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Comparative study of reactivity of (-)-*R*-carvone, (-)-*R*-linalool and (-)-(1*S*,4*S*)-camphor derivatives: Synthesis of new heterocycles

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ABSTRACT

Reactivity comparison by 1,3-dipolar cycloaddition of the three dipolarophiles (-)-*R*-Carvone (I), (-)-*R*-Linalool (II) and derivative of (-)-(1*S*,4*S*)-camphor (III) has been studied. By reactions of *p*-chlorophenylnitrile oxide, new heterocycles are obtained by stereospecific reactions for cyclic Terpenoids I and III (regardless of the length of the side chain). However the aliphatic dipolarophile II gives two diastereoisomers. Terpenoids (-)-*R*-Carvone I (-)-*R*-Linalool II and (-)-(1*S*,4*S*)-Camphor 1 are isolated respectively from Moroccan species *Mentha viridis* (L.), *Lavandula officinalis* (L.) and *Artemisia herba halba* (*Asso*). The new heterocycles obtained were identified by combination of chromatographic and spectroscopic methods.

1. Introduction

In the trials of valorisation of Moroccan plants traditionally known for their medicinal and aromatic power [1-13], we have undertaken a comparative study of reactivity of the major compounds of the essential oils from three different species. There are the (-)-*R*-Carvone (**I**) extracted from *Mentha viridis* (L.), (-)-*R*-Linalool (**II**) contained in *Lavandula officinalis* (L.) and dipolarophile (**III**) synthesized from (-)-(1*S*,4*S*)-Camphor, **1**. The latter is isolated from the species *Artemisia herba halba* (*Asso.*) (Scheme 1).

In literature, it is shown that there are many cycloaddition reactions on the terminal double bonds towards the nitrile oxides, both inter-molecular and intra-molecular. These reactions are often carried out on dipolarophiles whose stereochemistry is often not given [14-20].

In this work, we have tried to synthesize new molecules that may have some pharmacological applications, or that have interesting olfactory properties. To do this, we have chosen three dipolarophiles **I**, **II** and **III** (pure enantiomers) from the class of terpenoids where the terminal double bond fills various positions. In the dipolarophile **III**, the double bond is located on a long side chain compared to that of the dipolarophile **I** [1], while in the dipolarophile **II**, it fills an aliphatic chain. We first found that, from a stereo selective point of view, *p*-chloro phenylnitrile oxide oxygen atom always bonds to the most substituted carbon of the terminal double bond. Moreover, we noticed that the presence of the terpene cycle plays an important role in the stereospecificity of the reaction. The 1,3-dipolar cycloaddition on dipolarophile **I** and **III** (cyclic dipolarophiles) are indeed stereospecific; however dipolarophile **II** (aliphatic dipolarophile) provides a mixture of diastereoisomers.

We wanted to check, if the stereospecificity in dipolarophile **III** is due solely to the presence of the terpenic ring. For this, we did the epoxidation of the terminal double bond. This reaction provided a mixture of stereoisomers, which shows that the size of the isoxazolinic cycle also plays a certain role in the stereospecificity of the reaction. This result is consistent with the literary data regarding the epoxidation of the terminal double bonds in dipolarophile **I** and **II** [21-23].

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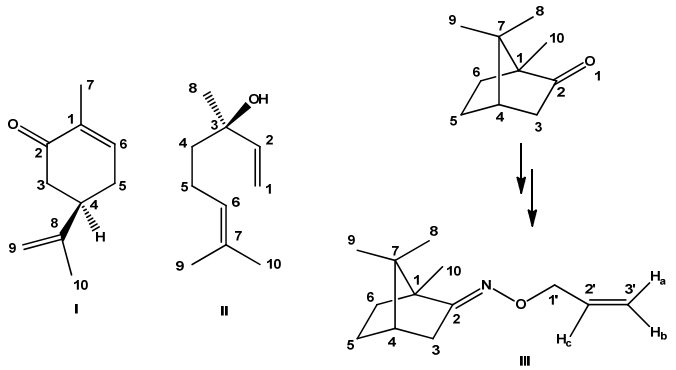


Scheme 1

2. Experimental

2.1. Instrumentation

Melting points were measured with Banc-Kofler and were confirmed on Buchi B-545. Infrared spectra were measured on Perkin-Elmer 577 and Bruker-Tensor 27. Products are dispersed solid phase in KBr. ^{1}H and ^{13}C NMR spectra were taken on Bruker Spectroscopin AC 200 and Perkin Elmer R24A in deuteriochloroform with Me_4Si as an internal standard. Chemical shifts are reported in ppm downfield from internal standard, with coupling constants in Hertz. Mass spectra were recorded with Wewlett-Packar 5995B. Optical rotations were measured on Perkin Elmer 141 polarimeter and were confirmed on electronic polarimeter ADP 220 Belligham.

2.2. Preparation of (R)-5-((S)-3-(4-chlorophenyl)-5-methyl-4,5-dihydroisoxazol-5-yl)-2-methylcyclohex-2-enone (I')

In a 200 mL erlenmeyer flack, equipped with a bromine funnel, were introduced 1.00 g of (-)-(*R*)-carvone (6.66 mmol) and 1.03 g of 4-chlorobenzaldehyde oxime in $CHCl_3$ (30 mL). The solution was stirred at 0 °C for 4 h, while 25 mL of Javel water 24° (NaOCl) were added dropwise. The mixture was stirred at room temperature for 48 h. The progress of the reaction was followed by TLC. The aqueous phase was washed with CH_2Cl_2 (50 mL), the combined organic phases were dried (Na_2SO_4) and evaporated to dryness. The oil residue was taken up with Et_2O (25 mL). A white solid appeared which was isolated by filtration (Scheme 2).

(R)-5-((S)-3-(4-chlorophenyl)-5-methyl-4,5-dihydroisoxazol-5-yl)-2-methylcyclohex-2-enone (**I'**): Color: White. Yield: 70%. M.p.: 165-167 °C. IR (KBr, ν, cm^{-1}): 1660 (C=O), 1620 (C=C). ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.82 (s, 3H, Me(12)), 1.53 (s, 3H, Me(13)), 2.20 (m, 2H, CH_2(11)), 2.32-2.83 (m, 3H, H-C(6), CH_2(7)), 3.09; 3.20 (AB, *J* = 16 Hz, 2H, CH_2(4)), 6.76-6.84 (m, 1H, H-C(10)), 7.41 (d, *J* = 9 Hz, 2H, H-C(3'), H-C(5')), 7.63 (*d*, *J* = 9 Hz, 2H, H-C(2'), H-C(6')). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm) : 16.06 (C(13)), 23.39 (C(12)), 27.52 (C(4)), 40.01 (C(6)), 44.21 (C(7)), 44.28 (C(11)), 88.82 (C(5)), 128.10 (C(3'), C(5')), 128.45 (C(4')), 129.43 (C(2'), C(6')), 135.95 (C(1')), 136.41 (C(9)), 144.72 (C(10)), 155.28 (C(3)), 199.12 (C(8)). MS (EI, *m/z* (%)): 303 (M$^+$, 80), 288 (34), 273 (28), 194 (60), 179 (40), 68 (56).

2.3. Preparation of compounds II_a and II_b

In a 200 mL erlenmeyer flack, equipped with a bromine funnel, were introduced 1.50 g of 4-chlorobenzaldehyde oxime in $CHCl_3$ (60 mL) and 1.50 mL of (-)-(*R*)-linalool. The solution was stirred at 0 °C for 45 min, while 50 mL of Javel water 24° (NaOCl) were added dropwise. The aqueous phase was washed with CH_2Cl_2 (50 mL), the combined organic phases were dried (Na_2SO_4) and evaporated to dryness. The obtained oil residue showed two separated spots on TLC (R_f : 0.52 and 0.62; $CHCl_3$, on Silica gel). The two products $\mathbf{II_a}$ and $\mathbf{II_b}$ are separated on a silica gel column (Eluent: $CHCl_3$:AcOEt, 90:10, *v:v*) (Scheme 3).

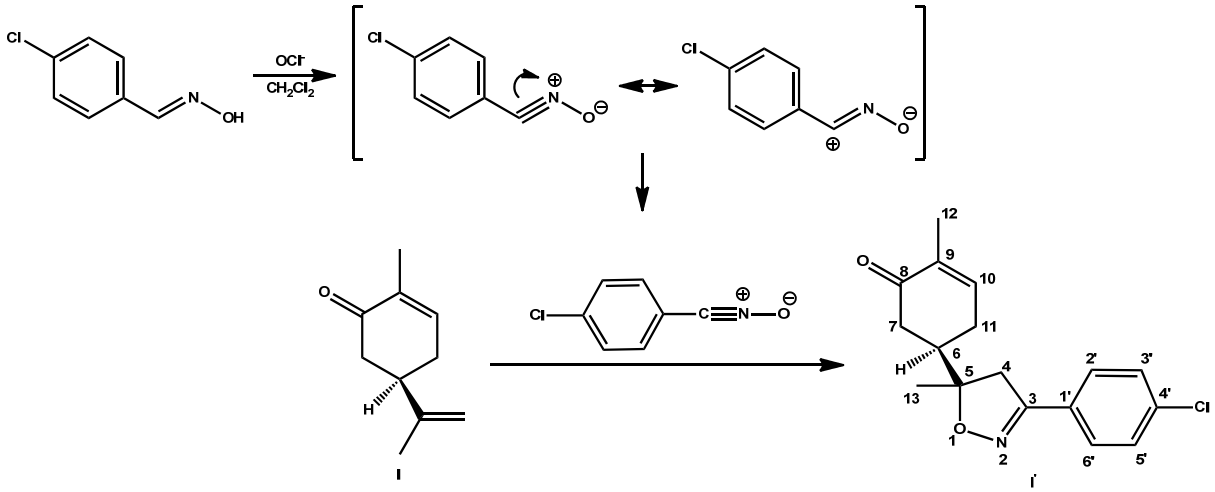
(R)-2-((S)-3-(4-chlorophenyl)-4,5-dihydroisoxazol-5-yl)-6-methylhept-5-en-2-ol ($\mathbf{II_a}$): Color: White. Yield: 70%. M.p.: 230-232 °C. IR (KBr, ν, cm^{-1}): 3330 (OH), 1600 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.15 (*s*, 3H, Me(11)), 1.44 (m, 1H, OH(6)), 1.66 (s, 3H, Me(12)), 1.71 (s, 3H, Me(13)), 1.87 (m, 2H, CH_2(7)), 2.13 (m, 2H, CH_2(8)), 3.22 (m, 2H, CH_2(4)), 4.59 (m, 1H, H-C(5)), 5.11 (m, 1H, H-C(9)), 7.26 (d, *J* = 9 Hz, 2H, H-C(3'), H-C(5')), 7.56 (d, *J* = 9 Hz, 2H, H-C(2'), H-C(6')). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm) : 21.59 (C(11)), 22.26 (C(7)), 22.42 (C(8)), 23.00 (C(12)), 35.05 (C(13)), 39.02 (C(4)), 72.82 (C(6)), 86.80 (C(5)), 123.84 (C(10)), 127.82 (C(2'), C(6')), 127.91 (C(4')), 128.50 (C(3'), C(5')), 131.99 (C(1')), 135.90 (C(9)), 156.32 (C(3)). MS (EI, *m/z* (%)): 307 (M$^+$, 90), 289 (65), 180 (45), 145 (48), 112 (40), 109 (20).

2-((R)-3-(4-chlorophenyl)-4,5-dihydroisoxazol-5-yl)-6-methyl hept-5-en-2-ol ($\mathbf{II_b}$): Color : White. Yield: 70%. M.p.: 204-206 °C. IR (KBr, ν, cm^{-1}): 3326 (OH), 1610 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.32 (s, 3H, Me(11)), 1.46 (m, 1H, OH(6)), 1.68 (s, 3H, Me(12)), 1.75 (s, 3H, Me(13)), 1.89 (m, 2H, CH_2(7)), 2.16 (m, 2H, CH_2(8)), 3.36 (m, 2H, CH_2(4)), 4.69 (m, 1H, H-C(5)), 5.15 (m, 1H, H-C(9)), 7.35 (d, *J* = 9 Hz, 2H, H-C(3'), H-C(5')), 7.59 (d, *J* = 9 Hz, 2H, H-C(2'), H-C(6')). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm) : 21.93 (C(11)), 22.42 (C(7)), 22.26 (C(8)), 23.18 (C(12)), 35.28 (C(13)), 39.05 (C(4)), 72.94 (C(6)), 86.83 (C(5)), 123.89 (C(10)), 127.61 (C(2'), C(6')), 127.91 (C(4')), 128.89 (C(3'), C(5')), 132.21 (C(1')), 134.20 (C(9)), 156.35 (C(3)). MS (EI, *m/z* (%)): 307 (M$^+$, 70), 289 (75), 180 (45), 145 (52), 112 (60), 109 (32).

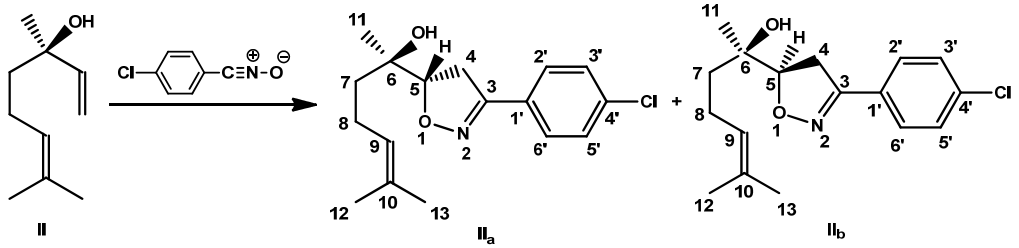
2.4. Preparation of (1S,4S,E)-1,7,7-trimethylbicyclo[2.2.1] heptan-2-one O-allyloxime (III)

In a balloon we dissolve 1.36 g of NaOH (34 mmol) and 2.26 g (32 mmol) of H_2NOH/HCl in 10 mL of distilled H_2O, then we add 2 g (13 mmol) of (-)-(1*S*,4*S*)-Camphor in 30 mL of ethanol, we obtain a limpid solution. 20 hours of reflux was necessary, then the ethanol was evaporated, the aqueous phase was cooled. It's form a crystal of oxime that we recrystallized in pentane (P.F.: 120 °C, Yield: 85%).

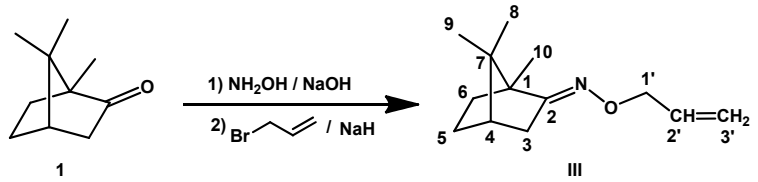
On a solution with 4 g (23.9 mmol) of oxime in 50 mL of toluene we add with little fraction 0.65 g (23.9 mmol) of NaH under nitrogen and agitation. After 5 min, 23 mmol of allylbromure was introduced; the mixture was left under agitation at room temperature for 12 hours. The organic phase extract was dried; the toluene was eliminated under low pressure. The residue was separated and purified on silica gel (Hexane:AcOEt, 95:5, *v:v*), to give compound **III**.



Scheme 2



Scheme 3



Scheme 4

(1S,4S,E)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one o-allyl oxime (**III**): Color: White. Yield: 72%. M.p.: 154-156 °C. IR (KBr, ν, cm^{-1}): 3010 (C-H), 1645 (C=N), 1640 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.82 (s, 3H, Me(10)), 0.94 (s, 3H, Me(8)), 1.02 (s, 3H, Me(9)), 1.55-1.92 (m, 5H, CH(4), CH_2(5), CH_2(6)), 2.22 (m, 2H, CH_2(3)), 5.12 (d, *J* = 3 Hz, 1H, CH_a(3')), 5.22 (d, *J* = 3 Hz, 1H, CH_b(3')), 5.43 (d, *J* = 2 Hz, 2H, CH_2(1')), 6.04 (m, 1H, CH_c(2')). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm) : 12.52 (C(4)), 18.62 (C(5)), 19.75 (C(6)), 27.50 (C(1)), 32.50 (C(3)), 34.56 (C(7)), 44.15 (C(10)), 48.22 (C(9)), 52.32 (C(8)), 74.54 (C(1')), 118.62 (C(2')), 135.24 (C(3')), 170.22 (C(2)).

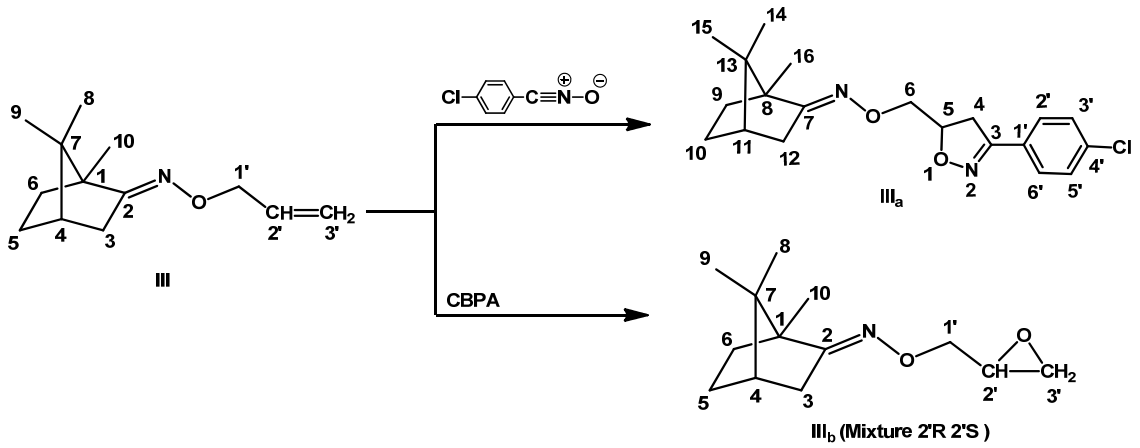
2.5. Preparation of compound III$_a$

In a 200 mL erlenmeyer flack, equipped with a Br_2 funnel, were introduced 1.30 g of 4-chlorobenzaldehyde oxime in $CHCl_3$ (80 mL) and 1.84 g (9.60 mmol) of **III**. The solution was stirred at 0 °C for 60 min. With the same **I'** obtention procedure, the reaction gave an isoxazolinic compound **III$_a$** in pure form for analysis (Scheme 4 and 5).

(1S,4S,E)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one o-((3-(4-chlorophenyl)-4,5-dihydroisoxazol-5-yl)methyl) oxime (**III$_a$**): Color: White. Yield: 82%. M.p.: 218-220 °C. IR (KBr, ν, cm^{-1}): 1640 (C=N), 1620 (C=C), 1045 (C-H). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.92 (s, 3H, Me(16)), 0.97 (s, 3H, Me(15)), 1.04 (s, 3H, Me(14)), 1.72-1.94 (m, 5H, CH(11), CH_2(9), CH_2(10)), 2.32 (m, 2H, CH_2(12)), 4.12 (d, *J* = 3 Hz, 1H, H-C(6)), 4.16 (d, *J* = 3 Hz, 1H, H-C(6)), 3.62 (m, 2H, CH_2(4)), 4.71 (m, 1H, H-C(5)), 7.42 (d, *J* = 9 Hz, 2H, H-C(3'), H-C(5')), 7.72 (d, *J* = 9 Hz, 2H, H-C(2'), H-C(6')). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm) : 20.74 C(13)), 21.40 (C(11)), 24.15 (C(10)), 27.94 (C(9)), 39.45 (C(8)), 44.20 (C(4)), 52.67 (C(15)), 54.20 (C(14)), 56.40 (C(16)), 67.82 (C(6)), 82.25 (C(5)), 127.41 (C(2'), C(6')), 128.15 (C(4')), 129.15 (C(3'), C(5')), 132.41 (C(1')), 158.21 (C(3)), 167.63(C(7)). MS (EI, *m/z* (%)): 360 (M^+, 94), 345 (38), 211 (40), 193 (60), 158 (30), 167 (75), 152(25), 149 (65).

2.6. Preparation of (1S,4S,E)-1,7,7-trimethylbicyclo[2.2.1] heptan-2-one O-oxiran-2-ylmethyl oxime (III$_b$)

Under moderate agitation and ambient temperature we dissolved 0.50 g (2.40 mmol) of the compound **III** and 0.83 g (4.80 mmol) of metachloroperbenzoic acid in 10 mL of CH_2Cl_2.



Scheme 5

The reaction is left overnight, the mixture is then cooled to remove the formed benzoic acid. The filtrate is washed by the sodium bisulfite 20%, then by Na_2SO_4 10% and finally by a saturated solution of NaCl. The organic phase is dried on $MgSO_4$ and evaporated to dry. The resulting residue provides **III$_b$** after purification on silica gel (Eluent, Hex:AcOEt, 90:10, *v:v*) (Scheme 4 and 5).

(1S,4S,E)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one o-oxiran -2-ylmethyl oxime (**III$_b$**): Color: Yellow. Yield: 70%. IR (Film, ν, cm^{-1}): 1075 (C-O-C), 1653 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.84 (s, 3H, Me(10)), 0.92 (s, 3H, Me(8)), 1.10 (s, 3H, Me(9)), 1.66-1.85 (m, 5H, CH(4), CH_2(5), CH_2(6)), 2.28 (m, 2H, CH_2(3)), 2.21, 3.22 (ABX, 3H, CH_2(3'), H-C(2')), 4.02 (d, *J* = 2 Hz, 2H, CH_2(1')). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm) : 13.04 C(4)), 19.12 (C(5)), 20.14 (C(6)), 28.12 (C(1)), 32.75 (C(3)), 35.22 (C(7)), 47.12 (C(10)), 50.22 (C(9)), 55.12 (C(8)), 62.20 (C(2')), 68.17 (C(3')) 70.40 (C(1'), 172.15 (C(2)).

3. Results and discussion

3.1. Formation of compound I'

(-)-*R*-Carvone **I**, $[\alpha]^{20}_D$ = -61±2 ° was isolated from *Mentha viridis* (L.), a plant cultivated in Morocco. It was identified by combination of chromatographic and spectroscopic methods. This compound alone represents 70% of the essential oil of the plant.

Addition of *p*-chlorophenylnitrile oxide to (-)-*R*-Carvone took place in a chloroform environment with stirring at 0 °C. The addition has affected only the double bond in C_8 to give isoxazoline **I'** (Scheme 2).

3.2. Formation of compounds II$_a$ and II$_b$

(-)-*R*-Linalool **II**, $[\alpha]^{20}_D$ = - 20±2 ° is the majority (60-70%) constituent of the essential oil from *Lavandula officinalis* (L.). It was isolated by fractionary distillation using a micro oven and identified by spectroscopic methods.

The addition of the dipole was held in chloroform medium, under agitation at 0 °C. The reaction has only affected the less substituted vinyl double bond, giving an appreciable quantity of two separable diastereoisomers (Scheme 3).

3.3. Formation of compound III

The natural camphor is a main constituent of several essential oil [8,11,12]. The dextrogyre isomeric is the most shed in nature, then that his enantiomeric levogyre is then rare. The Moroccan *Artemisia herba alba* (Asso) is rich into this last compound, and will present a particular interest [8]. In our study, our choice was tacked of levogyre camphor for two reasons: First, his rarity in nature then that Moroccan *Artemisia* contains about 70% of it into his essential oil. The second reason that it used rarely in organic synthesis. These two reasons give originality for our compounds that we have synthesised.

(-)-(1*S*,4*S*)-Camphre **1** was isolated from *Artemisia herba alba (Asso)* his natural site. This species harvested in Morocco at flowering period, was passed on hydro distillation in dry state. The essential oil obtained was distilled under moderate temperature until draining all light products. After cooling a residue, (-)-(1*S*,4*S*)-Camphre **1** deposit. Filtered and recrystallized in pentane, the (-)-(1*S*,4*S*)-Camphre **1** was obtained in a pure state. PF = 178 °C; $[\alpha]_D^{20}$ = -42.5±2° (c = 10, Ethanol).

When NH_2OH react on **1**, this reaction was followed by the action of the allylbromure into toluene in the presence of NaH, at ambient temperature; we got the compound O-alkylated **III** (Scheme 4).

3.4. Formation of compounds III$_a$ and III$_b$

In order to synthesize new molecules susceptible to present some pharmacodynamic applications from camphor derivative, we have added *p*-chlorophenylnitrile oxide to dipolarophile **III**. The reaction took place in the presence of Javel water 24° with stirring at 0 °C for 36 hours. We obtained new compound, with heterocyclic structure isoxazoline **III$_a$** (Scheme 5).

The same camphor derivative **III** furnish a mixture of epoxid (2'*R*,2'*S*) **III$_b$** after action of metachloroperbenzoic acid (CPBA) (Scheme 5).

4. Conclusion

Under identical operating conditions, we reacted in the presence of *p*-chlorophenylnitrile oxide, the constituents of the Moroccan medicinal plants, namely: (-)-*R*-Carvone, (-)-*R*-Linalool, and (-)-(1*S*,4*S*)-camphor. The new heterocycles obtained allowed us to obtain the following findings: from structural point of view, we noticed that the oxygen atom of the dipole always binds to the more substituted carbon. Stereochemical terms, we noticed that the presence of the terpene cycle (regardless of the length of the side chain) has played an important role in the guidance and the stereospecificity of the reaction.

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