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Research article

Chemical composition, Insecticidal and antifungal activities of *Pinus halepensis mill.* and *Acacia cyanophylla sp.* wood tars

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A R T I C L E I N F O

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A B S T R A C T

Pyrolysis of plant through the rotative oven is a promising and more eco-friendly way to produce charcoal, tar and pyroligneous acid, and other gaseous products with useful purposes. In this research using the Tar of 2 of the most common species in Tunisia *Pinus halepensis* and *Acacia cyanophylla* we tried to prove their Insecticidal and fungal activities. For that we started by assessing the Tars' secondary metabolites. Both tars presented important rates but *P. halepensis* tar presented higher levels of secondary metabolites especially flavonoids with 1.92 mg/ml QE comparing to 1.47 mg/ml QE for *A. cyanophylla* tar. The antioxidant activity and antioxidant capacity of the 2 tars revealed more pronounced antioxidant activity of *P. halepensis* tar with 89.5% (%DPPH) and 2.91 mg/ml AAE compared to 75.70% (%DPPH) and 2.72 mg/ml AAE for *A. cyanophylla* tar. The insecticidal activity against *Aphis spiraecola* showed faster and stronger efficiency of *A. cyanophylla* tar extract 25% inducing 73.3% mortality within 2 Hours of exposure and reached 100% mortality after 10H. *P. halepensis* tar extract 75% showed slower response with 73.3% mortality after 6H of exposure. The results of the antifungal activity of *P. halepensis* tar extract 10% and *A. cyanophylla* tar extract 0.75% revealed that *P. halepensis* tar was more inhibiting of the mycelium growth of many fungi including F.solani, F.nyagami and M.nivale with an inhibition rate of 77% but less effective on other like F.rodelens that reached 77% mycelium growth. On the other hand, *cyanophylla* tar extract 0.75% was less effective with only 30% inhibition rate of Phoma sp. the other fungi had more than 79% mycelium growth.

1. Introduction

Forests and trees have a paramount role, not only from an ecological standpoint, as they help preserve biodiversity and limit the desertification, but also economically, as they are a vital source of income, livehood and well-being for the rural populations. In the timeframe between 2010 and 2020, the world and especially Africa had the highest annual rate of forest loss with 3.9 million hectares caused by various reasons like fires and acts of vandalism [1] In fact, both commercials and rural population use many forest-extracted

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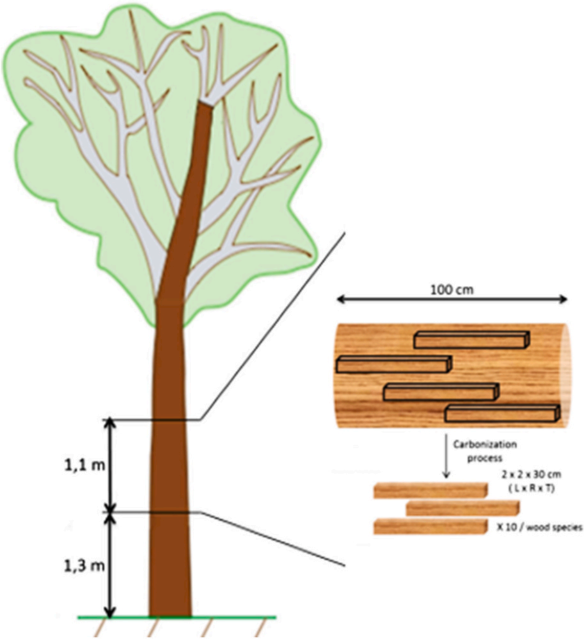

Fig. 1. Illustration of the method used to distribute wood samples.

goods, including Timber and Non- Timber Forest product in addition to the main product: wood [2].

However, forests overexploitation through tree cutting for industrial and energy purposes, resulted in an environmental offset. [3] Thus, the human activities that includes incomplete lignocellulosic biomass combustions, carbonization, and forest fires caused nitrogen oxide, carbon monoxide, and other noxious gases emitting into the atmosphere, contributing to climate warning. Nevertheless, between the year of 1997 and 2010, the demand for coal increased significantly from 148,000 tons to 201,000 tons, an increase of 53, 000 tons in 13 years. Consequently, an additional consumption of primary wood that reached 265,000 tons [4].

The anaerobic thermal decomposition reactions of wood, generates solid fuels like coal and liquid ones in form of pyroligneous acids also known as Tar, in addition to some other valuable products. The pyroligneous acids also Known as Wood Vinegar, are brown liquids produced by the distillation of wood in absence of air. When the gas generated by the combustion is cooled, it condenses into liquid. Tar is defined as a complex mixture of condensable hydrocarbons, which may be composed of 1–5 aromatic ring compounds along with other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PHA); its composition strongly depends on the reaction conditions as a consequence of the complex reactions that take occur during the pyrolysis and gasification processes [5]. Also, tars are a complex mixture of secondary metabolites and comes mainly from the lignin decaying [6]. Due to their richness in phenolic compounds they were being used as pesticides, in medicine as antiseptics, as an anti-inflammatory and for their wood preservation properties [7] Therefore, Wood tar, with its chemical composition, has the potential to be a chemical wood preservative. It has long been known that wood pyrolysis products, such as tar, can be used to protect wood. The literature also describes the product's long history of use and its positive results. Because of its toxic fungal and insecticidal properties, it is being developed as a new environmentally friendly wood preservative as a natural product.[8] [9]Wood vinegars derived from a variety of wood sources are recognized as safe natural inhibitors with a wide range of applications, including antifungal, termiticidal, and insect repellent properties [10].

Nevertheless, traditional technique performed to obtain charcoal and other carbonization products generates significant atmospheric pollution in addition to poor conversion efficiency. The consequence is dramatic on both the environment and the wood resources. [11]Thus, the need to develop new eco-friendly biomass thermochemical conversion pilots [12]. Considerable improvements have been made through the years to create new technologies and equipment for clean charcoal and its deriving production.

Tunisia has an estimated 8% of the country's surface for forests, shrubs and wooded lands. The forests species are numerous but are mainly composed of Aleppo pine (Pinus halepensis) with over 361.221 ha, Acacias (37.963ha) along with other coniferous and deciduous species [13] These species are most commonly used is many aspects including fuel and fencing.

The main aim of this study is to valorize wood tar from Aleppo pine (*Pinus halepensis)* and *Acacia cyanophylla*.and that by (i) assessing and comparing their secondary metabolites contents then (ii) testing their biological activity; First, the tar's insecticide activity on *Aphis spiraecola patch, also* known as spirea aphid, of the Aphididae family, a polyphagous species with a worldwide distribution and a pest for over 20 botanical families including citrus, apples and ornamentals in addition to transmitting a number of plant viruses [14]. The damage includes curled leaves, honeydew of shoots and fruits. It is likely for this pest to infest at least 50% of the shoots on a mature tree [15]. Many studies have demonstrated that Aphis spiraecola have the least susceptibility to several insecticides among other Aphis [16]. This can be the result of many factors including the inherent ability to detoxify potential poisonous

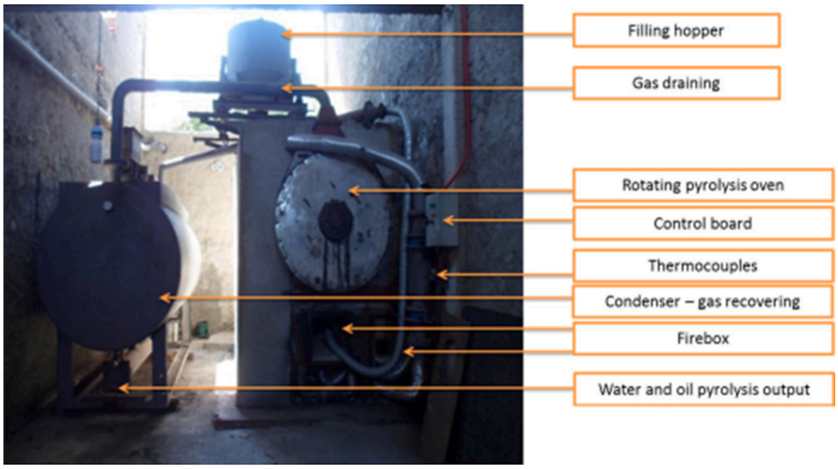

Fig. 2. Rotatable pyrolysis system used to carbonize different Tunisian wood species.

substances they encounter in the environment [17].

Second, Tar's antifungal activity against various phytopathogenic fungi that have been a devastating threat to agriculture, 70%–80% are caused by pathogenic fungi with adverse effects on crop growth and yield [18]. In the past two decades, the severity of disease outbreaks caused by virulent fungal plant pathogens has been steadily rising, as has been the incidence of new emergent diseases [19] In this study we tested 10 strains; 6 are from Fusarium genus (F.verticillioides, F. oxysporum, F. poae, F. ygamai, F. solani, F. redolens). These are very strong pathogens capable of causing devastating losses. Plants systemically infected with Fusarium pathogens cannot be cured and must be destroyed as soon as possible [20]. In addition to them we studied the response of Bipolaris sorokiniana, Phoma sp, Microdochium nivale and Stemphylium.

2. Materials and methods

2.1. Wood sampling process

Relating to the method developed by Oger and Leclercq [21], one tree without defects (knots, biotic and abiotic alterations, …), with a perfect rectitude and which represented at best the global quality of the tree species involved was selected for each studied wood species. At 1.30 m of the ground one log of 1.10 m long is cuted from each selected tree. Then divided into parts where the 1 m log will be used for the carbonization process (Fig. 1)

2.2. Carbonization process

Carbonization was carried out in a single batch, on all wood samples. The process used a rotatable pyrolysis oven system heating by combustion gas. The pyrolysis process was carried out in a horizontal stainless-steel reactor where the bottom part of the reactor (firebox) was loaded with a small wood quantity to heat the oven. The upper compartment (rotator pyrolysis room) was loaded with the feedstock to be treated (Fig. 2).

Each wood sample was bundled according to their wood species initially and placed in the oven. The reactor was tightly sealed in order to avoid the entrance of air into the feedstock compartment and its temperature was slowly increased by 10C/min from ambient to 200C. After 4 h of drying at 200C, temperature oven was increased by 10C/min from 200 to 550C to perform the carbonization step, and the temperature was maintained for 6 h. The heating system was then stopped and wood samples were allowed to cool down to room temperature under an inert atmosphere composed of combustion gas. A thermocouple was used to measure the temperature and the heating rate of the feedstock. The carbonization system was equipped with a gases output, condensation system, and liquids collection that were used in the carbonization processed [22].

2.3. Determination of total phenolic contents

The total phenolic content of *P. halepensis* end *A. cyanophylla* wood tar extracts were determined by Folin-ciocalteau method described by Singleton and Rossi [23] The extracts were diluted in Dimethylsulfoxide DMSO; a polar aprotic organic solvent with strong affinity to both polar and non-polar compounds. 100 μl of that extract was used. The reaction needed 2 ml of Na_2CO_3 and 150 μl of Folin ciocalteau (50%). After 30 min incubation the absorbance of each solution was determined at 760 nm using a UV-VIS spectrophotometer. To ensure accurate results of each tar extract 3 replicates were prepared and evaluated. Gallic acid with known concentration (10–500 μg/ml) was used for the preparation of standard calibration curve. The results were expressed as μg Gallic acid equivalent (μg GAE/ml of extract)

Table 1
Selected fungi for the antifungal activity.

Phytopathogenic fungi	Impact and Effected Plants
Fusarium verticillioides	Pathogen of Corn; Leaf spot and stem rot [30]
Fusarium oxysporum	Vascular wilts of palms, banana and tomato, root and stem rots, crown rot of tomatoes, cucumber, sweet potato, asparagus … [20]
Fusarium poae	Central bud rot of carnations, attack cereals … [20]
Fusarium nygamai	Fungus of seeds
Fusarium solani	Root and shoot rot of legumes and other crops, crown disease of oil palm … [20]
Fusarium redolens	yellowing and wilt of chickpea [31]
Bipolaris sorokiniana	Roots and shoot rot, leaf black spots of wheat and oats [32]
Phoma sp	Roots and shoot rot, leaf black spots of red beet [33]
Microdochium nivale	Pink snow mold disease of wheat, rye, barley, oats, turf and forage grasses [34]
Stemphylium	Black fungus of Oat and wheat, black dots and rot of the wheat ears [35]

2.4. Determination of flavonoids contents

Using the method of Aluminum trichloride $AlCl_3$ and after adding 75 µl of $NaNO_2$ (5%), 150 µl of $AlCl_3$ (10%) and 500 µl of NaOH to the diluted tar extracts, the solution absorbance is determined at 510 nm. The standard calibration curve is prepared through different concentration of Quercetin. The results are generally stated as milligram Quercetin Equivalent (mg EQ/g of extract) [24]The sampling process used 3 replicates of each extract to be tested for more accurate results.

2.5. Determination of condensed tannins contents

Resorting to the Vanillin method, described by Hagerman AE [25] and after mixing the extracts with 1.5 ml of HCl and 3 ml of Vanillin (2%) the final solution absorbance is rated at 500 nm. As for the standard calibration curve is prepared with different Catechin solutions with known concentration and the results are expressed as mg Catechin Equivalent.

2.6. Antioxidant activities

2.6.1. DPPH free radical scavenging

This assay was used in order to evaluate the antioxidant capacity of various extracts and plant materials including wood tar. The following method war reported by Katalinic et al. [26] In fact, the reaction of the mixture of 1.5 ml DPPH in ethanol (0.004%) and 15 µL the extract takes place in the dark at room temperature then the absorbance was measured at 517 nm. In addition to the tars extracts samples, 3 control samples were prepared using the same volume of ethanol instead of the extrats. A successful scavenging of the radical changes the purple color of the mixture to yellow with a consequent decrease in the absorbance. The free radical-scavenging activity is expressed as percentage inhibition of DPPH and calculated according to the formula:

$$\%\mathrm{DPPH} = \frac{(Abs\ controle - Abs\ sapmle)}{Abs\ controle} \times 100$$

2.6.2. Total antioxidant capacity TAC

According to the technique given by Prieto et al. [19], this activity tests the propensity of plant extracts and fractions to diminish molybdate ions. The antioxidant capacity is measured spectrophotometrically through phoshpomolybdenum method, based on the formation of a bluish green phosphate/Mo (V) compounds at 695 nm absorption. This procedure needs the add of H_2SO_4, the sodium phosphate and the ammonium molybdate to the tested sample. The mixture is incubated et 95 °C for 90 min. Once cooled to the room temperature, the absorbance is measured. Ascorbic acid with different concentration (0.3–2.4 mg/ml) was used as standard and the total antioxidant capacity is stated as Equivalent of Ascorbic acid [27].

2.7. Insecticidal activity

Tested insects: *Aphis spiraecola,* from a field located in Cap Bon, Tunisia.

Plant material: *Cestreau Nocturne* leaves collected and maintained at 4 °C before using them.

Extract preparation: *P. halepensis* and *A. cyanophylla* tar extracts were diluted using DMSO to obtain 3 doses to be tested against *Aphis spiraecola:* 25%, 50% and 75%

Bioassay and toxicity: both *P. halepensis* Tar and Acacia Tar extracts on *Aphis spearicola,* were assayed using impregnated paper essay. The 2 types of Tar were diluted using DMSO and applied to whatman No.1 filter paper and the leaf of *Cestreau Nocturne* placed in Petri dishes along with 10 adult *Aphis spearicola* insects. The toxicity levels to the 2 tars were evaluated through the insects' percentage of mortality within 10 Hours after exposure and comparing it to the control sample containing DMSO.

2.8. Antifungal activity

This activity was conducted against 10 phytopathogenic fungal strains (Table 1) on a PDA medium prepared out of potato infusion

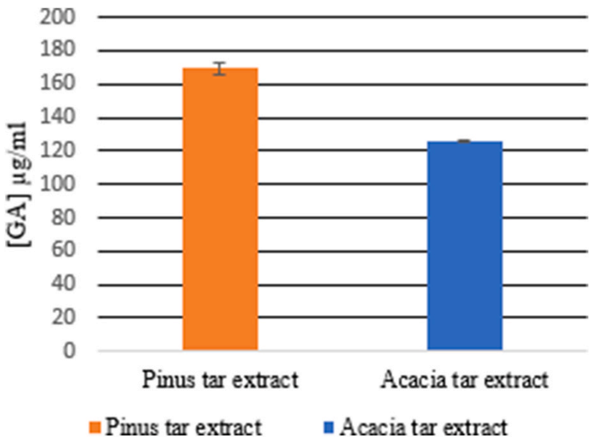

Fig. 3. Total phenols content of Acacia and Pinus tar extract.

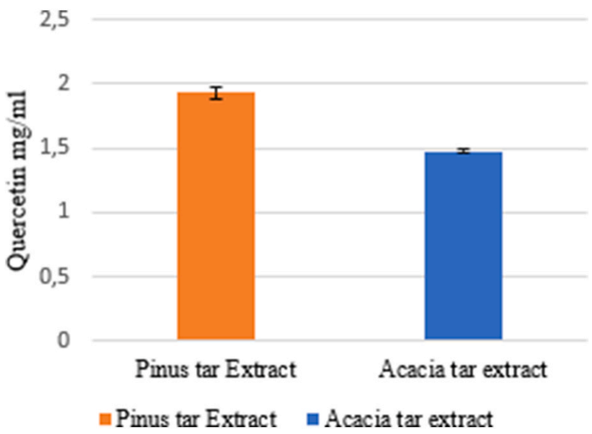

Fig. 4. Flavonoid content of Acacia and Pinus tar extract.

and Potato Dextrose Agar. The antifungal activity was determined through the Poisoned food method described by M.S. Ali-Shtayeh and S.I. Abu Ghdeib [28] and Mounyr Balouiri et al. [29] which is the most used technique.

The extracts were diluted in DMSO; Acacia Tar extract to 0.75% and 10% for Pinus halepensis tar extract. The extracts were incorporated into the melted agar and mixed well. Then, the medium is poured into Petri dishes until it cools down. The fungal strains were prepared 7 days beforehand in an agar culture at 28 °C in an appropriate medium. The inoculation was done by a 5 mm mycelia disc deposited in the center of each Petri dish containing the extracts. After incubation in 25 °C temperature, the diameters of fungal growth in control and sample Petri dishes are measured each 2 days until the control sample dish is fully colonized by the tested fungus. The antifungal effect is estimated via mycelium growth percentage calculated using the following equation:

$$\text{Mycelium growth percentage} = \frac{\text{Mycelium growth with extract}}{\textit{Mycelium control sample maximum growth}} \times 100.$$

The collected data were analyses using SPSS ((Statistical Package for the Social Sciences) using different tests and POST HOC in order establish an understanding of the correlation between the tested parameters.

3. Results and discussion

3.1. Secondary metabolites

Phenolic compounds have the ability to reduce Folin ciocalteau reagent and the reaction is followed by measuring a change in color of the solution from intense yellow to blue spectrophotometrically. Quantitively, the phenols content is determined through the quantity of Gallic Acid. Our results showed that the highest content is in *P.alepensis* tar extract with 169 µg/ml GAE to 125 µg/ml GAE for *A.cyanoplylla* tar extract (Fig. 3)

Flavonoids are evaluated through quercetin, one of the most common flavonoids isolated from the bark of conifers. Which explains the elevated rate of Pinus tar extract quercetin levels with 1.9 mg/ml QE to 1.4 mg/ml for Acacia tar extract (Fig. 4)

For the tannins, this metabolite assassment showed almost similar contents for both Acacia and Pinus tar content with 0.2 mg/ml

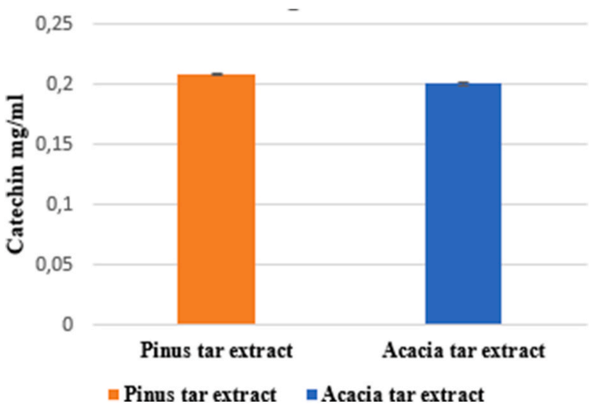

Fig. 5. Condensed Tannin content of Acacia and Pinus tar extract.

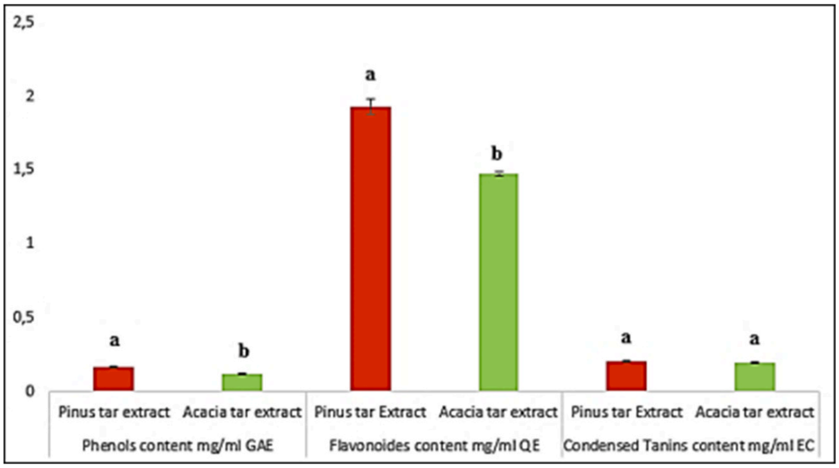

Fig. 6. Secondary metabolites content of both Acacia and Pinus tar extracts Results correspond to the mean estimated from extracts analyzed in triplicate. Different letters indicate a significant difference ($p < 0.05$) between different extracts using ANOVA and Duncan test.

EC (Fig. 5)

After quantifying the secondary metabolites rates for both species, the results in Fig. 6, revealed that the extract of pyroligneous acid from Aleppo pine is richer in phenolic compounds than that of acacia. This could be explained by the fact that coniferous trees are richer in phenolic compounds. The concentration of these metabolites in trees is not uniform; generally, higher amounts occur in bark, heartwood, roots, branch bases and wound tissues. These variations also occur among species, from tree to tree, and from season to Ref. [36]. A study by Deba et al. [37] mentioned that these metabolites levels are affected by their chemical nature, the solvent as well as the protocol used during their extraction. Also, the Phenolic compounds are distributed in different plant tissues and have a fundamental input in the efficiency of most bioactive molecules.

In similar research [38], stated that pyroligneous acid (PA) consist of more than 200 water-soluble chemical compounds with 80–90% water and 10–20% organic chemical compounds comprising organic acids, alkane, phenolic, alcohol and ester. These components endow woods with their many colors and hues, and scents [39].

3.2. Antioxidant activities

In the present investigation antioxidant activities of different tar extracts of the 2 species *Pinus halepensis* and *Acacia cyanophylla* were subjected to antioxidant screening against the DPPH radical and Total Antioxidant Capacity TAC (phosphomolybdenum), since these assays have been widely used to determine the free radical-scavenging activity of various pure compounds or extracts. The ability of different extracts to reduce free radicals was measured by using UV-VIS spectrophotometry [40].

The inhibition percentage calculated for Pinus and Acacia tar revealed high levels exceeding 70% and the highest percentage was for Pinus's tar with 89.57%–75.70% for Acacia tar (Fig. 7). This proves that Tars of pyroligneous acid have high inhibition capacity of the DPPH radical. A.Y. Loo et al. [41], stated similar values in his work on PA of mangrove plant (Rhizophora apiculate) with a high % DPPH of 80%.

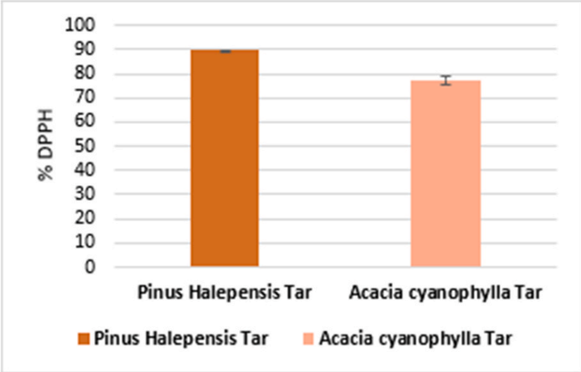

Fig. 7. DPPH free radical percentage of the Pinus and Acacia Tar extracts.

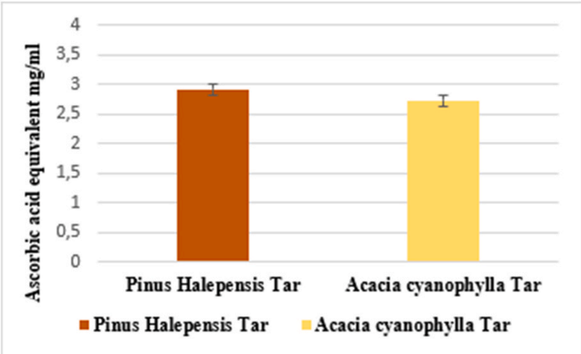

Fig. 8. Total antioxidant capacity of *P. halepensis* and *Acacia cyanophylla* Tar extracts.

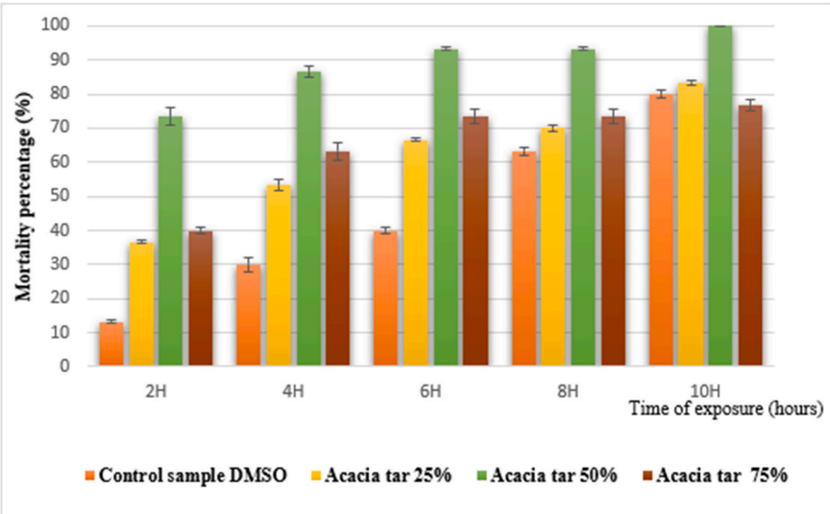

Fig. 9. Effect of the different doses of Acacia tar extract on Aphis spiraecola.

The phosphomolybdate method is quantitative; therefore, the total antioxidant capacity (TAC) is stated as ascorbic acid equivalent. This method is based on the redox antioxidant reaction in order to assess the reduced concentration of Phosphate-Mo. A higher degree of color creation designates the more reducing power of analyte, it gives a direct estimation of reducing the capacity of antioxidant [42].[43]

After using Ascorbic acid as a standard to determine the TAC we were able to find that Pinus halepensis tar has higher quantities of

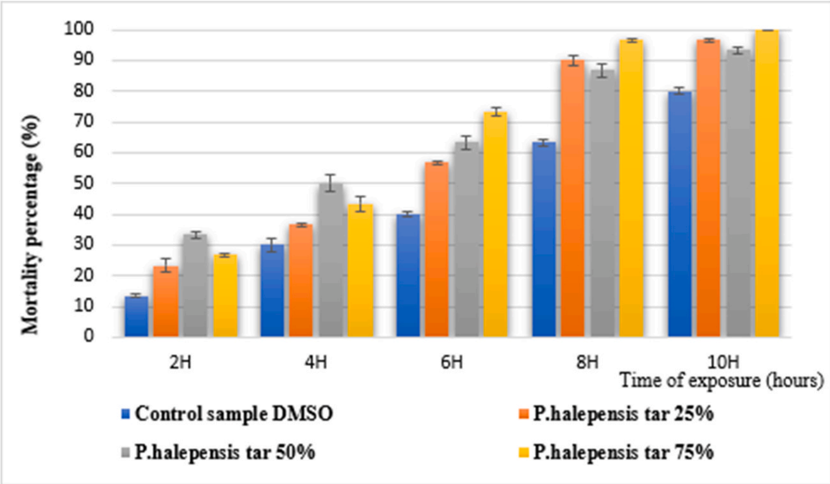

Fig. 10. Effect of the different doses of P. halepensis tar extract on Aphis spiraecola.

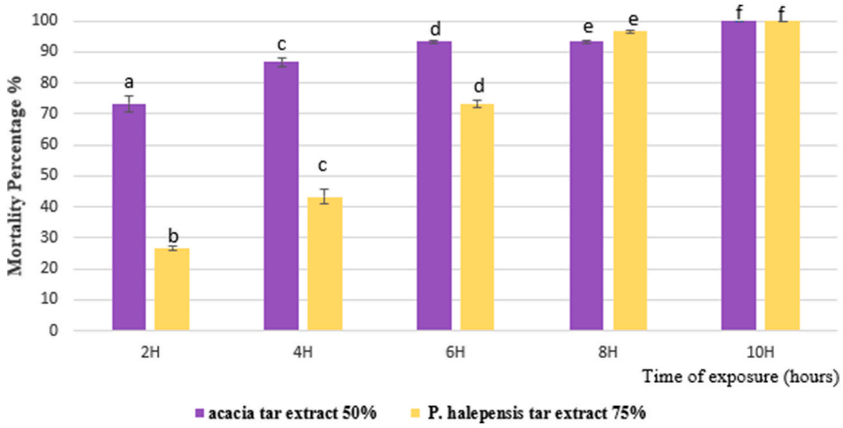

Fig. 11. Influence of the Acacia and Pinus most efficient Tar extract dose against Aphis spiraecola Results correspond to the mean estimated from extracts analyzed in triplicate. Different letters indicate a significant difference ($p < 0.05$) between different extracts using ANOVA.

Ascorbic acid with 2.91 mg/ml to 2.72 mg/ml for Acacia extract (Fig. 8). the same study by Loo et al. [41], confirmed that an increase in the standard (Ascorbic acid) indicates elevated antioxidant activity.

Accordingly, in a work of Chunhui et al., 2013 on pyroligneous acid (PA) from *Rosmarinus officinalis* leaves suggested that many flavonoid and related polyphenols contribute expressively to the phosphomolybdate scavenging activity. [44]These results, alongside with the work reported by some research teams on walnut shell [45][46] and hickory shell [47] indicate that PA has the potential to be a source of natural antioxidants, and can be used as a source of food antioxidants in addition to other uses in different domains.

3.3. Insecticidal activity

This test was conducted on adult Aphis spiraecola insects, on which we applied different doses of both Tars. The difference in Aphis spiraecola mortality were detected among doses across observation times.

The use of doses from 25% to 75% of Acacia tar, and when comparing it to the control, showed a high efficiency of the 50% dose with mortality percentage of 73% within 2 Hours and reaching 100% after 10H. A higher dose of 75% exhibited less mortality with 76% after 10H of exposure to the tar extract (Fig. 9).

These results have proven that Acacia tar have an effect on Aphis spiraecola viability, with 50% doses to be the optimal dose used.

For Pinus tar the same doses were used 25%, 50% and 75%. After 10H of exposure, we were able to observe a high effect of the highest dose of 75% that reached 100% mortality after 10H of exposure (Fig. 10) this showed that 75% dose of Pinus halepensis tar is the optimal dose used.

After optimizing the best dose to use for each tar, we tried to compare the effectiveness of the 2 species types of tars (Fig. 11). The results revealed a long-term effect on insects for both tars with 100% mortality after 10H, never the less Acacia 50% tar extract showed

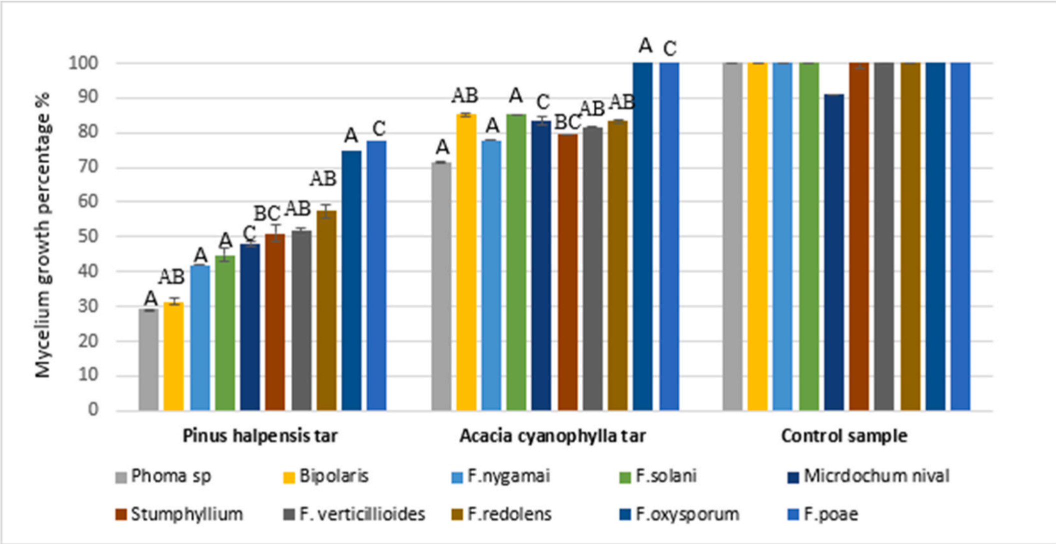

Fig. 12. Effect of Pinus and Acacia Tar extracts on the Mycelium growth percentage of the 10 tested fungi Results correspond to the mean estimated from extracts analyzed in triplicate. Different letters indicate a significant difference ($p < 0.05$) between different extracts using DUNCAN post-hoc to verify groups homogeneity.

a quicker response on Aphis spiraecola, with 73% mortality to 26% after 2 h of exposure which was proved statistically by a significant difference between the 2 tars through their p-value ($p = 0.035 < 0.05$)

Although the significant difference of the level of impact of the 2 Tars but their outcome is the same; proving the efficiency of wood Tar (PA or wood vinegar) against insects. In fact, there have been numerous studies using the combusted wood products. A study by Pangnakorn et al. [48] used the wood vinegar to test its toxicity on *Culex quinquefasciatus* (Diptera insect vector of several diseases including West Nile fever) with 2 application methods one Topical (through contact) the other is a drops method (ingestion). The results revealed that the ingested poison is more effective than through contact only. thus, wood vinegar was a highly acive poison. Another research elaborated by Kim D.H. [24], where an insecticide-coupled wood tar was tested on 2 homopteran insects *Nilaparvata lugens* and *Laodelphax striatellus* showed that tar could improve the penetration of carbosulfate into leafhoppers as it contains a large amount of acetic acid that may influence the permeability of the cuticular layer making the insecticide more effective with the lowest doses. Mmojieje and Hornung [49] also investigated the insecticidal effect of PA obtained from mixed wood biomass against green peach aphid (Myzus persicae) and red spider mite (Tetranychus uriticae) in the UK and found more than 90% mortality for both pests. Even in early studies like that of Strong R.G. back in 1973 [50]reported good results when wheat seed were treated with hardwood tar oil to repel birds, rodents and insects.[51] Very similar effects were found when using pyroligneous acid for controlling insects from sweet corn plots [48] Also, preliminary investigation in Greece [52] showed that one spray application with birch tar oil (1% v/v aquaous solution) killed 95% of aphids (*Myzus persicae*) on eggplant in a greenhouse experiment. These researches and many more testify on the positive impact of using Tar (PA, wood vinegar). *Pinus halepensis* and *Acacia cyanophylla* tars could be alternatives to the widespread use of synthetic pesticides as "green chemicals" with less damage on the environment.

3.4. Antifungal activity

For this test the mycelium growth was noted until full colonization. The incubation period was up until 10 days. Then the extracts inhibition ability was noted. Through the collected data and after performing ANOVA with DUNCAN post-hoc we were able to class the fungi strains.

After the Data analysis, we were able to deduce that: when using the P. halepensis tar extract (10%) The mycelium growth of the tested strains was restricted significantly down to 30% for Phoma. sp and Bipolaris sorokiniana, meaning an inhibition rate of 70%, in second comes F.nyagami, F.solani and Microdichium nival with less than 50% growth rate (41%,44% and 48%) indicating a 52–59% inhibition rate. nevertheless, P. halepensis tar was less effective on F. rodelens, F.oxysporum and F.poae with mycelium growth that reaches 77% for F.poae. leading to less than 30% inhibition rate (Fig. 12). We can conclude that Phoma. sp, Bipolaris sorokiniana, F. nyagami, F.solani and Microdichium nival are the fungi that are significantly effected by the use of P.halepensis tar. As for Acacia cyanophylla tar extract (0.75%) the mycelium growth was more elevated where the most effected fungus by the use of the tar is Phoma. sp with 71% growth which means 29% inhibition strength, seconded by F.nyagami with77% growth (23% inhibition rate). The other strains were less inhibited by the tar leading to high growth rates up to 100% for F.oxysporum and F.poae. these results showed that Pinus halepensis tar was more effective against the tested fungi and proved to have higher antifungal activity compared to Acacia cyanophylla tar. This could be the outcome of using different doses of both extract and a lesser dose of Acacia tar. In fact, a higher dose could have more repercussion on the mycelium strains development. Using the DUNCAN test we were able to rank the fungi strains

Table 2
DUNCAN test, effect of the tars extract on mycelium growth of the tested fungi strains.

Fungi	N	DUNCAN group
Phoma sp	3	A
Microdichium nival	3	A
Fusarium nyagami	3	A
F.solani	3	A
Fusarium redolens	3	AB
Fusarium verticillioides	3	AB
Bipolaris	3	AB
Stumphyllium	3	BC
Fusarium oxysporum	3	C
Fusarium poae	3	C

from the most vulnerable fungi the most resistant one (Table 2) with *Phoma* sp*, Microdechium nival, Fusarium solani* and *Fusarium nygami* most inhibited and affected fungi by the Aleppo pine tar.

These results showed a promising effect of Pinus tar on many phytopathogenic fungi. For that many publications cite that pyrolysis liquid may be effective fungicides in agriculture applications [53].reported that, the wood vinegars produced from biomasses such as inner coconut shells, bamboo and Eucalyptus wood effectively controlled fungal growth. Murat Kizil et al., [54] tested the tar of *P. brutia* (roots and stems) which exhibited high activity. In another study, *Juniperus oxycedrus* Tar was used against 6 strains of Fusarium including F. oxysporum. the fungi growths were completely inhibited by the tar. Even in recent research, by Khadidja Bendjima et al. [55], Olea europaea subsp. sylvestris tar was used against Fusarium oxysporum f. sp. albedinis, one of the most damaging diseases of date palm in Algeria, and proven significally effective with a minimal inhibition concentration value of 2,1 μg/ml these researches and more demonstrated the importing effect of tar on many fungi and phytopathogenic ones. This activity is strongly linked to the levels of phenolic compounds in each Tar. This fact was reported by many studies like that of Inoue et al. [56] and Yatagi M. et al. [57] suggesting that activity could be due to more than one compound. Murat Kizil et al. [54] work results also suggested that, the flavonoids, terpenoids and alkaloids present in the plant appear to be responsible for biological activity.

4. Conclusion

Tar is a dark, oily material produced by slow pyrolysis of wood, coal, or peat, separated from pyrolysis liquids by sedimentation. It's a viscous liquid with a smoky odor and acrid, slightly aromatic taste. It's known to have antifungal, antioxidant, pesticidal and properties. The present study used Pinus halepensis an Acacia cyanophylla wood to produce tar and test its effectiveness on *Aphis spiraecola* in addition to numerous fungi strains specially from Fusarium species. What we have achieved through the tests allowed us to affirm that these 2 tars have important biological activities derived from their high phenolic compounds' contents. However, Pinus halepensis tar showed better results and more effectiveness that could be from the fact that conifers are reported to have antibacterial activities. Pyrolysis technology may offer a "greener" solution to produce chemicals using local resources: plant material, labor and solar energy absorbed by plant cells. These Tars may be an ecological and sustainable tool for farmers, if earlier reports on its beneficial effects are substantiated in further detailed studies through additional tests which are required specially with a direct apply on crops of these tars in order to prove their effectiveness and the fact that they cause no harm on the applied crops.

Data availability statement

All data associated to this paper is available for revision or consult at Carthage University site: www.UCAR.rnu.tn.

Additional information

No additional information is available for this paper.

CRediT authorship contribution statement

Fedia Derbali: Writing – original draft, Writing – review & editing. **Soumaya Torkia Hammami:** Methodology. **Methaq Algabr:** Project administration. **Mohamed Taher Elaieb:** Resources. **Lamia Hamrouni:** Supervision, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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