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SELECTIVE TRANSFORMATION OF MENTHONE FROM THE ESSENTIAL OIL OF *MENTHA PIPERATA* L. INTO MENTHONE 2,4 DINITROPHENYLHYDRAZONE AND UV-VISIBLE SPECTROPHOTOMETRIC ANALYSIS

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ABSTRAT: *The essential oil of Mentha piperata L., brown in color, was extracted by hydrodistillation from leaf stems collected in the southern district of Brazzaville (Bacongo), with a yield of 0.42 %. Analysis by gas chromatography (GC) and by gas chromatography coupled with mass spectrometry (GC/MS) revealed the presence of thirty (30) constituents of which twenty (20) were identified representing a proportion of (93.26 %) of the chemical composition of the total essential oil. The essential oil consists mainly of monoterpenes (92.47 %) with a predominance of oxygenated monoterpenes (89.43 %) dominated by menthol (44.08 %), followed by menthone (14.49 %), menthyl acetate (13.54 %)), mint furanone 1 (7.81 %) and menthofuran (3.04 %). Hydrocarbon monoterpenes occupy a low level of (3.04 %) characterized by limonene (2.71 %), orthocymene (0.37 %), β-pinene (0.35 %) and α-pinene (0.15 %). Concerning the group of sesquiterpenes, this represents a minimal rate (0.79 %), oxygenated compound are predominant (0.57 %) marked by caryophyllene oxide (0.40 %) and viridiflorol (0.17 %). We note the presence of a single hydrocarbon sesquiterpene, E caryophyllene occupying a small proportion of (0.22 %).Menthone 2,4-dinitrophenylhydrazone was hemi-synthesized by reacting the essential oil of Mentha piperata with 2,4-dinitrophenylhydrazine in the presence of sulfuric acid, a simple, easy method occurring in a rapid time (five minutes). The rate of conversion of menthone to menthone 2,4-dinitrophenylhydrazone of orange color is 29 %.Analysis of menthone 2,4-dinitrophenylhydrazone by UV-visible spectrophotometry showed an absorption maximum wavelength of 356 nm. The UV-visible spectrophotometric method employed for the determination of this hydrazone is convenient, fast and simple. The hemi-synthesized menthone 2,4-dinitrophenylhydrazone could be useful in the pharmaceutical, agrochemical, perfume and cosmetic industries*

KEYWORDS: Mentha piperata L., essential oil, menthone, menthone 2,4dinitrophenylhydrazone, UV-visible spectrophotometry, wavelength.

INTRODUCTION

Essential oils contain a diverse range of organic compounds, including ketones. Among these is menthone; one of the main constituents of essential oils of certain species of the genus Mentha belonging to the family Labieaes or Lamiaceaes [1] including *Mentha piperata* L. with considerable proportions [2; 3; 4].

It is a cyclic ketone (carbonyl compound), more precisely a cyclohexanone substituted by isopropyl and methyl groups in positions 2 and 5 respectively. It is of great interest in cosmetics, perfumery, agrifood and pharmacy. Indeed, it enters into the composition of natural perfumes and aromas [5; 6]. It has various chemical properties due to the presence of the C=O double bond giving rise to several nucleophilic and electrophilic addition reactions [7]. However the main or disadvantage of this is its instability which often results in oxidations, hence the need to convert it into hydrazones, crystalline compounds more stable than their precursors (carbonyls) [8; 9].

Hydrazones are organic compounds of the general formula: RR'C = N-N-R''R ''.

2,4-Dinitrophenylhydrazones are substituted hydrazones, derived from the condensation of an aldehyde or a ketone with 2,4-dinitrophenylhydrazine [10] (figure 1); a reversible reaction subjected to acid catalysis [11]. They play an important role in the protection of carbonyl compounds [12]. They are also used for the isolation, purification and characterization of the carbonyl group [13] and as an intermediate in organic synthesis [14]. Furthermore, hydrazones are used for the extraction or determination of transition metals such as iron [15], molybdenum [16], by formation of hydrazonic metal complexes.

Menthone 2,4-dinitrophenylhydrazone, for its part, results from the condensation of menthone (a cyclic monoterpene ketone) with 2,4-dinitrophenylhydrazine.

In pharmacology, numerous studies carried out affirm that menthone hydrazone exhibits various biological activities, among others, anticonvulsant [17;18] antibacterial [19]; antimicrobial and cytotoxic [20]; antifungal [21]; anticancer; antidepressive; analgesic and antiviral [22].
In addition, it should be noted that hydrazide hydrazone derived from cyclohexanan-1,3-dione is endowed with anticancer activity [23].
Furthermore, thiosemicarbazone and semicarbazone derived from menthone have shown significant anti-HIV and analgesic activities [24, 25].
Also, menthopyrazole derived from menthone is endowed with electrochemical; inter alia, anticorrosive properties [26]. While hydrazone derived from formylmenthone has electrochemical complexing properties towards metals such as Cu (II) and Ni (II) [27].

Several synthesis of 2,4-dinitrophenylhydrazones from menthone have been reported in the literature [28; 29; 21; 30 ; 31; 32].

Very few studies of the hemi-synthesis of hydrazones derived from essential oil ketones are described in the literature.
To our knowledge, the hemi-synthesis of menthone 2,4-dinitrophenylhydrazone from essential oils are not known.

Various analytical methods are used for the determination of hydrazone ketones, among them, HPLC-UV is the technique of choice for the determination of the latter [33]. To this are added HPLC-MS [34], RRLC-UV and RRLC-MS (/ MS) | 35], LC-MS [36], as well as GC-MS [37; 38]. In addition, APPI-MS [39] and HPLC [40; 41] are also involved in the analysis of 2, 4-dinitrophenylhydrazones ketones.
Besides these methods, UV-visible spectrophotometry also is widely used for the determination of hydrazone ketones [42; 43; 44]. However, some of these analytical methods involve long analysis time, tedious sample pre-treatment, and high product cost.
The aim of this present work is to extract the essential oil of *Mentha piperata*, to make the hemi-synthesis and to characterize the menthone 2,4-dinitrophenylhydrazone by UV-Visible spectrophotometry, a simple and fast method.

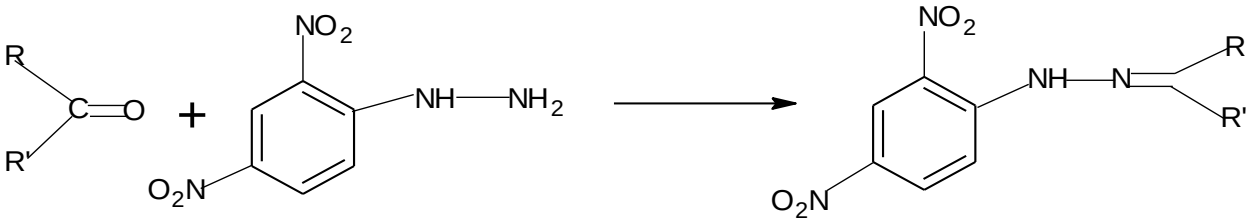

Figure 1: Reaction of a carbonyl compound with 2,4-dinitrophénylhydrazine.

MATERIALS AND METHODS

Vegetable material

The samples of *Mentha piperata* (figure 2) were collected in april 2019 in the southern districts of Brazzaville (Bacongo). They were identified by botanists from the National Herbarium of the Congo. Only leaf stems were selected for the study.

Figure 2: Leaves of *Menta piperata* L.

Extraction of essential oils:

After eight (8) days of drying at room temperature, in a ventilated room, the samples of *Mentha piperata* made up of the leaf stems are subjected to hydrodistillation for four (4) hours using a Clevenger type extractor [45], fitted with a two (2) liters balloon. The condensate loaded with essential oil and hydrolate is collected. The essential oil is separated from the hydrolate by decantation. The extraction with diethyl ether is carried out to isolate the aqueous phase of the essential oil followed by drying the ether phase with anhydrous sodium sulfate. Twenty-four (24) hours after evaporation of the diethyl ether in air, the essential oil is recovered. These operating conditions are summarized in Table I. The yield Y in essential oil is calculated according to the following formula:

$$Y = \frac{\text{Masse d'huile essential (g)}}{\text{Masse of plant material used (g)}} \text{ x } 100$$

Table I: Operating conditions for hydrodistillation of *Mentha piperata* L.

Plant material	***Mentha piperata***
Organs	Leaf stems
Quantity of matter dry (g)	131
Quantity of water (L)	1
Execution time of operation (h)	4

Organoleptic characteristics

The organoleptic properties (appearance, colour, smell) were evaluated based on the sensory method involving sight and smell.

Physicochemical parameters

Refractive index:

The refractive index is the ratio between the sine of the angles of incidence and refraction of a light ray of a given wavelength, passing from the air in the essential oil maintained at a constant temperature [46]. It is linked to the chemical function to which the essential oil belongs and also depends on the acidity, the polymerization of the essential oil.The measurement was carried out using a Novex Abbé refractometer. The method described by AFNOR was applied [46]. It consisted of putting two (2) to three (3) drops of essential oil on the prism of the refractometer. Look through the eyepiece by rotating the adjustment knob until the dividing line of the bright and dark areas is in the center of the reticle. Read the refractive index value of the essential oil on the reading scale. The index is given by reading on the refractometer at the temperature T at which the reading is taken. This is brought to 20 °C according to the following formula:

$n20 = nT + 0.00045 (T-20)$

With T: temperature on reading is taken

Acid index:

The acid Index (Ia) is the number of milligrams of potash (KOH) required to neutralize the free acids contained in 1 gram of essential oil [46]. It makes it possible to check the quality of an essential oil, in particular its deterioration and aging during storage time. The method described by AOAC [47] was applied to determine the refractive index. It consists of placing 1 gram of essential oil in an Erlenmeyer flask in which 5 milliliters (mL) of 95 % ethanol and 5 drops of phenolphthalein are added. The mixture is warmed in a water bath to about 65 °C for 10 minutes. After cooling, it is titrated with a 0.1 N solution of potassium hydroxide (KOH) using a burette, until the solution turns pink. The operating conditions are summarized in Table II.
Thus, the acid index is determined by the following formula:

$Ia = 0.56 \times V/m$ in which:
V: volume of the KOH solution.
m: mass of essential oil in gram

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Table II: Operating conditions for determining the acid index of essential oil of *Mentha piperata* L.

Parameter	Values
Mass of essential oil in (g)	1
KOH cencentration (mol/L)	0.1
Volume of ethanol (mL)	5
Amount of phenolphthalein (drops)	5

Analysis of essential oils

Analysis by gas chromatography

Quantification of the constituents was performed using a Hewlett Packard HP 5890 type chromatograph equipped with a flame ionization detector fitted with HP ChemStation data acquisition software. The different constituents are separated using a DB5 capillary column (30 mx 0.25 mm), (film thickness 0.25 µm) under the following operating conditions: helium carrier gas (1 mL.min-1), temperature injector temperature: 280 °C, detector temperature: 280 °C. The oven is programmed at 50 ° C for 5 minutes with a gradient of 5 °C.min-1 from 50 to 300 °C, 5 minutes at 300 °C with a split mode injection of 1-20.

Analysis by gas chromatography-mass spectrometry

Analysis by gas chromatography-mass spectrometry was carried out using a Hewlett Packard HP 6890 brand chromatograph coupled to an HP 5973 mass spectrometer. The separation of the different constituents is carried out using a DB5 capillary column (30m x 0.25 mm), (film thickness 0.25 µm) under the following experimental conditions: carrier gas: (helium: 1 mL.min-1), energy ionization (70 eV), injector temperature (280 °C), detector temperature (280 °C). The oven is programmed at 50 °C for 5 minutes with a gradient of 5 °C.min-1 from 50 to 300 °C, 5 min at 300 °C with an injection mode split1-10.

Identification of constituents

The different constituents of essential oil have been identified on the basis of their retention indices and their mass spectra by comparison with data from the literature [48; 49; 50].

Hemi-synthesis of menthone 2,4-dinitrophenylhydrazone

2,4-Dinitrophenylhydrazine reagent and essential oil from the species *Mentha piperata* are used for the preparation of menthone 2,4-dinitrophenylhydrazone. The method used was reported by Leclercq [51]. It consists in dissolving 0.25 g of 2,4-dinitrophenylhydrazine in 5 mL of methanol, followed by the addition of 0.5 mL of concentrated sulfuric acid, then filtration of the lukewarm solution. To this solution is added 0.2 g of essential oil solubilized beforehand in a small volume of methanol. After about five (5) minutes, the solid formed is filtered off and

washed in a little methanol. If there is no solid, the solution is acidified with sulfuric acid. The precipitate is then recrystallized from ethanol and then dried. These conditions are summarized in Table III.

Table III: Operating conditions for the hemi-synthesis of menthone 2,4-dinitrophenylhydrazone

Essential oil	Quantity of reagent	Quantity of essential oil (g)	Quantity of MeOH (mL)	Quantity of H_2SO_4 (mL)
Mentha piperata	0.25	0.2	5	0.5

Characterization of 2,4-dinitrophenylhydrazone

Determination of melting points

The measurement of the melting temperature of the prepared hydrazone is carried out using the kofler bench. The method consists of calibrating the device with benzoic acid which has a melting point of 122.35 °C. The carriage is moved horizontally until the cursor is at the border between solid and liquid. Then the movable index is moved vertically until it indicates the melting point of the standard. The hydrazone's melting point is then taken by depositing it at the cold end of the kofler bench and moving it towards the hot zone until the first drops of liquid appear. The carriage is then moved horizontally until the cursor is at the border between solid and liquid. The moving index then indicates the melting point. Three tests are carried out,

UV-visible spectrophotometric analysis

Analysis of 2,4-dinitrophenylhydrazone is done by a WPA Lightwawe II UV-visible spectrophotometer, connected to an HP computer.

Preparation of solutions

2,4-Dinitrophenylhydrazine solution

The 2,4-dinitrophenylhydrazine solution is prepared by dissolving 0.3 g of 2,4-dinitrophenylhydrazine in 100 mL of 0.05 M sulfuric acid solution.

Essential oil solution

The essential oil (10 to 20 mg) is placed in a 10 mL flask in which methanol is added to the mark.

Spectral scan

2.4-dinitrophenylhydrazones can

0.5 mL of the 2,4-dinitrophenylhydrazine solution is added to 0.5 mL of the essential oil solution. An orange precipitate forms. The precipitate is left to stand for 10 minutes at room

temperature and 5 ml of methanol are added to it: This is the solution of menthone 2, 4-dinitrophenylhydrazone.

We put in the reference tank:

• 1 mL of the 30 % (V/V) water/ethanol solvent

and in the measuring tank:

• 1 mL of the 2,4-dinitrophenylhydrazone solution

RESULTS AND DISCUSSION

Extraction and yield of essential oils

Hydrodistillation extraction from the leaf stems of *Mentha piperata* produced the chestnut essential oil '(table IV) with a yield of 0.43 % (table V). This result is close to the results published in India [52] and Egypt [53] with respective yields of 0.42 % and 0.45 %. In addition, this yield complies with the standards described by the French Standardization Association (AFNOR) in 2000 which include the yield of essential oil of *Mentha piperata* between 0.38 % and 1.2 %.

Table IV: Organoleptic characteristics of the essential oil of *Mentha piperata* L.

Species	AFNOR standards (AFNOR, 2000)			Essential oil studied		
	Aspect	**Colour**	**Odour**	**Aspect**	**Colour**	**Odour**
Mentha piperata L.	Mobile liquid	Yellow pale	Fresh characteristic more or less minty depending on the origin	Liquid	Chestnut	Minty

Table V: Extraction yield of the essential oil of *Mentha piperata* L.

Species	yield %		
	Our study	**Previous studies/origin**	**Standards (AFNOR, 2000)**
Mentha piperata L.	0.43	0.42 [52]/Inde 0.45 [53]/Egypte	0.38 à 1.2

Physico-chemical parameter

Refractive index

The refractive index obtained at 20 °C of the essential oil of *Mentha piperata* is 1.4707 (table VI). Analysis of this table shows that this index is high. Indeed, the refractive index values of essential oils are generally high, higher than those of water at 20 °C (1.333) and olive oil at 20 °C (1.4684).

The value of this refractive index at 20 °C complies with AFNOR standards; this proves its good quality. Indeed, the standards of the French Standardization Association (AFNOR, 2000) set the refractive index of *Mentha piperata* between 1.4600 and 1.5000. Also, by comparing the value of our index to those of the literature, we find that our value is close to the values of the literature. This is the case for the refractive index value of the essential oil of *Mentha piperata* from Egypt whose $IR_{20°C}$ = 1.4927 [53].

Acid index

The acid value of *Mentha piperata* essential oil is 0.672 (table VI). These values are low, less than unity. A low value of the acid number of less than 2 is proof of good preservation of the essential oil [54], that it does not deteriorate or degrade. That is, the oil is stable and is not oxidized. The essential oil stored in anti-actinic tinted bottles protected from light are protected from all attacks and possible reactions. Light, in fact, promotes the alteration of the structure of essential oils and the development of acids. Fresh essential oil is low in free acids | 54]. The value of this index compared to that of previous studies shows little difference. Indeed, the acid index of *Mentha piperata* from Egypt Ia = 0.560 [53] for which the value is also low and less than 2.

Table VI: Refractive index and acid index of essential oil of *Mentha piperata* L.

Species	Refractive index at 20 ° C	Acid index	AFNOR Standards		Previous studies	
			Refractive index	Acid index	Refractive index	Acid index
Mentha piperata L.	1.4707	0.672	1.4600-1.5000	2	1.4927[53]/ Egypte	0.560[53]/ Egypte

Chemical composition

Mentha piperata

The results of the analysis of the essential oil extracted from the leaf stems of *Mentha piperata* are shown in table VII. Figures 3 and 4 show the chromatograms (GC-MS) and (GC-FID) of the essential oil. Chemical analysis revealed the presence of thirty (30) constituents of which twenty (20) was identified representing a proportion of (93.26 %) of the chemical composition of the total essential oil. The essential oil consists mainly of monoterpenes (92.47 %) with a predominance of oxygenated monoterpenes (89.43 %) dominated by menthol (44.08 %), followed by menthone (14.49 %), menthyl acetate (13.54 %), mint furanone 1 (7.81 %) and menthofuran (3.04 %). Hydrocarbon monoterpenes occupy a low level of (3.04 %) characterized by limonene (2.71 %), orthocymene (0.37 %), β-pinene (0.35 %) and α-pinene (0.15 %). Concerning the group of sesquiterpenes, this represents a minimal rate (0.79 %), oxygenated compounds are predominant (0.57%) marked by caryophyllene oxide (0.40 %) and viridiflorol (0.17 %). We note the presence of a single hydrocarbon sesquiterpene, E caryophyllene occupying a small proportion of (0.22 %). The chemical composition of this

sample presents a qualitative resemblance to that of the essential oil of *Mentha piperata* described in Iran [55] dominated by menthol (53.28 %), menthyl acetate (15.10 %), menthofuran (11.18 %). Menthol is the major characteristic component of most of the essential oils *of Mentha piperata* in the world [56].

On the other hand, this chemical composition is qualitatively different from that of another sample of Iranian origin [57] with α-terpene (19.70 %), Isomenthone (10.30%) and β caryiophyllene (7.60 %) as major components. Also the presence of piperitone oxide (16.00 %), 1, 8 cineole (7.03 %), α-3-carene (3.27 %) in the extract of Indian origin [52] shows a different essential oil. qualitatively from our extract. Furthermore, there is also a qualitative difference with essential oil of Moroccan origin which is rich in linalool (60.72 %) and lynalyl acetate (20.79 %) [58].

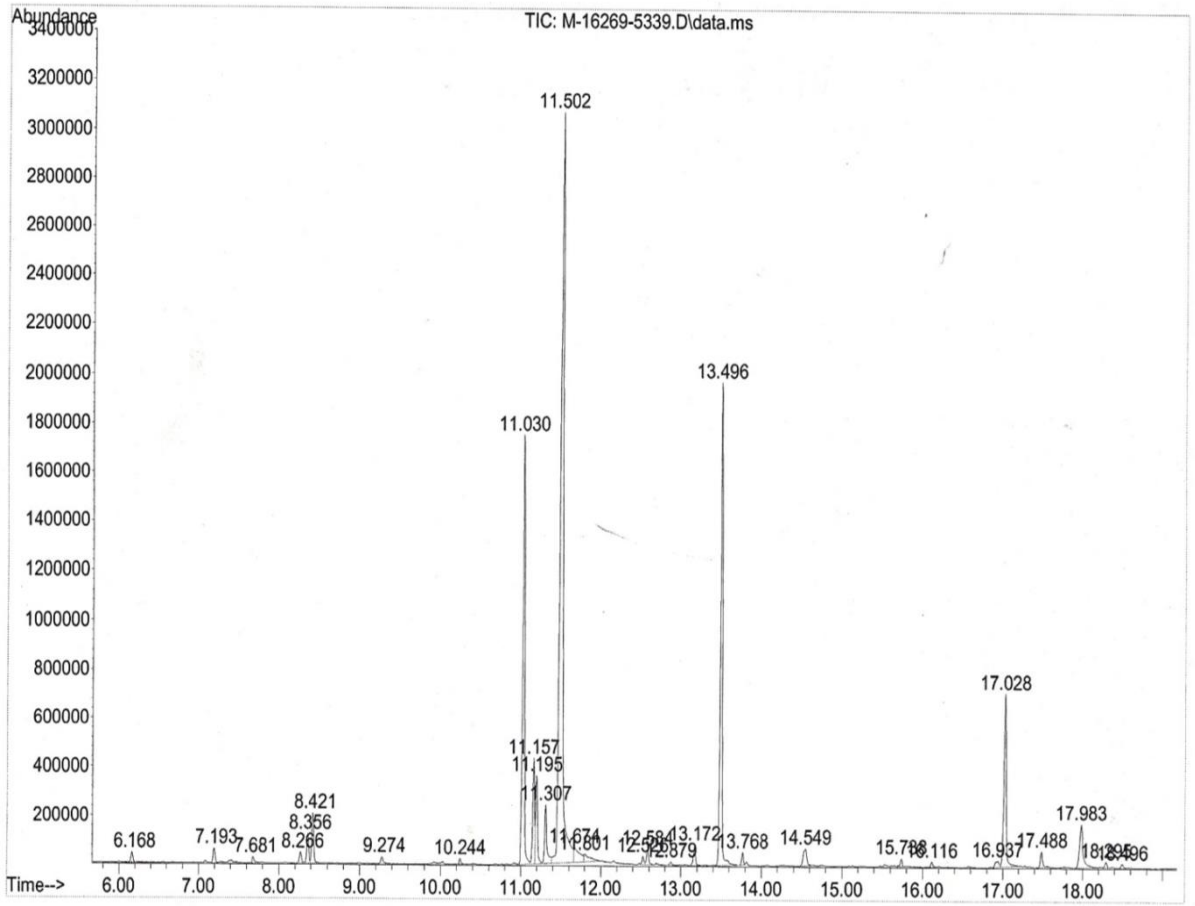


Figure 3: Chromatogram (GC-MS) of essential oil of *Mentha piperata* L.

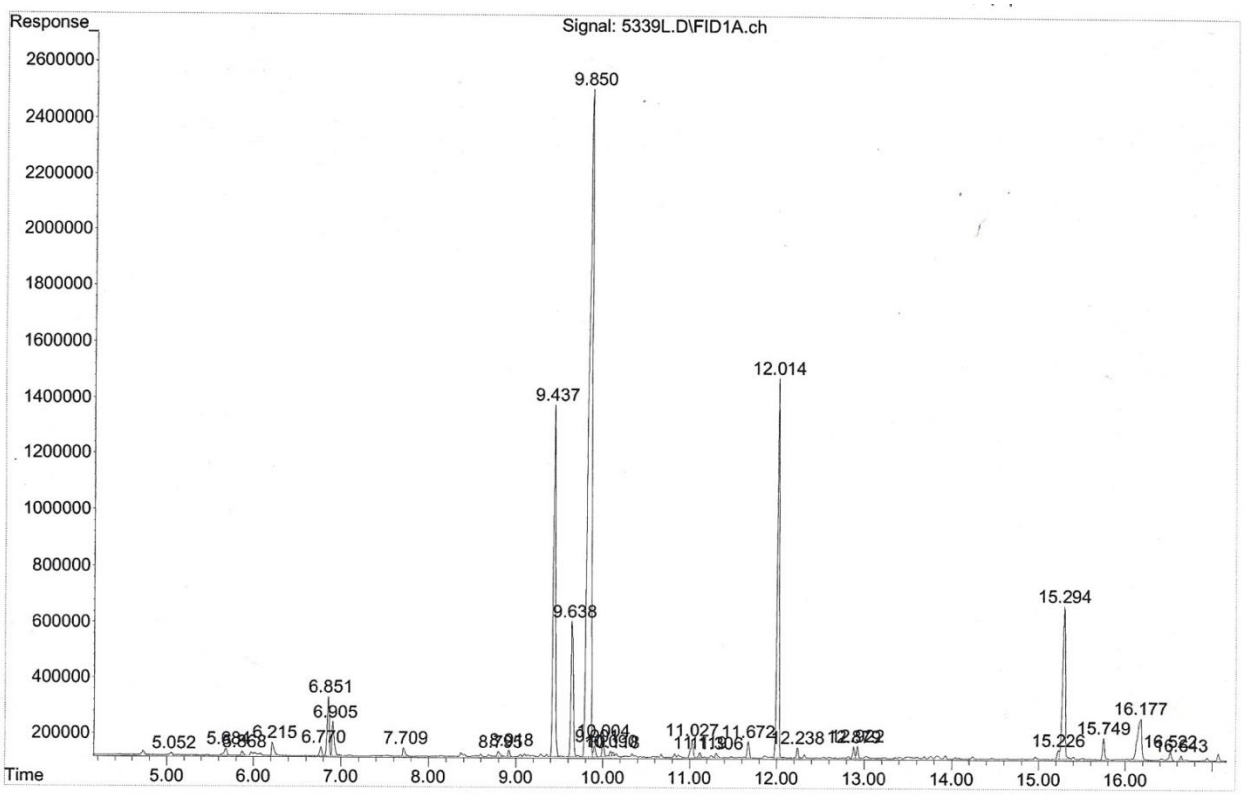
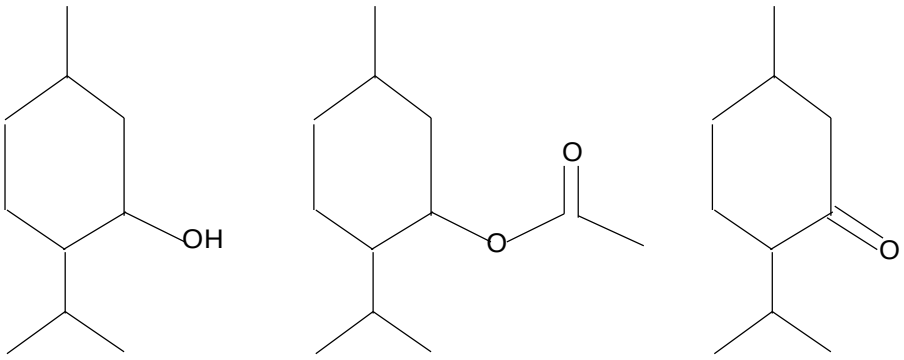
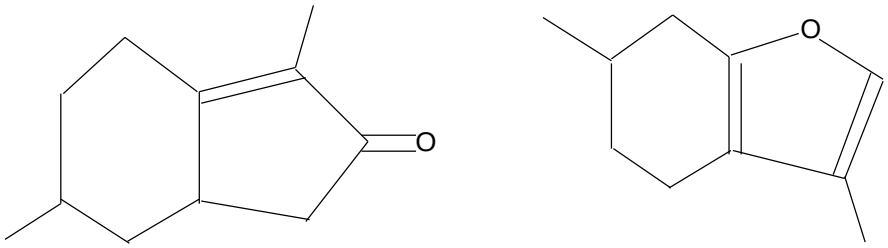


Figure 4 : Chromatogramm (GC-FID) of essential oil of *Mentha piparata* L.



Menthol Menthyl acetate Menthone



Mint furanone 1 Menthofurane

Figure 5: Chemical structures of major compounds in the essential oil of *Mentha piperata* L.

Table VII: Chemical composition of essential oil of *Mentha piperata* L.

N°	Compounds	IK	*Mentha piperata* L.
1	α-Pinene	933	0.15
2	β-Pinene	977	0.35
3	Orthocymene	1026	0.37
4	Limonene	1030	2.17
5	1,8 cineole	1033	1.36
6	Cis sabinene hydrate	1069	0.34
7	**Menthone**	1157	**14.29**
8	**Menthofurane**	1166	**3.04**
9	Isomenthone	1168	2.81
10	Neomenthol	1174	0.02
11	**Menthol**	1180	**44.08**
12	Pulegone	1242	0.55
13	Piperitone	1259	0.20
14	**Menthyl acetate**	1293	**13.54**
15	Isomenthone acetate	1308	0.35
16	E Caryophyllene	1426	0.22
17	**Mint furanone 1**	1508	**7.81**
18	Mint furanone 2	1539	0.84
19	Caryophyllene oxyde	1589	0.40
20	Viridiflorol	1603	0.17
Total compounds identified **Oxygenated monoterpenes** **Hydrocarbons monoterpenes** **Oxygenated sesquiterpenes** **Hydrocarbon sesquiterpenes** **Aliphatic compounds**			**93.26** **89.43** **3.04** **0.57** **0.22** **-**

Hemi-synthesis of menthone 2, 4-dinitrophenylhydrazone

Physical characterization

Table VIII shows the results of the hemi-synthesis of menthone 2,4-dinitrophenylhydrazone and their measured melting points. The reaction of 2,4-dinitrophenylhydrazine in the presence of sulfuric acid on the essential oil of *Menha piperata* gives rise to an orange-colored precipitate. This color is characteristic of menthone 2,4-dinitrophenylhydrazone. *Mentha piperata* essential oil contains a diverse range of chemical constituents, menthone 2,4-dinitrophenylhydrazone forms after five (5) minutes, kinetics are slow so extraction is also slow. In addition, the hemi-synthesis yield of 2,4-dinitrophenylhydrazone menthone is 29 %. This yield is low, and could be explained by the influence of the different constituents of the essential oil during the reaction. Indeed, the presence of the different constituents in the

essential oil changes the speed of the extraction, resulting in slow kinetics. This slowing down means that there is competition or hindrance between the compound to be extracted and the other constituents of the mixture. This Competition is linked to steric and electronic effects [59]. The melting point of hydrazone in *Mentha piperata* essential oil is 145 °C. This melting point is approximate to that of the literature [60], and corresponds respectively to that of menthone 2,4-dinitrophenylhydrazone.

Table VIII: Yield and physical properties of the menthone 2,4 dinitrophenylhydrazone

Compound of essential oil converted into 2,4-dinitrophenylhydrazo-ne	**Aspect**	**Colour**	**Yield (%)**	**Melting point Measured (°C)**	**Melting point of literature (°C)**
Mentha piperata L. (menthone)	Précipitate	Orange	29	145	146

Characterization by UV-visible spectrophotometry

Menthone 2,4-dinitrophenylhydrazone

The maximum wavelength of menthone 2,4-dinitrophenylhydrazone derived from the essential oil of *Mentha piperata* of 356 nm was recorded (table IX). This value is characteristic of the C=N chromophore of 2,4-dinitrophenylhydrazones whose maximum absorption wavelength is (λmax = 360-370 nm) [61; 62; 63].

Table IX: Maximum absorption wavelength of menthone 2,4-dinitrophenylhydrazone

2,4-dinitrophenylhydrazone derivative	**λmax (nm)**
Menthone 2,4-dinitrophénylhydrazone	356

The UV-visible spectrum of menthone 2,4-dinitrophenylhydazone (figure 6) shows two main bands:

- A low intensity band at 270 nm corresponding to the n → σ * transition relating to the aniline aromatic system;
- A very intense band at 356 nm attributable to the n → π * transition of the C=N group of the hydrazone.

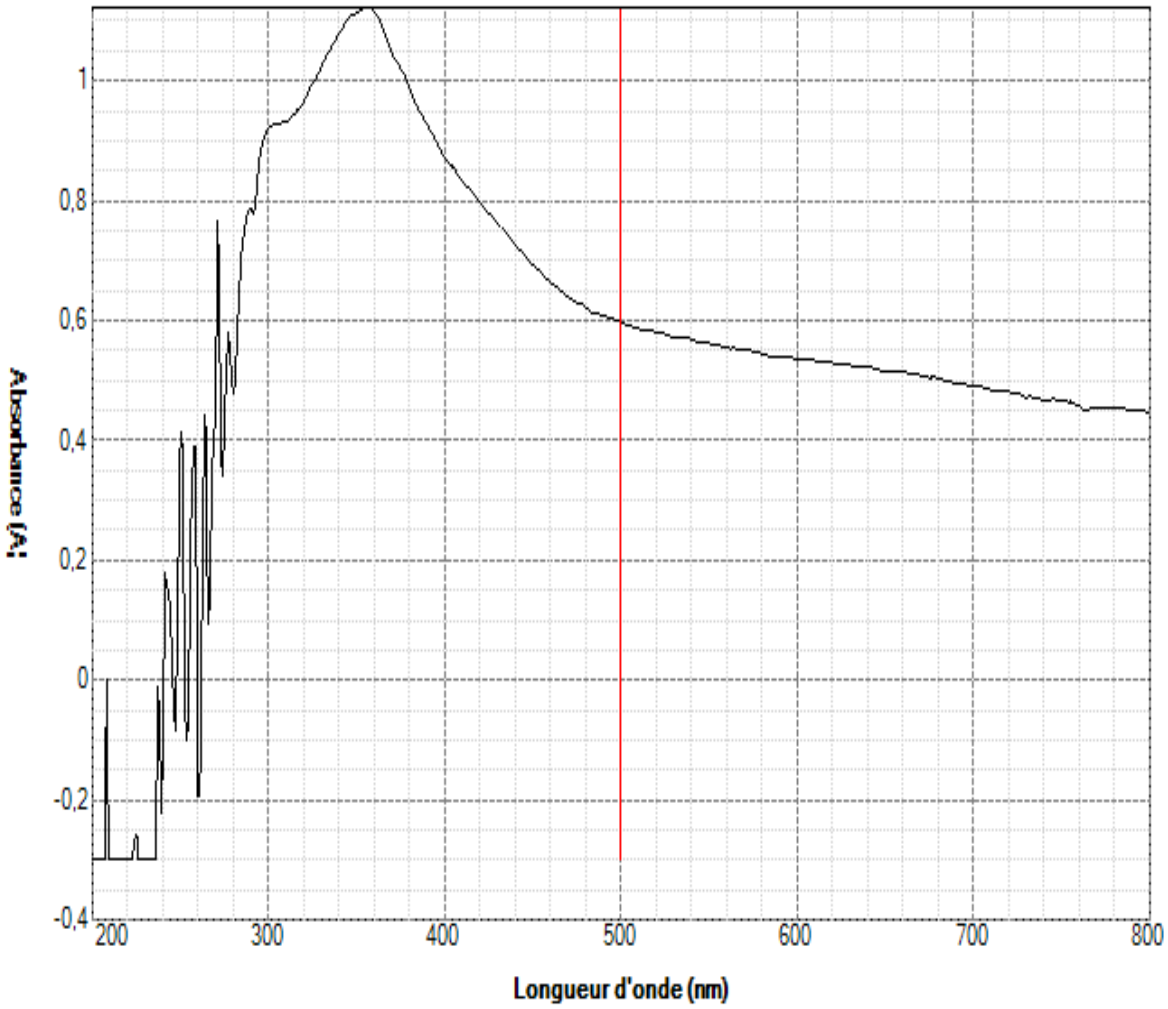


Figure 6: UV-visible spectrum of menthone 2,4-dinitrophenylhydrazone

The different absorption bands of menthone 2,4-dinitrophenylhydrazone, their chromophores and their groups are shown in table X.

Table X: Different absorption bands of menthone 2,4-dinitrophenylhydrazone

2,4-dinitrophénylhydrazone derivative	**Absorption band λ(nm)**	**Transition et Chromophore**	**Group**
Menthone 2,4-dinitrophénylhydrazone	**270** Not very intense	n→σ* (C-NH-)	aniline aromatic system
	356 Very intense band	n→π* (C=N)	Hydrazone

 https://doi.org/10.37745/gjpacr.2013

2,4-dinitrophenylhydrazine

The UV-visible spectrum of 2,4-dinitrophenylhydrazine shown in figure 7 shows three main bands at 346 nm, 360 nm and 377 nm due to chromophoric groups C-N and NO_2 substituted at the aromatic ring.

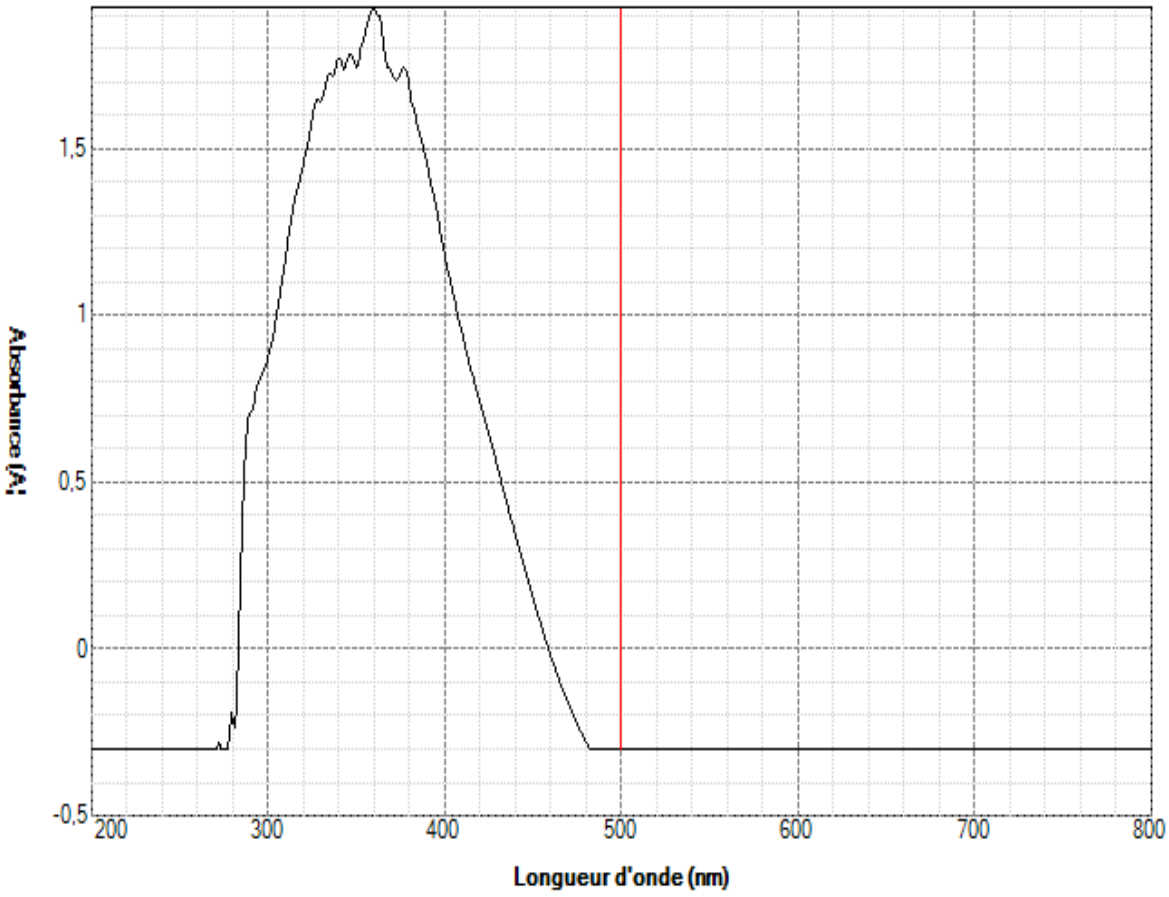


Figure 7: UV-visible spectrum of 2,4-dinitrophenylhydrazine

CONCLUSION:

Mentha piperata L. essential oil is an abundant and important source of menthone, a high added value molecule useful in the perfume, pharmaceutical, cosmetic and chemical industries. This interest has motivated our efforts to transform this molecule into hydrazone in order to enhance its economic and biological value. Menthone 2,4-dinitrophenylhydrazone was hemi-synthesized by a simple, easy method from essential oil of *Mentha piperata* with a conversion rate (yield) of 29 %, in a short time of five (5) minutes. Analysis of menthone 2,4-dinitrophenylhydrazone by UV-visible spectrophotometry showed an absorption maximum wavelength of 356 nm. The UV-visible spectrophotometric method employed for the determination of this hydrazone is convenient, fast and simple. The hemi-synthesized menthone

2,4-dinitrophenylhydrazone could be useful in the pharmaceutical, agrochemical industries [64] and in cosmetics.

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