the phytotoxic effect depends on the origin of the essential oil, as the oil extracted from flowers is the most phytotoxic [29][30]. The caryophyllene oxide, b-caryophyllene, germacrene D, and hexahydrofarnesyl acetone presented in the essential oil may be responsible for such a phytotoxic effect [30][35][36]. Additionally, the complete inhibition of the germination of target plants is achieved after the application of 400 to 600 µg/mL hydrodistilled leaf residues [29].

Phytotoxicity of Polar *Ailanthus altissima* Extracts

The juglone index [37] of *A. altissima* has been assessed as very high (0.80–1.40 depending on the extract concentration [38][39][40]. The plant produces allelopathic substances that inhibit the seed germination and seedling growth of competing species. They are located mostly in the bark and the roots, but also occur in the leaves, seeds, and wood. The inhibitor(s) can readily be extracted from *A. altissima* with methanol, but not dichloromethane, indicating the plant's polar characteristics. The experimental tests show “striking” postemergence effects, with a nearly complete mortality of all the receiver plant species [41].

The compounds of the methanolic extracts from *A. altissima*'s fresh leaves and some sub-fractions have strong inhibitory effects on plant growth. Some fractions show a regulatory effect on plant by inhibiting the growth of radicles at higher concentrations and enhancing their growth at lower concentrations [42]. The compounds of the aqueous extracts from *A. altissima*'s fresh leaves and bark negatively influence the growth of the treated seedlings of *Sinapis alba* L. and *Brassica napus* L. regardless of the dilution [43]. The aqueous extracts of *A. altissima* leaves have a concentration-dependent herbicidal effect on *Medicago sativa* L. seed germination [44].

Ailanthone is highly phytotoxic, with concentrations of 0.7 mL/L causing 50% inhibition of radicle elongation in a standardized bioassay with garden cress (*Lepidium sativum* L.) seeds [45]. The quassinoids (from the root bark of *A. altissima*), e.g., ailanthone, ailanthinone, and ailanthinol; the alkaloids such as 1-methoxycanthin-6-one; and the phenolic constituents of the leaves are potent phytotoxins [29][46][47][48][49][50][51]. A significant pre-emergence herbicide activity is found for most of the bark dichloromethane extracts, which is directly correlated with the ailanthone concentration. A remarkable combined pre- and post-emergence herbicidal activity was found for a specific fraction. These results indicate that the bark of *A. altissima* is a potential source for the production of natural herbicides for use in agriculture [52]. Methanol bark extract with the main component ailanthone was tested for herbicidal effects under field conditions. The results show that it was quite efficient against the weeds but also caused serious injuries to the crops. Thus, a weakness of ailanthone is its non-selectivity, but a positive feature lies in its ephemeral effects. Ailanthone is easily degradable by soil microorganisms [44][53]. It is necessary to note, however, that ailanthone is an acute toxic triterpene and should be used with caution [54].

5.2. Antifungal Activity

The antifungal activity test results are contradictory and depend on the extraction methods and reagents. The methanol and ethanol *A. altissima* leaves' extracts have fungicidal activity only against *Cladosporium cladosporioides* of all the tested nine species belonging to *Fusarium*, *Penicillium*, *Aspergillus*, and *Giberella*—the toxic microfungi found in cereals used for livestock and human food. However, this activity is weaker compared to the *Juglans regia* leaves' extracts [55]. Ethanol, methanol, and aqueous extracts of *A. altissima* were tested against *Ceratocystis manginecans* (the causal agent of Mango Sudden Death) using a poisoned food technique and the treatments result in thin, collapsed/damaged hyphae compared to the control. Phytochemical profiling of the most effective extracts revealed that 9-octadecanoic acid and l-(+)-ascorbic acid 2, 6-hexadecanoate possibly contribute to the antifungal effect [56]. Both acetone and methanol from the leaves' extracts have activity against *Candida albicans*, which is higher than amphotericin B, a gold standard in antifungal therapy [9]. Although *C. albicans* is not a crop pathogen, the result shows that further antifungal activity is worth testing. The chloroform extract of *Ailanthus excelsa* stem bark shows fungistatic and fungicidal activity against *Aspergillus niger*, *A. fumigatus*, *Penicillium frequentence*, *P. notatum*, and *Botrytis cinerea* [57]. It is the quassinoids that have been found to have inhibitory activities against plant fungal pathogens [58].

5.3. Fumigant and Insect Repellent Activity

Essential Oil Fumigant and Insect Repellent Activity

The essential oil of *A. altissima* bark has a fumigant activity against some pest beetles. One possible application of *A. altissima* bark essential oil is for killing insects that damage stored foods or seeds, as it causes 99.3 and 81.9% mortality to *Oryzaephilus surinamensis* (Linnaeus) (Coleoptera: Silvanidae) and *Sitophilus oryzae* (Linnaeus) (Coleoptera: Curculionidae) with within 24 h, respectively [2][59][60]. In addition, Lü and his co-workers revealed that despite its weak fumigant activity against *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae) and *Liposcelis paeta* Pearman (Psocoptera: Liposcelididae) adults, it notably repels *T. castaneum* adults and *L. paeta* nymphaea [2][59][60]. Additionally, *A. altissima* bark oil possesses high fumigant activity against *Lasioderma serricorne* (Fabricius 1792) (Coleoptera: Anobiidae) adults with a mortality of 100% at 8 µL/L air within 48 h of exposure; thus, it is obviously a strong repellent of these pests [61]. (Z)-3-hexen-1-ol, which is one of the main components of the essential oil extracted from *A. altissima* stems [29], is known as a key herbivore-induced plant volatile. There is no doubting its role as an indirect defense and this compound is a good candidate for novel insect pest control strategies [62]. Additionally, caryophyllene and caryophyllene oxide, which are the main constituents of the essential oil of *A. altissima* leaves and samara [29], are attractive to green lacewings [63]. Green lacewing larvae are predators of many soft-bodied insect pests such as: aphids, thrips, whiteflies, leafhoppers, spider mites (especially red mites), and mealybugs, and consequently they participate in biological control [64]. Caryophyllene and caryophyllene oxide stimulate oviposition in green lacewings, which leads to increased larval predation against pest insects [63]. *A. altissima* contains compounds with strong acaricidal activity against the parasitic mites that cause skin disease, namely, *Psoroptes cuniculi* and *Sarcoptes scabiei* var. *cuniculi* [65]. It was also found to have activity towards nematodes of the *Meloidogyne* genus [66].

Polar Extracts' Fumigant and Insect-Repellent Activity

The methanol extracts of *A. altissima* fresh leaves are practically non-toxic to the mosquito *Aedes aegypti* larvae [42] and the leaves are even used for feeding silkworms [67]. However, the methanolic extract of *A. altissima* leaves causes the malformation and mortality of the larvae of the moth *Agrotis ipsilon*, (Lepidoptera: Noctuidae), which are known to cause considerable damage to crops by severing young plants at the ground level. Aqueous extracts of *A. altissima* leaves have oviposition-deterrence effects against *Spodoptera frugiperda* (Smith) (Noctuidae), causing delays in the time to pupation and emergence in addition to reduced larval and pupal biomasses [68][69]. This moth is considered a noxious pest because the larvae cause massive damage to various crops; consequently, insecticide sprays are employed against it [70]. In addition, 0.5, 1, and 2% ethanol (70%) extracts of *A. altissima* bark and leaves have strong antifeeding activity against and significant insecticidal effects on gypsy moth (*Lymantria dispar* (L.)) larvae—insects known as voracious defoliating pests of deciduous trees.

The diethyl ether extract of *A. altissima* possesses an extremely strong repellent effect and to a certain extent a contact-killing effect on *Oryzaephilus surinamensis* (Linnaeus), the saw-toothed grain beetle [71]. The ethanol extract of *A. altissima* leaves possess strong acaricidal activity (97.4%) against the spider mite, *Tetranychus urticae* (Koch), a plant-feeding mite generally considered to be a pest [72]. The extract has no direct toxic effect on the pest but reduces its fertility about threefold and suppresses the development of larvae from eggs. The maximum efficiency of the extract was observed after 7–10 days when a filial generation of the spider mites started developing [73].

Quassinoids extracted both from leaves and roots have insecticidal, antifeedant, and insect-growth-regulatory activity, and aianthone, in particular, was found to be efficient against the aphid *Acyrtosiphon pisum* [46]. There is a high mortality rate of aphids, pests of peas, when treated with aianthone [74]. Methanol extracts or active substances such as aianthone, chaparinone, glaucarubinone, and 13 (18)-dehydroglaucarubinone obtained from *A. altissima* leaves can be recommended for the development of new botanical insecticides targeted against the phytophagous larvae of *Spodoptera littoralis*, a moth referred to as the African cotton leafworm [75]. At the same time, quassinoids seems to be nontoxic for bees as they are found in propolis [46][53][76][77][78][79]. In addition, *A. altissima* bark-based hexane and methanol extracts do not possess any genotoxic, mutagenic, or carcinogenic effects on *Saccharomyces cerevisiae*, which was used as a test object to evaluate the potential harm to human health [80].

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