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ACTIVITIES**

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THIONATION OF ESSENTIAL OILS FROM ALGERIAN *ARTEMISIA HERBA-ALBA* L. AND *RUTA MONTANA* L.: IMPACT ON THEIR ANTIMICROBIAL AND INSECTICIDAL ACTIVITIES

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Abstract. Essential oils were extracted from *Artemisia herba-alba* L. and *Ruta montana* L. by means of steam distillation and thionated with a reagent combination of phosphorus pentasulfide and sodium bicarbonate. Both parent essential oils and their modified ones were screened for their biological and insecticidal activities. The results showed that essential oils were composed mainly of ketones; essential oils from *Artemisia herba-alba* L. and those from *Ruta montana* L. consisted of bicyclic monoterpenes and acyclic aliphatic ketones (thujone, camphor and 2-undecanone), respectively. The antimicrobial activity of essential oils was substantially improved upon thionation (from 10 to 34 mm and from 11 to 32 mm). The insecticidal effect of the thionated essential oil from *Ruta montana* L. was observed to be very significant, but that of the essential oil from *Artemisia herba-alba* L. was observed to decrease (from 100% to 70% after 24 hrs. The extracted essential oils as well as their thionated forms were characterized by GC-MS, FT-IR, and UV-visible.

Keywords: essential oil, thionation, *Artemisia herba-alba* L., *Ruta montana* L., GC-MS analysis.

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Introduction

Biologically active molecules from essential oils are known for their pharmacological [1], antimicrobial [2], insecticidal [3], and antioxidant [4] activities. Essential oils, acting as homogeneous matrixes, consist chiefly of hydrocarbon and oxygenated mono- and sesquiterpenes [5] and, in some instances, of aliphatic terpenes (2,4-dimethyl hexane) as in *Ruta* type [6]. Apart from the bioactive molecules, essential oils composed of tolerable terpenoids such as alcohols and aldehydes [7], and of toxic terpenes such as ketones [8]. A variety of ketones with different structures are present in variable proportions in the chemical compositions of essential oils of some species like *Absinthe* [9], *Artemisia* [10], *Salvia officinalis* L. (sage) [11], *Peppermint* [12], and *Ruta* [13].

Overall, the difference in the chemical compositions of essential oils would impart different biological activities. Some bacterial strains and fungi exhibit some resistance against some essential oils, as they are fitted with suitably

adapted protecting systems. Similarly, some insects develop a certain defensive behavior against some essential oils and can be thus unaffected when treated with.

Sulfur-containing compounds are widely known for their biological and pharmacological activities [14]. Henceforth, one of the objectives is to test different essential oils and to determine which are the most effective against bacteria, fungi and insects, that is, alleviating the relative resistance of these species towards the treating molecules, that thionation of the essential oils of *Ruta Montana* L. (*Rutaceae*) and *Artemisia herba-alba* L. was undertaken. By doing so, the physicochemical properties of the essential oils from these plants, and their hydrophobicity and volatility are expected to be enhanced as a result of the formation of thioketones (or thiones), less polar groups than ketones; this would induce a hydrogen bonding lowering, in addition to the displacement of the tautomeric equilibrium towards the formation of the enethiol.

Experimental

Materials

Camphor ($\geq 98\%$), 2-undecanone ($\geq 98\%$), P_2S_5 (99%), $NaHCO_3$ (99%), CS_2 (99.5%), and DMSO (99%) were purchased from Cheminova, Sigma-Aldrich, Biochem, Riedel-de Haen AG, and Panreac, respectively.

The plants *Artemisia herba-alba* L. and *Ruta montana* L. were harvested in March 2016 at Djelfa (North-central Algeria) and Hammam Melouane (Northern Algeria), respectively. Two plants of each species were identified at the "Department of Process Engineering" of the University of Blida 1 (Algeria). The selected vegetal parts of the plants were shade-dried in a well-aerated space, and then thoroughly stored before use.

Analytical apparatus

The GC-MS analysis of the *Artemisia herba-alba* L. and *Ruta montana* L. steam distilled and thionated essential oils was carried out on an Shimadzu HP 6890 equipped with a quadrupole TQ8030 Mass-Selective Detector (GC-MSD) equipped with split-splitless injector (splitless, $250^\circ C$, $1 \mu L$) and Rtx-5 ms capillary calibrated column (30 m x 0.25 mm x 0.25 mm); The carrier gas: helium 1 mL/min; oven: $60^\circ C$ -2 min, $2^\circ C/min$ - $270^\circ C$ -5 min; MSD in scan 35-550 amu, solvent (methanol) delay 3.5 min.

The ionization type was electron impact and the intensity of the filament of the MS part was 70 eV. The temperatures of the source and the interface were maintained at 230 and $280^\circ C$, respectively.

Infrared spectra were recorded at neat liquids on BRUKER FT/IR. UV-visible spectra were registered with Shimadzu UV-1800 (double beam) using spectroscopic grade methanol.

Extraction of essential oils

The extraction of essential oils from the selected vegetal parts was performed by means of steam distillation. The extracted essential oils (EO) from *Artemisia herba-alba* L. and *Ruta montana* L. are herein designated EO_{Aha} and EO_{RM} respectively. The chemical compositions of these essential are given in Tables 1 and 2.

Thionation of essential oils

Prior to thionation, the essential oil (1.43 and 1.59 g) was dried over Na_2SO_4 then dissolved in CS_2 (30 mL). A 250 mL three-necked round bottom flask equipped with a condenser, a thermometer, and a magnetic stirrer, was charged with this solution, 2.1 g of P_2S_5 (Scheme 1) (4.7 mmol) and 0.438 g of $NaHCO_3$ (5.2 mmol). The system was then refluxed by means of a thermostated water bath ($50^\circ C$) under continuous

stirring for 6 and 11 h for *Artemisia herba-alba* L. and *Ruta montana* L., respectively. The monitoring of the progress of the reaction was carried out by means of thin layer chromatography (TLC) analysis. After cooling the reaction mixture to room temperature, the solvent was evaporated and the thionated essential oil was stored at $4^\circ C$ until use. The thionated EO_{Aha} and EO_{RM} are herein called $S-EO_{Aha}$ and $S-EO_{RM}$, respectively.

Antimicrobial assay

Two microbial and one fungal strains, referenced as American Type Culture Collection (ATCC) and employed in the present study were obtained from the clinical bacteriology laboratory of the hospital of Boufarik (Northern, Algeria): *Staphylococcus aureus* ATCC 6538 (gram-positive), *Escherichia coli* ATCC 10536 (gram-negative), and *Candida albicans* ATCC 10231 (fungus).

Bacterial suspensions were obtained by sampling 3 to 5 well-isolated and morphological identical colonies from 18 h cultures for bacteria and 48 h for fungi, and adding them to 9 mL of physiological water. The obtained systems were vortex-stirred for a few seconds. Optical densities were measured using the UV spectrophotometer set at the wavelength of 620 nm. The readings of optical density must be in the spectrum of 0.22 and 0.32 for bacteria with the exception of *Staphylococcus aureus*, which must be between 0.3 and 0.4. Those of fungi must be between 2 and 3, corresponding to 10^7 - 10^8 germs/mL.

First, 15 mL of the liquefied Muller-Hinton agar medium (for bacteria) or Sabouraud one (for fungi) were poured into Petri dishes. Then, the culture media were seeded with 200 μL of the above-mentioned suspensions.

Sterile cellulose disks were soaked with an amount of essential oil solution and then deposited on the agar surface; the solution was allowed to diffuse throughout for 30 min at ambient temperature. The incubation was performed in an oven incubator at $37^\circ C$ for 24 h for bacteria and at $25^\circ C$ for 48 h for fungi. The testing solutions were prepared by dissolving the virgin EO_{Aha} and EO_{RM} and the thionated ones, $S-EO_{Aha}$ and $S-EO_{RM}$, in DMSO.

The formation of a translucent halo on the disk suggested the absence of microbial growth; the diameter of the halo in mm was measured by means of a caliper or a ruler. The results are expressed as diameters of the inhibition zones.

Insecticidal assay

The insects were collected at OAIC (Algerian Interprofessional Office for Cereals).

They were reared on infested-*Sitophilus oryzae* wheat grains in an aerated room at a temperature range of 24-28 °C and a relative humidity of 70%.

The insecticidal activity test was conducted by fumigation of essential oil on the *Sitophilus oryzae* adults. Hermetically sealed transparent vials of 250 mL capacity were used as fumigation chambers. Essential oil (or modified one) (1.5 mL/L of air) was deposited onto a piece of filter paper which was then placed at the bottom of the vial. Each vial contained 30 insects. One control test was done under identical conditions but in the absence of essential oil. The mortality rate was appreciated by counting the dead insects every hour of the first day of treatment, until the death of all of them, and the vials being kept closed.

The mortality rate was corrected using the Schneider-Orelli formula Eq.(1) which takes into account the natural death (the control test).

$$M_{cr}(\%) = \frac{M - M_{cn}}{100 - M_{cn}} \quad (1)$$

where, M_{cr} is the mortality rate;

M is the mortality rate of the fumigated population;

M_{cn} is the mortality rate of the control population.

Results and discussion

Essential oils from *Artemisia herba-alba* L. and *Ruta montana* L. were obtained in yields of 1.5 and 1.8%, respectively, after 1 h of extraction, using steam distillation process (refractometric index: 1.4691 and 1.4351). It is worth noting that the essential oil from *Ruta montana* L. is composed of acyclic aliphatic ketones: 2-nonanone, 2-decanone, 2-undecanone, 2-dodecanone, and 2-tridecanone (Table 1). However, *Artemisia herba-alba* L. consists mainly of bicyclic monoterpene ketones (filifolone, α -thujone, β -thujone and camphor) (Table 2); chemical compositions of EO_{Aha} and EO_{RM} consist chiefly of camphor (33%) and 2-undecanone (71%), respectively. According to authors EO_{RM} from the region of Tipaza (70 km east of Algiers, Algeria) was reported to contain about 67% of 2-undecanone as major component [13]. Moreover, the essential oil of *Ruta graveolens* was found to be composed mainly of 2-undecanone [13]. Also, EO_{Aha}'s from different regions of Algeria were found to contain camphor as the major constituent in about 33% [15].

The second step of this research was to thionate the extracted essential oils, EO_{Aha} and

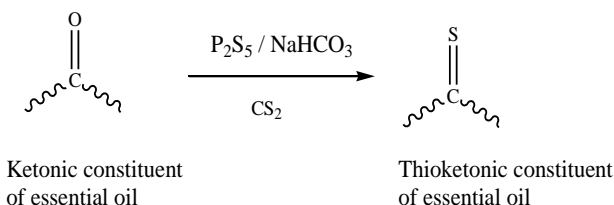
EO_{RM}, in the aim to assess their biological and insecticidal activities. Thionation of carbonyl compounds could be achieved with Lawesson's reagent [16] or with systems containing phosphorus pentasulfide such as phosphorus pentasulfide / hexamethyldisiloxane [17]. In our case, thionation was carried out with phosphorus pentasulfide / sodium bicarbonate system in CS₂, converting all the ketones to their corresponding thioketones as shown in Scheme 1.

Table 1

Chemical composition of essential oil from <i>Ruta montana</i> L. (EO _{RM}).			
Component	Retention time (min)	Kovats retention index (min) [20-22]	Composition (%)
2-Nonanone	6.6	1091	2.11
2-Decanone	8.1	1190	5.36
1-Undecanol	8.9	1380.4	0.82
2-Undecanol	9.3	1287	1.06
3-Undecanol	9.6	1308	0.73
2-Undecanone	14.6	1291	71.37
2-Dodecanone	18.9	1348	8.08
2-Tridecanone	20.5	1496	10.47

Table 2

Chemical composition of essential oil from <i>Artemisia herba-alba</i> L. (EO _{Aha}).			
Component	Retention time (min)	Kovats retention index (min) [20-22]	Composition (%)
Artemisiatriene	5.6	929	0.28
Mesitylene	6.5	994	2.38
Terpinolene	7.1	1088	1.95
<i>p</i> -Cymene	7.3	1026	13.19
1,8-Cineole	7.5	1033	7.78
Filifolone	8.4	1083	6.4
β -Thujone	9.4	1102	16.62
α -Thujone	9.8	1102	18.43
Camphor	10.7	1143	32.98



Scheme 1. Thionation of essential oils.

The success of thionation of the essential oils (Figures 1S and 3S, see *Supplementary Material*) was confirmed by infrared spectroscopy. A new absorption band at

1018 cm^{-1} appeared that was attributed to thioketone group ($\text{C}=\text{S}$), and the intensity of the band for ketone group decreased (as can be seen in Figure 2S and 4S from *Supplementary Material*). In addition, the spectra profiles for the thionated essential oils are clearly different from those of the non-modified ones.

Figure 1 illustrates the UV-visible spectra of the essential oils from *Artemisia herba-alba* L. and *Ruta montana* L. and their thionated ones. The bands appearing at 216-218 nm are assigned to $\pi \rightarrow \pi^*$ transition of the double bonds ($-\text{C}=\text{C}-$) of the alkenylic components of the EOs such as terpinolene (olefin) and *p*-cymene (aromatic) in EO_{Aha} and terpineol (olefin) in EO_{RM} (Figure 1, spectra **a** and **c**). The characteristic band of ketone group in the ketonic ($-\text{C}=\text{O}$) components fluctuated between 270 and 280 nm, corresponding to $n \rightarrow \pi^*$ electronic transition. The spectra of the thionated EOs (Figure 1, spectra **b** and **d**) revealed a lower absorption intensity of the band of the corresponding thioketone group ($-\text{C}=\text{S}$); the extinction coefficient of the latter group is weaker than that of the ketone one. However, the absorption band of alkenyl group was maintained and became more intense due to $\sigma \rightarrow \pi^*$ transition, resulting from the coexisting enethiol tautomer of thioketone.

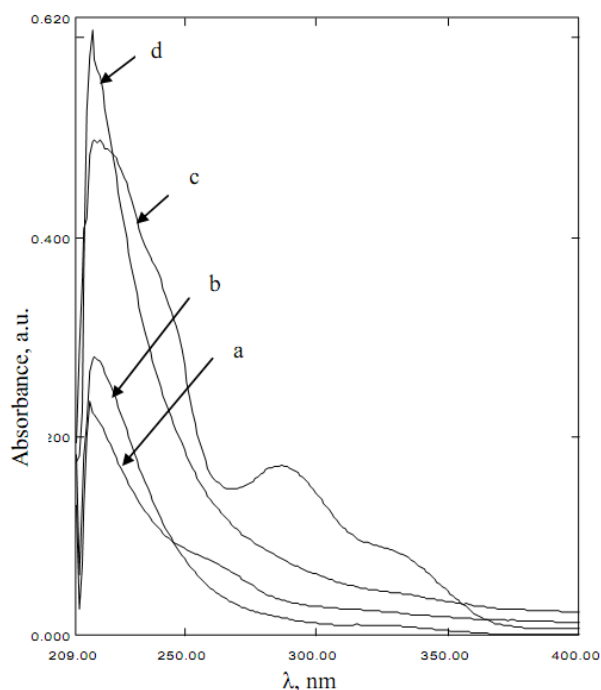


Figure 1. UV-visible spectra: a) essential oils from *Artemisia herba-alba* L.; b) thionated essential oils from *Artemisia herba-alba* L.; c) the essential oils from *Ruta montana* L.; d) thionated essential oils from *Ruta montana* L.

The chemical compositions of S-EO_{Aha} and S-EO_{RM} are gathered in Tables 3 and 4. The trends in compositions followed generally the same order as those of the non-thionated ones (Tables 1 and 2); that is, thiocamphor with its tautomer and 2-undecanethione with its tautomers are the major components, respectively.

Table 3

Chemical composition of thionated essential oil from *Ruta montana* L.

Component	Retention time (min)	Composition (%)
1-Undecanol	8.9	0.80
2-Undecanol	9.3	1.04
3-Undecanol	9.6	0.72
Nonan-1-ene-2-thiol	11.4	0.07
Undecan-2-en-2-ol	11.8	0.88
Nonan-2-ene-2-thiol	12.1	0.57
2-Nonanethione	12.2	1.43
Decan-1-ene-2-thiol	14.3	1.09
2-Undecanone	14.6	0.68
Decan-2-ene-2-thiol	15.0	2.57
2-Decanethione	15.1	1.59
Undecan-1-ene-2-thiol	17.3	28.86
Undecan-2-ene-2-thiol	18.1	35.20
2-Undecanethione	18.5	5.38
Dodecan-1-ene-2-thiol	19.8	1.04
Dodecan-2-ene-2-thiol	20.5	3.71
2-Dodecanethione	20.6	3.19
Tridecan-1-ene-2-thiol	22.4	1.17
Tridecan-2-ene-2-thiol	22.9	6.67
2-Tridecanethione	23.0	3.33

Table 4

Chemical composition of thionated essential oil from *Artemisia herba-alba* L.

Component	Retention time (min)	Composition (%)
Artemisiatriene	5.6	0.28
Mesitylene	6.5	2.38
Terpinolene	7.1	1.95
1,8-Cineol	7.3	13.19
<i>p</i> -Cymene	7.5	7.78
Filifolone	8.9	1.97
α -Thujone	9.5	6.40
β -Thujone	9.8	6.64
Camphor	10.7	14.43
α -Thuj-1-en-2-thiol	11.1	0.60
β -Thuj-1-en-2-thiol	11.2	0.71
Camphan-2-en-2-thiol	11.8	5.69
Filifolenthilol	12.1	2.86
α -Thuj-2-en-2-thiol	13.0	2.68
β -Thuj-2-en-2-thiol	13.3	6.71
Thiocamphor	13.6	12.86
Thiofilifolone	15.3	1.57
α -Thiothujone	16.1	6.94
β -Thiothujone	17.5	4.37

Gas chromatography analysis of the S-EO_{Aha} and S-EO_{RM} revealed the emergence of new peaks, assigned to the corresponding thiones (Figures 2 and 3). As can be noticed, the thiones are eluted at longer retention times than those for the corresponding precursors. This could be related to the difference in polarity between ketone group and thione towards the column stationary phase. The chromatographic analysis revealed peaks assigned to the enethiol tautomers of some of the obtained thioketones, a result that was confirmed by mass spectrometry analysis. The stability of enethiol tautomers, hence their detection, has been demonstrated [18]. Indeed, the peaks at retention times 13.6 and 11.8 min corresponded to thiocamphor and its enethiol

tautomer (see Figure 2), respectively, and the 2-undecanethione and its two enethiol tautomers (see Figure 3) were eluted at, 18.5, 18.1, and 17.3 min, respectively.

In addition, the thio-compounds were featured by mass spectrometry peaks greater than those of their precursors by an increment of 16 amu, a result of the substitution of oxygen atom by sulfur one (Figures 5S-8S, see *Supplementary Material*). The parent peaks corresponding to molecular masses of the thiones of S-EO_{Aha} were found: 166 for thiofilifolone against 150 for filifolone, 168 for α - and β -thiothujones against 152 for α - and β -thujones, 168 for thiocamphor (Figure 6S) against 152 for camphor (Figure 5S).

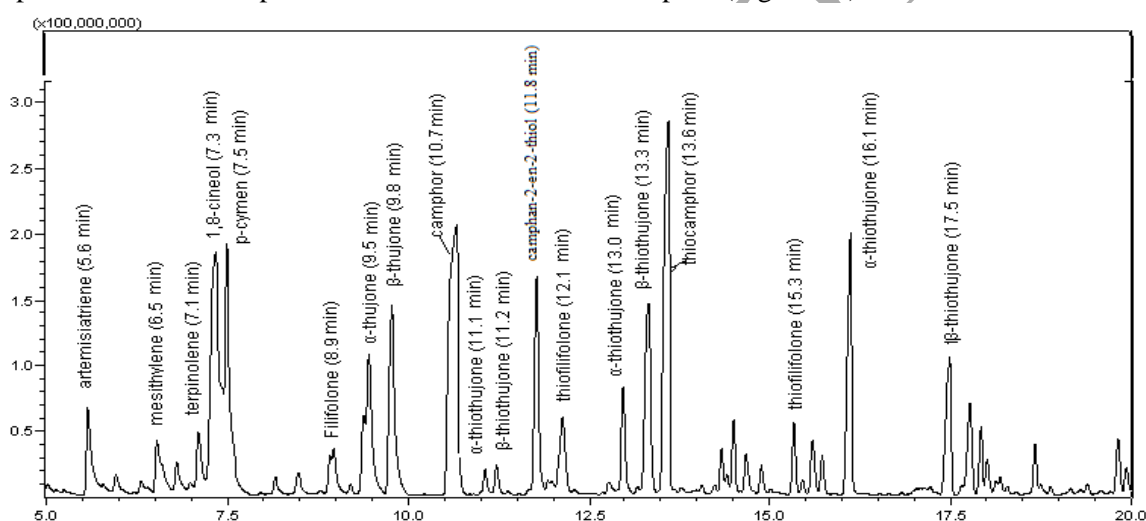


Figure 2. Chromatogram of thionated essential oils from *Artemisia herba-alba* L.

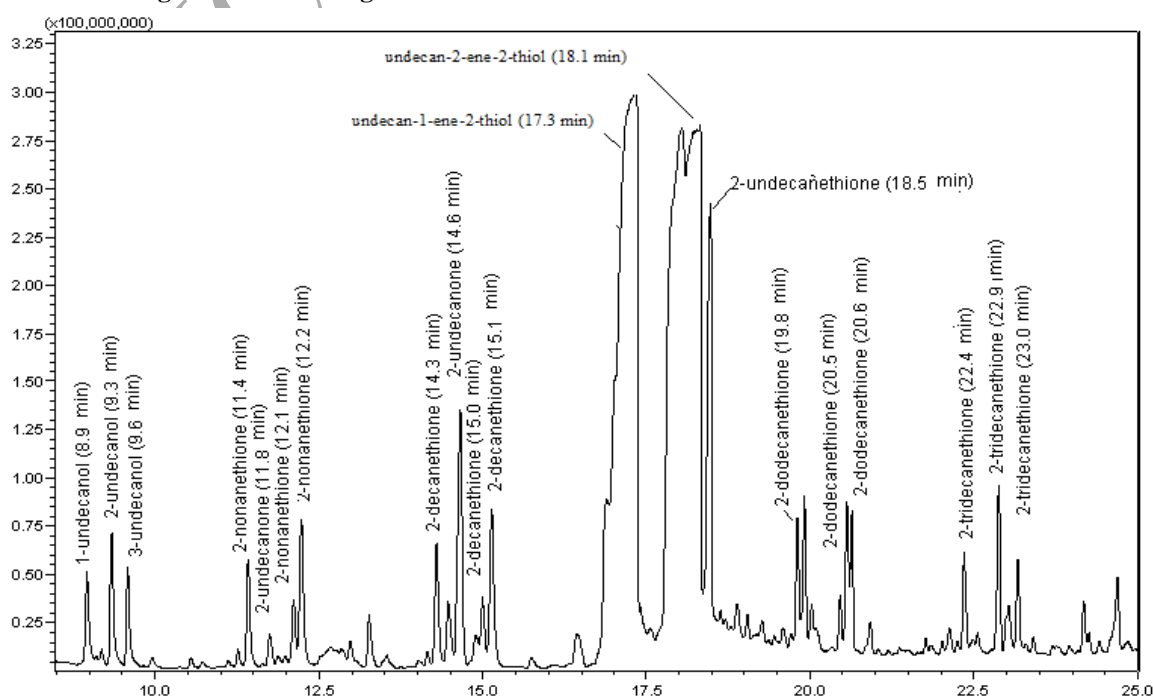


Figure 3. Chromatogram of thionated essential oils from *Ruta montana* L.

Those of S-EO_{RM} were: 158 for 2-nonanethione against 142 for 2-nonanone, 172 for 2-decanethione against 156 for 2-decanone, 186 for 2-undecanethione (Figure 8S) against 170 for 2-undecanone (Figure 7S), 200 for 2-dodecanethione against 184 for 2-dodecanone. Worthy of note is that the ketonic constituents of EO_{RM} were almost entirely converted into their corresponding thioketones and the relative tautomers, whereas the conversions of those of EO_{Aha} were only in the range of 55-70% (Tables 2, 4 and 5). Such a difference in the conversion extents seemed to be linked to the structure nature of the ketones; that is, the alicyclic aliphatic ketones as in EO_{RM} were easily converted to thioketones than the cyclic ones of EO_{Aha}.

Antimicrobial activity

EO_{Aha} and EO_{RM} were screened for their antimicrobial activity against two strains of bacteria and one of a fungus. The results are compiled in Table 6. It was found that the EO_{Aha} and EO_{RM} could not inhibit the bacterial growth

from *Escherichia coli* G(-). However, they became efficient after being thionylated. A positive action of the pure EO_{RM} and EO_{Aha} was observed against *Staphylococcus aureus* G(+), by inhibiting the growth. Conspicuously, this activity towards this bacterium was remarkably enhanced upon thionation, starting at a minimum concentration of 1% for the essential oil from *Artemisia herba-alba* L. and 0.1% for the essential oil from *Ruta montana* L. It is important to note that the antimicrobial activity of aliphatic thiones is greater than that of bicyclic monoterpene thiones. Antifungal activity of the bare essential oils towards *Candida albicans* was observed at concentrations of 1 and 0.1% for EO_{Aha} and EO_{RM}, respectively. This activity was visibly improved upon thionation of the oils; for the same respective concentrations, the diameters increased from 10 to 34 mm and 11 to 32 mm for S-EO_{Aha} and S-EO_{RM}, respectively.

Table 5

Estimated conversions of ketonic components of the essential oils from *Ruta montana* L. and *Artemisia herba-alba* L.

Ketonic components of essential oil from <i>Ruta montana</i> L., EO _{RM}	Conversion to the corresponding thiones and their tautomers (%)	Ketonic components of essential oil from <i>Artemisia herba-alba</i> L., EO _{Aha}	Conversion to the corresponding thiones and their tautomers (%)
2-Nonanone	100	Filifolone	69.22
2-Decanone	100	β-Thujone	61.49
2-Undecanone	99.05	α-Thujone	63.97
2-Dodecanone	100	Camphor	56.25
2-Tridecanone	100	-	-

Table 6

Results of antimicrobial activity test of essential oils and thionylated essential oils (mm)*.

Concentration of EO and S-EO(%)		Microbial strains		
		<i>Escherichia coli</i> ATCC 10536 G (-)	<i>Staphylococcus aureus</i> ATCC 6538 G (+)	<i>Candida albicans</i> ATCC 10231
EO _{RM}	0.1	-	-	11
	1.0	-	-	12
	2.0	-	-	15
	100.0	-	18	>40
S-EO _{RM}	0.1	-	18.5	32
	1.0	-	22.5	34
	2.0	-	24.0	35
	100.0	25	>40	>40
EO _{Aha}	0.1	-	-	-
	1.0	-	-	10
	2.0	-	-	16
	100.0	-	15	>40
S-EO _{Aha}	0.1	-	-	-
	1.0	-	12	34
	2.0	-	28	36
	100.0	10	>40	>40

*Tests with pure solvent (DMSO) were negative

Insecticidal activity

The insecticidal activities of EO_{Aha} and EO_{RM} towards *Sitophilus Oryzae* adults are different (Figures 4 and 5). Indeed, while the first oil brought to death all the tested insects within 12 h, only 13% of them were dead after 24 hrs of fumigation with the last one. It was observed that the insects demonstrated a higher resistance towards aliphatic ketones than towards bicyclic monoterpenes; in fact, about 70% (Figure 4) of the insects became extinct after 12 h of fumigation with EO_{Aha}, whereas none was dead after the same time of fumigation with EO_{RM}. The biological activity of long aliphatic chain ketones, such as 2-undecanone, was previously reported [19]. Surprisingly, the thionation of EO_{Aha} imparted a negative insecticidal effect; that is, a better resistance was noticed with S-EO_{Aha} as compared to that of the non-thionated oil (Figure 4). That is, the toxicity of EO_{Aha} was reduced upon thionation. However, the toxicity of EO_{RM} rose upon thionation as noticed in Figure 5.

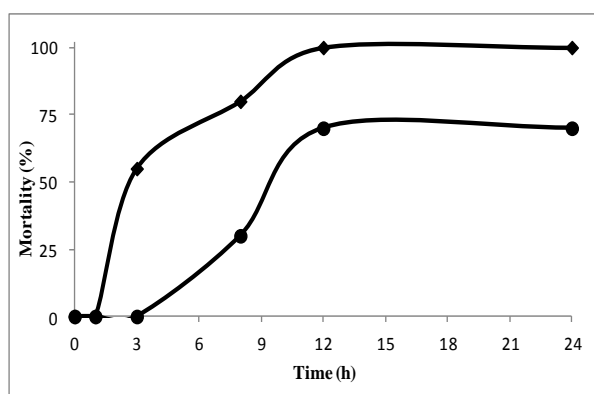


Figure 4. Mortality of the insects from *Sitophilus Oryzae* upon fumigation with: (♦) essential oils from *Artemisia herba-alba* L.; (●) thionated essential oils from *Artemisia herba-alba* L.

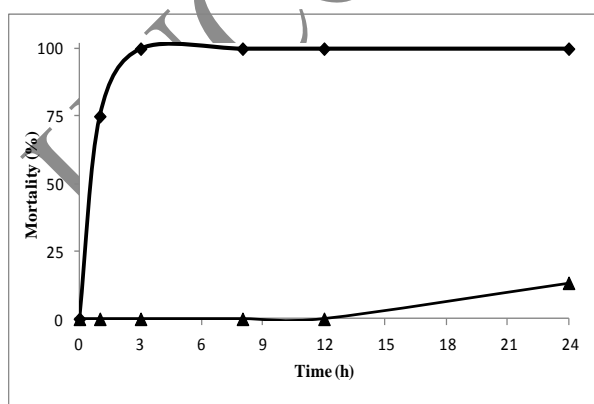


Figure 5. Mortality of the insects from *Sitophilus Oryzae* upon fumigation with: (▲) essential oils from *Ruta montana* L.; (◆) thionated essential oils from *Ruta montana* L.

The toxicity of the aliphatic ketones was tremendously increased when converted to their corresponding thiones; the insecticidal potential of S-EO_{RM} was 100% after 3 h only.

Conclusions

The antimicrobial and insecticidal properties of the essential oils from *Artemisia herba-alba* L. and *Ruta montana* L. is due to their ketonic components. These properties proved to be structure-dependent of the ketones; the acyclic aliphatic ketones are more effective than the cyclic ones towards the bacteria, but the effectiveness towards insects from *Sitophilus Oryzae* is the opposite. The corresponding thiones, generated by thionation of the essential oils, demonstrate greater antibacterial, antifungal and insecticidal activities than the ketonic species.

Supplementary information

Supplementary data are available free of charge at <http://cjm.asm.md> as PDF file.

References

- Fu, Z.; Wang, H.; Hu, X.; Sun, Z.; Han, C. The pharmacological properties of salvia essential oils. *Journal of Applied Pharmaceutical Science*, 2013,3, pp. 122-127. DOI: [10.7324/JAPS.2013.3723](https://doi.org/10.7324/JAPS.2013.3723).
- Andrade, B.F.M.T.; Barbosa, L.N.; da Silva Probst, I.; Júnio, A.F. Antimicrobial activity of essential oils. *Journal of Essential Oil Research*, 2014, 26, pp. 34-40. DOI: <http://dx.doi.org/10.1080/10412905.2013.860409>.
- Abd-Elhady, H.K. Insecticidal activity and chemical composition of essential oil from *Artemisia judaica* l. against *Callosobruchus Maculatus* (F.) (Coleoptera: Bruchidae). *Journal of Plant Protection Research*, 2012, 52(3), pp. 347-352.
- Gürsoy, N.; Tepe, B.; Akpulat, H.A. Chemical composition and antioxidant activity of the essential oils of *Salvia palaestina* (Benth) and *S. ceratophylla* (L.). *Records of Natural Products*, 2012, 6(3), pp. 278-287.
- De Falco, E.; Mancini, E.; Roscigno, G.; Mignola, E.; Tagliatela-Scafati, O.; Senatore, F. Chemical composition and biological activity of essential oils of *Origanum vulgare* L. subsp. *vulgare* L. under different growth conditions. *Molecules*, 2013, 18(12), pp. 14948-14960. DOI: [10.3390/molecules181214948](https://doi.org/10.3390/molecules181214948).
- Zellagui, A.; Belkassam, A.; Belaidi, A.; Gherraf, N. Environmental impact on the chemical composition and yield of essential oils of Algerian *Ruta Montana* (Clus.) L and their antioxidant and antibacterial activities. *Advances in Environmental Biology*, 2012, 6(10), pp. 2684-2688.

7. Ali, B.; Al-Wabel, N.A.; Shams, S.; Ahamad, A.; Khan, S.A.; Anwa, F. Essential oils used in aromatherapy: A systemic review. *Asian Pacific Journal of Tropical Biomedicine*, 2015, 5(8), pp. 601-611. DOI: <https://doi.org/10.1016/j.apjtb.2015.05.007>.
8. Knobloch, K.; Pauli, A.; Iberl, B.; Weigand, H.; Weis, N. Antibacterial and antifungal properties of essential oil components. *Journal of Essential Oil Research*, 1989, 1(3), pp. 119-128. DOI: [10.1080/10412905.1989.9697767](https://doi.org/10.1080/10412905.1989.9697767).
9. Rezaeinodehi, A.; Khangholi, S. Chemical composition of the essential oil of *Artemisia absinthium* growing wild in Iran. *Pakistan Journal of Biological Sciences*, 2008, 11(6), pp. 946-949.
10. Mohammadhosseini, M. Essential oils extracted using microwave-assisted hydrodistillation from aerial parts of eleven *Artemisia* species: Chemical compositions and diversities in different geographical regions of Iran. *Records of Natural Products*, 2017, 11(2), pp. 114-129.
11. Khalil, R.; Li, Z.-G. Antimicrobial activity of essential oil of *Salvia officinalis* L. collected in Syria. *African Journal of Biotechnology*, 2011, 10, pp. 8397-8402. DOI: [10.5897/AJB10.2615](https://doi.org/10.5897/AJB10.2615).
12. El-Ghorab, A.H. The chemical composition of the *Mentha pulegium* L. essential oil from Egypt and its antioxidant activity. *Journal of Essential Oil Bearing Plants*, 2006, 9(2), pp. 183-195. DOI: <http://dx.doi.org/10.1080/0972060X.2006.10643491>.
13. Boutoumi, H.; Moulay, S.; Khodja, M. Essential oil from *Ruta Montana* L. (Rutaceae) chemical composition, insecticidal and larvicidal activities. *Journal of Essential Oil Bearing Plants*, 2009, 12(6), pp. 714-721. DOI: <http://dx.doi.org/10.1080/0972060X.2009.10643780>.
14. Rezanka, T.; Sobotka, M.; Spizek, J.; Sigler, K. Pharmacologically active sulfur-containing compounds. *Anti-Infective Agents in Medicinal Chemistry*, 2006, 5(2), pp. 187-224. DOI: <https://doi.org/10.2174/187152106776359002>.
15. Belhattab, R.; Amor, L.; Barroso, J.G.; Pedro, L.G.; Figueiredo, A.C. Essential oil from *Artemisia herba-alba* asso grown wild in Algeria: Variability assessment and comparison with an updated literature survey. *Arabian Journal of Chemistry*, 2014, 7(2), pp. 243-251. DOI: <https://doi.org/10.1016/j.arabjc.2012.04.042>.
16. Cava, M.P.; Levinson, M.I. Thionation reactions of Lawesson's reagents. *Tetrahedron*, 1985, 41(22), pp. 5061-5087. DOI: [https://doi.org/10.1016/S0040-4020\(01\)96753-5](https://doi.org/10.1016/S0040-4020(01)96753-5).
17. Krstić, N.M.; Bjelaković, M.S.; Dabović, M.M.; Pavlović, V.D. Thionation of some α,β -unsaturated steroidal ketones. *Molecules*, 2010, 15(5), pp. 3462-3477. DOI: [10.3390/molecules15053462](https://doi.org/10.3390/molecules15053462).
18. Allegretti, P.E.; Schiavoni, M.M.; Di Loreto, H.E.; Furlong, J.J.P.; Della Védov, C.O. Separation of keto-enol tautomers in β -ketoesters: a gas chromatography-mass spectrometric study. *Journal of Molecular Structure*, 2001, 560(1-3), pp. 327-335. DOI: [https://doi.org/10.1016/S0022-2860\(00\)00773-0](https://doi.org/10.1016/S0022-2860(00)00773-0).
19. Chatzivasileiadis, E.A.; Sabelis, M.W. Toxicity of methyl ketones from tomato trichomes to *tetranychus urticae* Koch. *Experimental and Applied Acarology*, 1997, 21, pp. 473-484. DOI: <https://doi.org/10.1023/A:1018436113892>.
20. Adams, R.P. Identification of essential oil components by gas chromatography/mass spectrometry: Carol Stream. Illinois, USA, 1995, 469 p.
21. Kuhn, E.R. Selectivity vs. polarity: the fundamentals of chromatographic separation. *Journal of Separation Science*, 2001, 24(6), pp. 473-476. DOI: [10.1002/1615-9314\(20010601\)24:6<473::AID-JSSC473>3.0.CO;2-Y](https://doi.org/10.1002/1615-9314(20010601)24:6<473::AID-JSSC473>3.0.CO;2-Y).
22. Didaoui, L.; Touabet, A.; Meklati, B.Y. Comparison of mathematical methods for the calculation of retention indices at high temperature in gas chromatography. *Journal of Separation Science*, 1997, 20(11), pp. 605-610. DOI: [10.1002/jhrc.1240201107](https://doi.org/10.1002/jhrc.1240201107).