

**UNIVERSITE DE CORSE PASCAL PAOLI
FACULTE DES SCIENCES ET TECHNIQUES**

**CARACTERISATION PAR CPG/IK, CPG/SM
ET RMN DU CARBONE-13
D'HUILES ESSENTIELLES DE MADAGASCAR**

Jean-François CAVALLI

Madagascar

Capitale : Antananarivo

Superficie : 587 041 km²

Population : 13 500 000 h.

Relief : Plateau (1000 à 1500 m) surmonté de reliefs volcaniques (Tsaratanana, 2886 m) et bordé de plaines littorales.

Climat : Tropical humide à l'Est (cyclones), sec à l'Ouest.

Économie : Agriculture vivrière (riz, manioc) et commerciale (café, épices, tabac, coton).

Plantes aromatiques : huiles essentielles.

Déforestation et surpâturage menacent les sols.



Huiles essentielles de Madagascar

- ◆ Les méthodes d'analyses d'un mélange complexe
- ◆ CPG/SM
- ◆ RMN du carbone-13

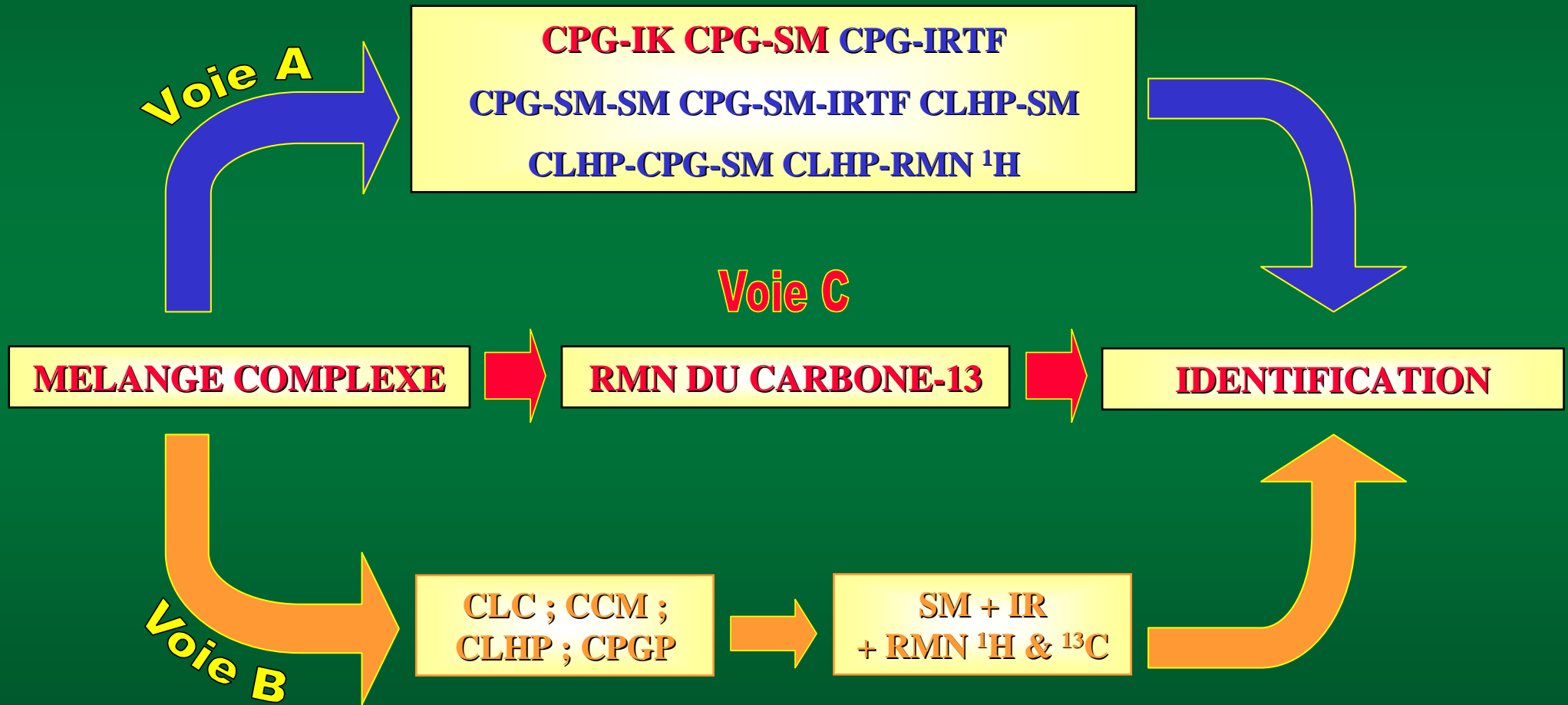
◆ Diverses huiles essentielles de Madagascar : *Cinnamomum camphora*, *Cupressus lusitanicus*, *Tagetes bipinata*, *Lantana camara*, *Eucalyptus citriodora* et *Chenopodium ambrosioides*.

◆ L'huile essentielle d'écorce de *Cedrelopsis grevei*.

◆ *Helichrysum* de Madagascar : *H. gymnocephalum*, *H. bracteiferum*, *H. faradifani*, *H. selaginifolium*, *H. cordifolium*, *H. hypnoides* et *Helichrysum* sp.

◆ Conclusion

Les méthodes d'analyse d'un mélange complexe

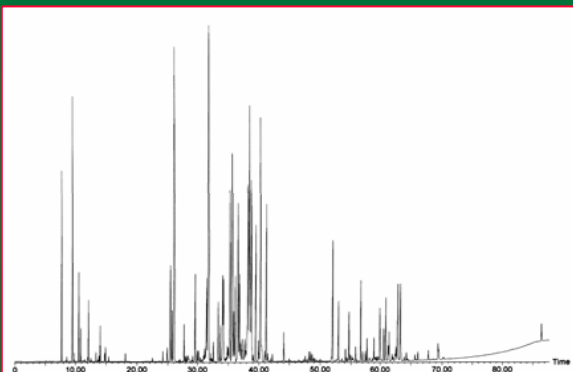


Identification des composés d'une huile essentielle par CPG/IK et CPG/SM

HUILE ESSENTIELLE

CPG/IK

CHROMATOGRAMME DE
L'HUILE ESSENTIELLE

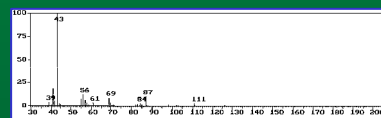
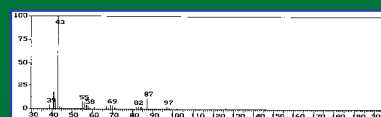
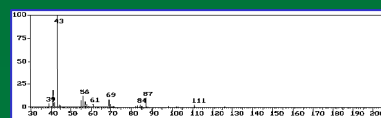
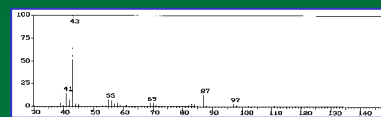
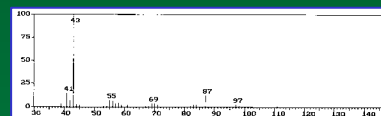


- IK POLAIRE
- IK APOLAIRE
- QUANTIFICATION

IDENTIFICATION

CPG/SM

Spectres de masse
de chaque composé
du mélange complexe



BANQUES DE
SPECTRES

Informatisées

- ARÔMES
(Composés terpéniques)
- NIST
- WILEY
- KÖNIG

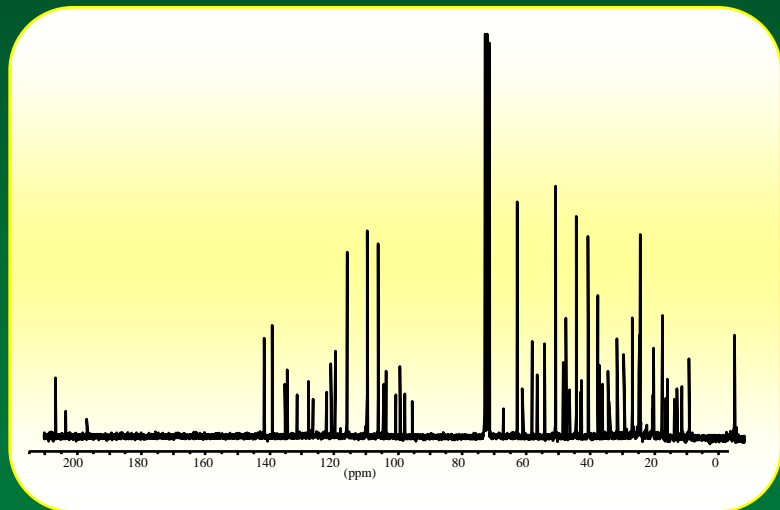
Non informatisées

- WILEY
- JOULAIN
- ADAMS

LOGICIEL D'AIDE A L'IDENTIFICATION

- COMPARAISON DES DIFFERENTS
SPECTRES DE MASSE
- PROPOSITION D'UNE STRUCTURE
(NOTE DE CONCORDANCE)

Identification des constituants d'un mélange complexe par RMN du carbone-13



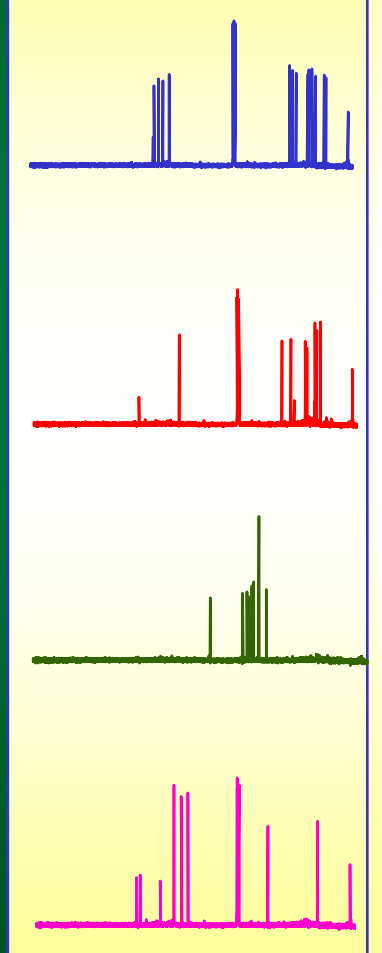
SPECTRE DU MELANGE COMPLEXE



LOGICIEL D'AIDE A L'IDENTIFICATION

BIBLIOTHEQUES DE SPECTRES

- COUMARINES
- TRIGLYCERIDES
- PHENOLS
- SUCRES
- TERPENES

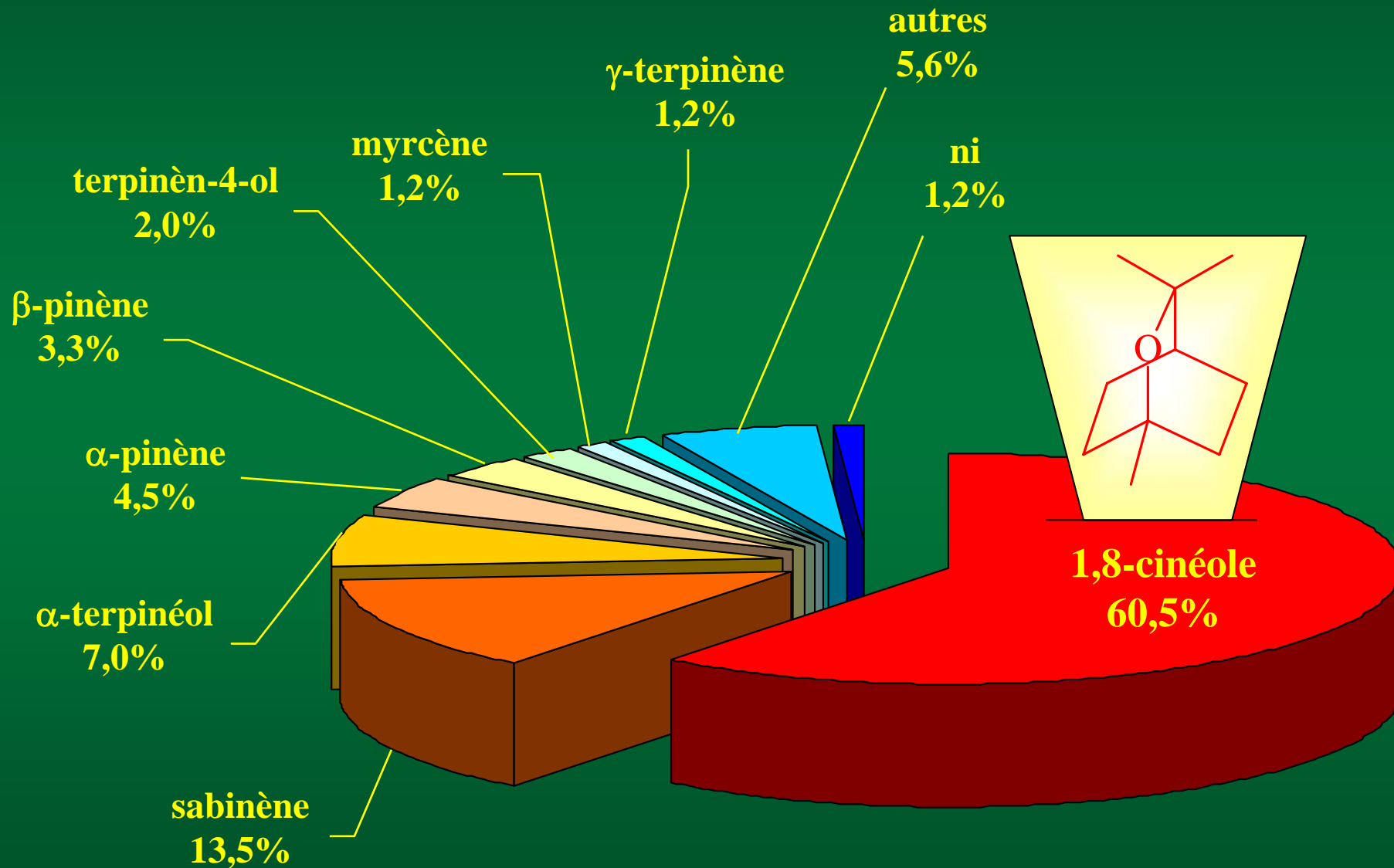


A vertical stack of four 13C NMR spectra, each corresponding to a different chemical class: blue (top), red, green, and magenta (bottom). Each spectrum shows a unique pattern of peaks characteristic of that class.

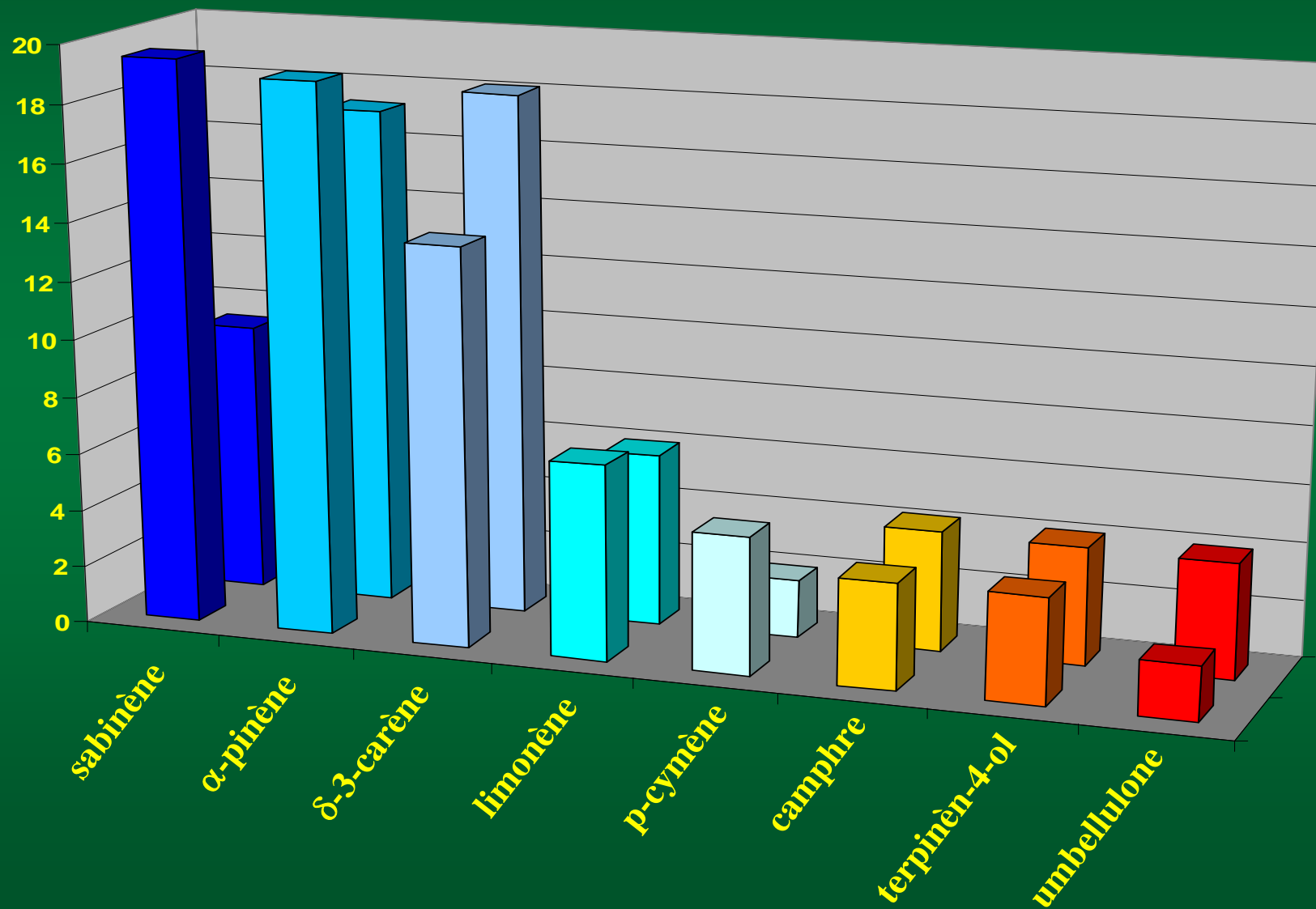
NOMBRE DE CARBONES OBSERVES
NOMBRE DE SUPERPOSITIONS
VARIATIONS DES DEPLACEMENTS CHIMIQUES

IDENTIFICATION

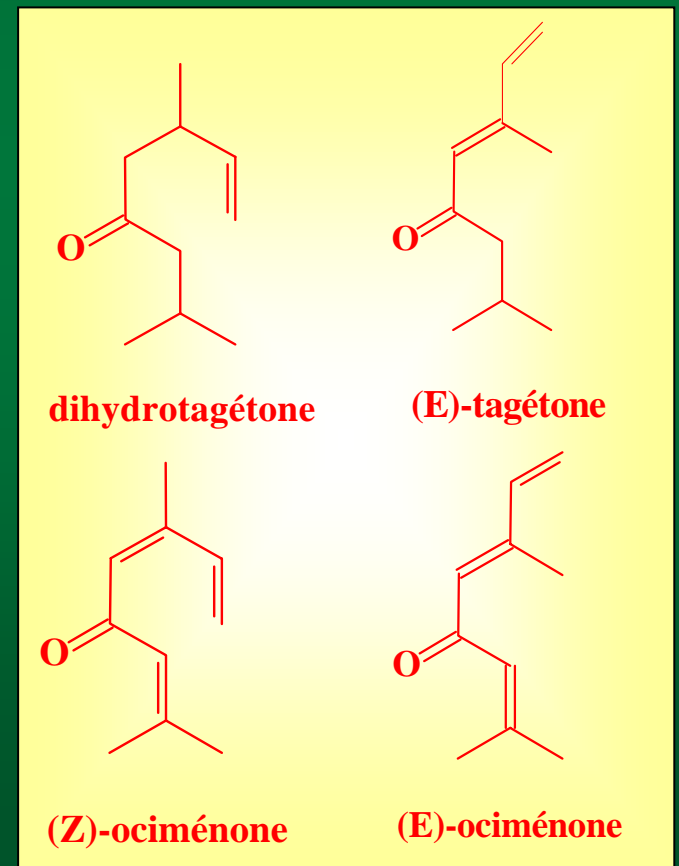
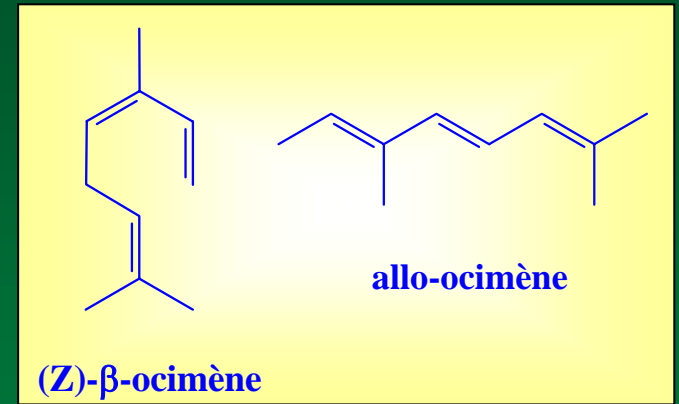
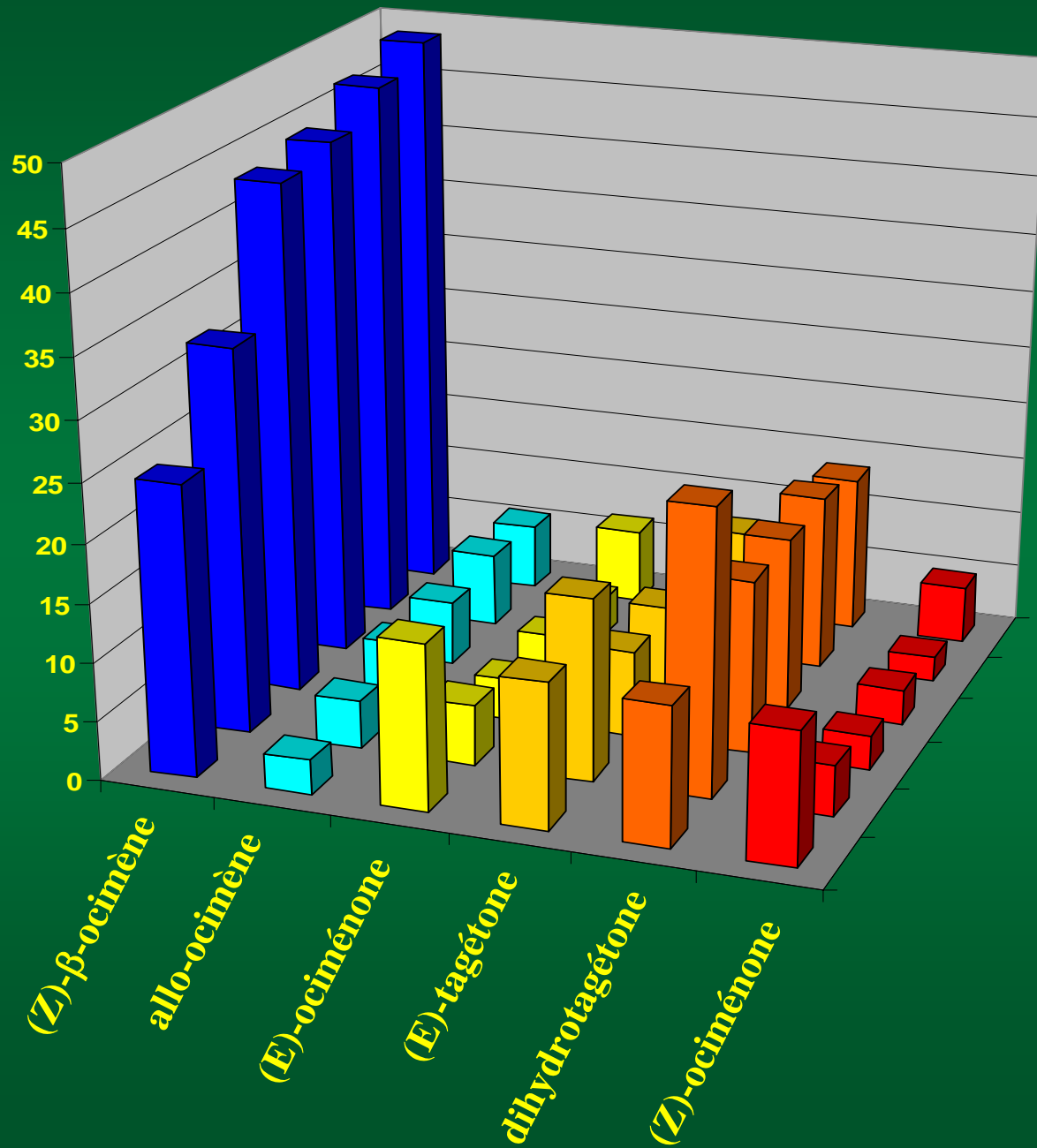
L'huile essentielle de *Cinnamomum camphora*



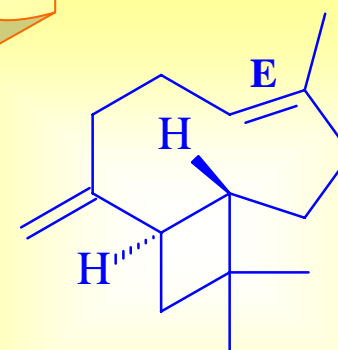
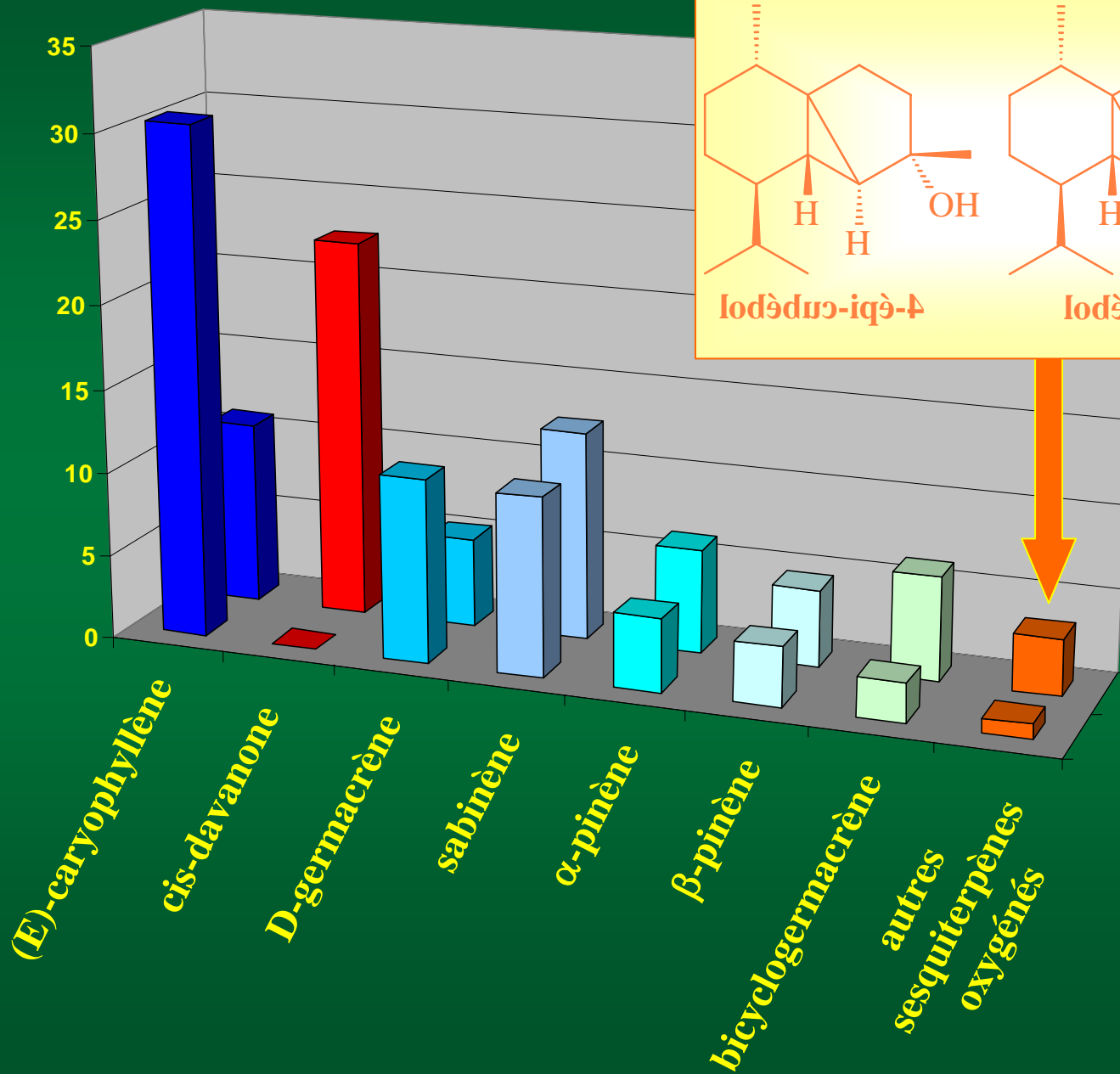
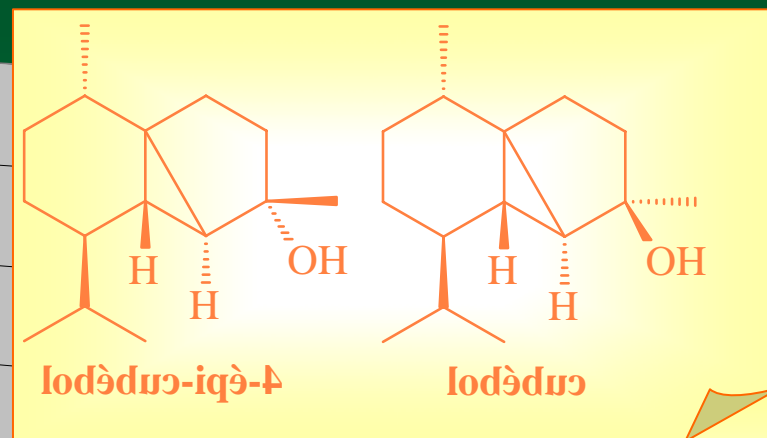
L'huile essentielle de *Cupressus lusitanicus*



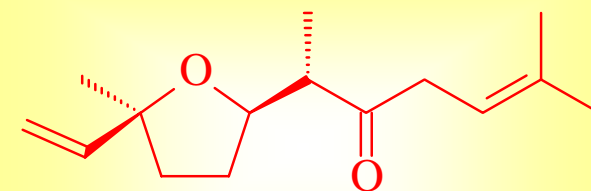
L'huile essentielle de *Tagetes bipinata*



L'huile essentielle de *Lantana camara*



(E)-caryophyllène



cis-davanone

L'huile essentielle d'*Eucalyptus citriodora*

acétate de citronellyle 4,3%

β -pinène 1,2%

autres 5,3%

ni 8,7%

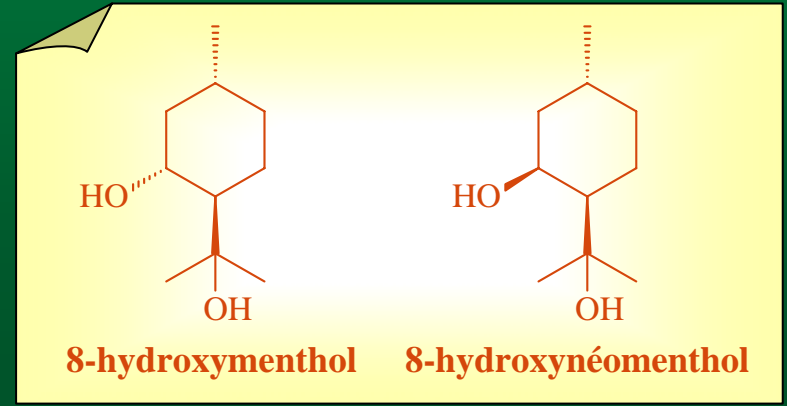
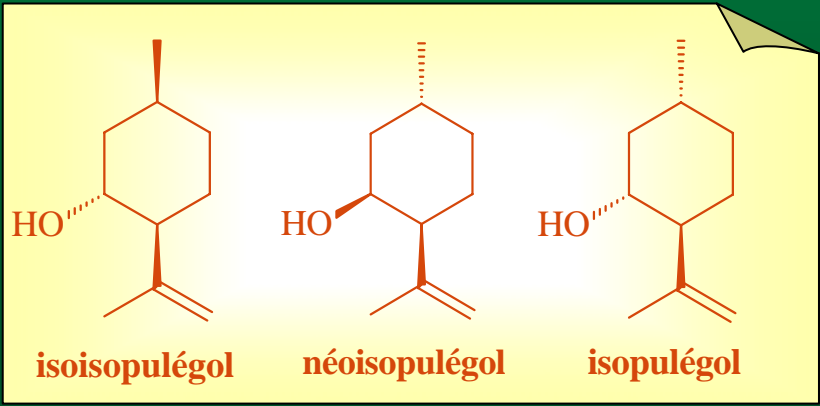
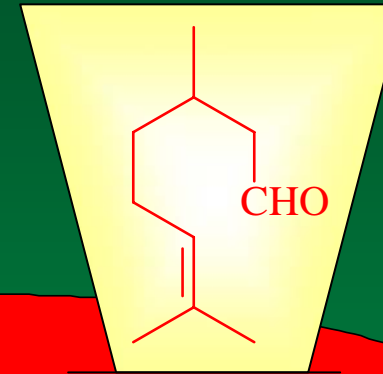
citronellol 6,7%

isoisopulégol 1,0%

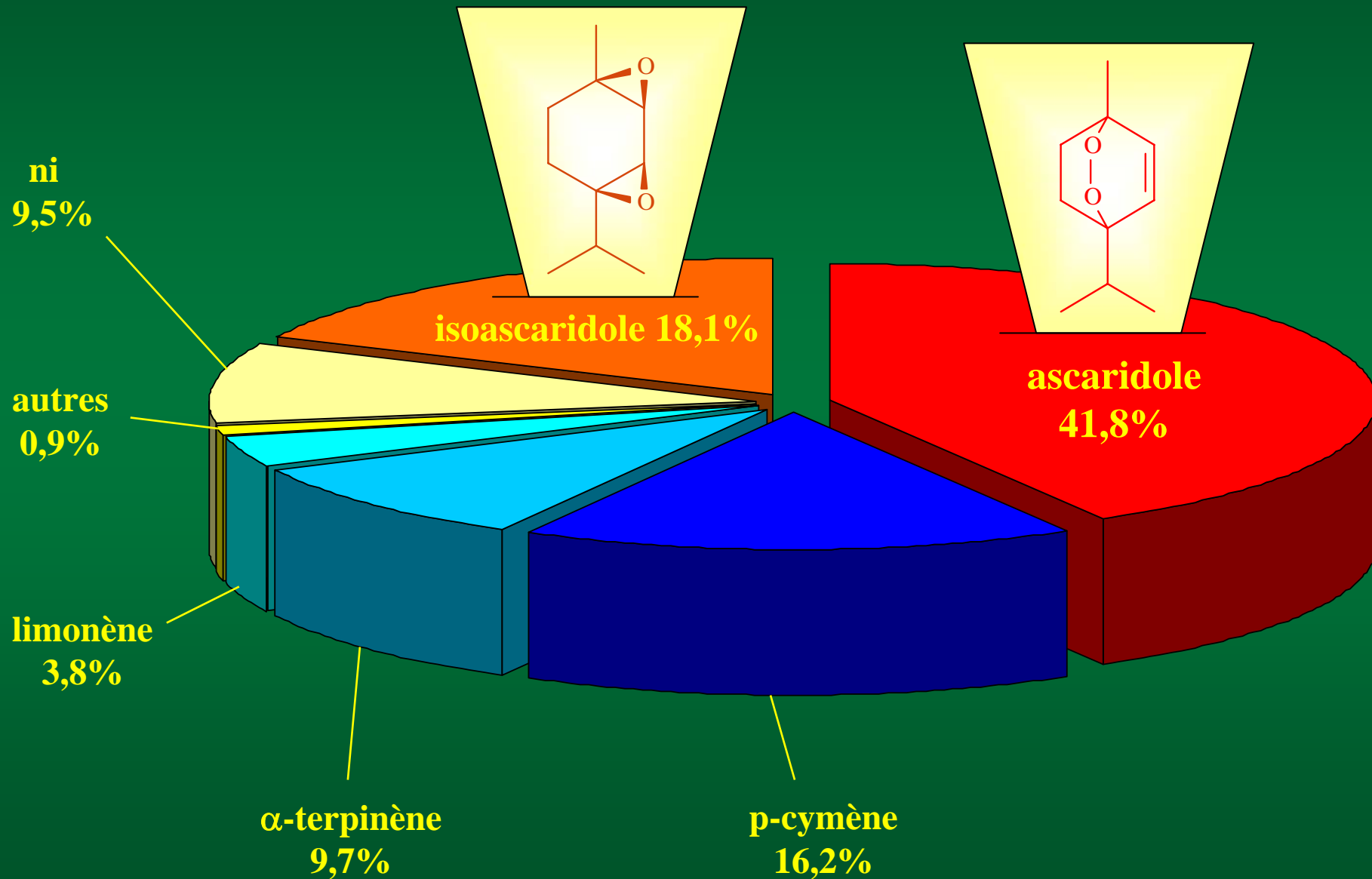
néoisopulégol 9,0%

isopulégol 16,9%

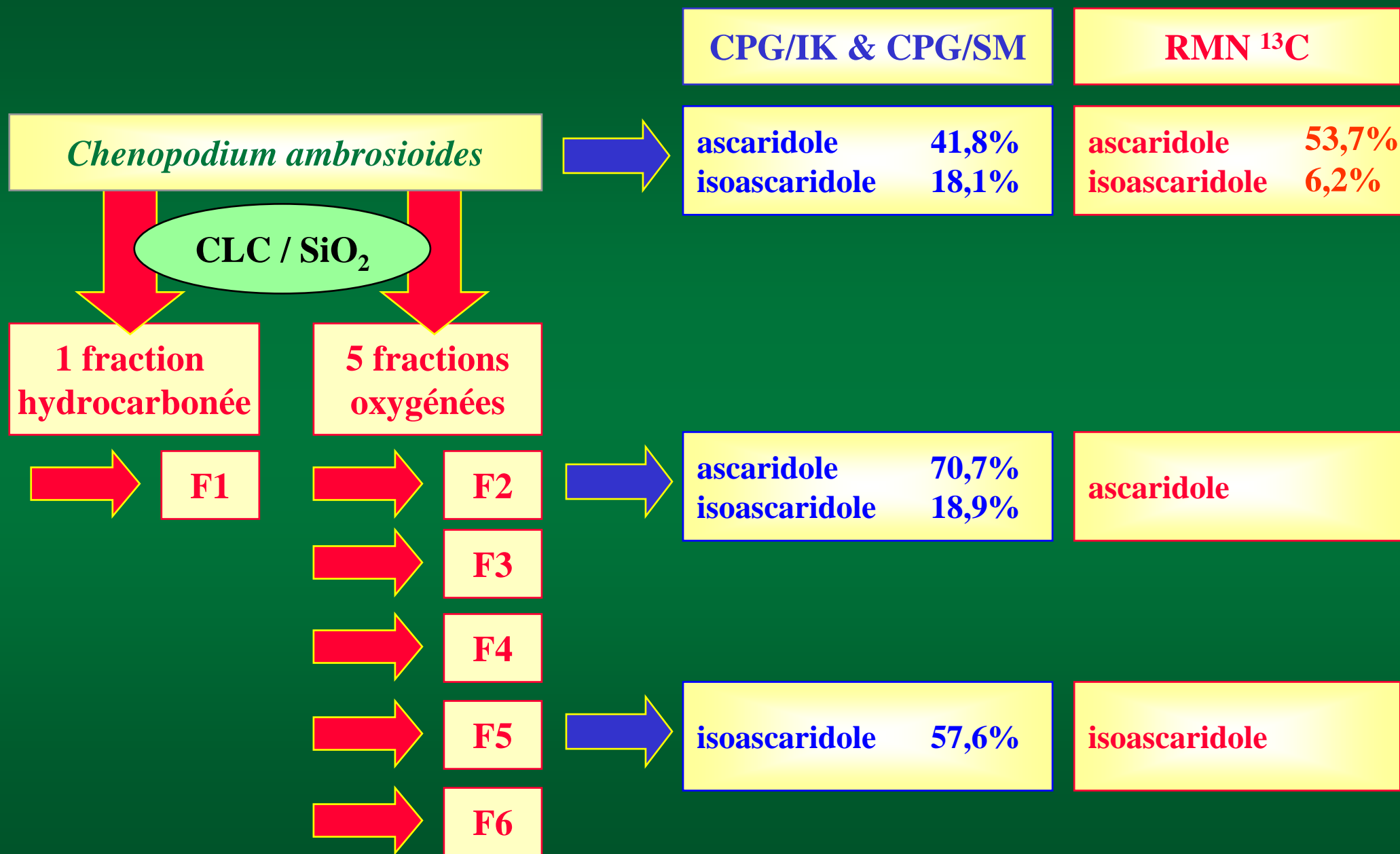
citronellal 46,9%



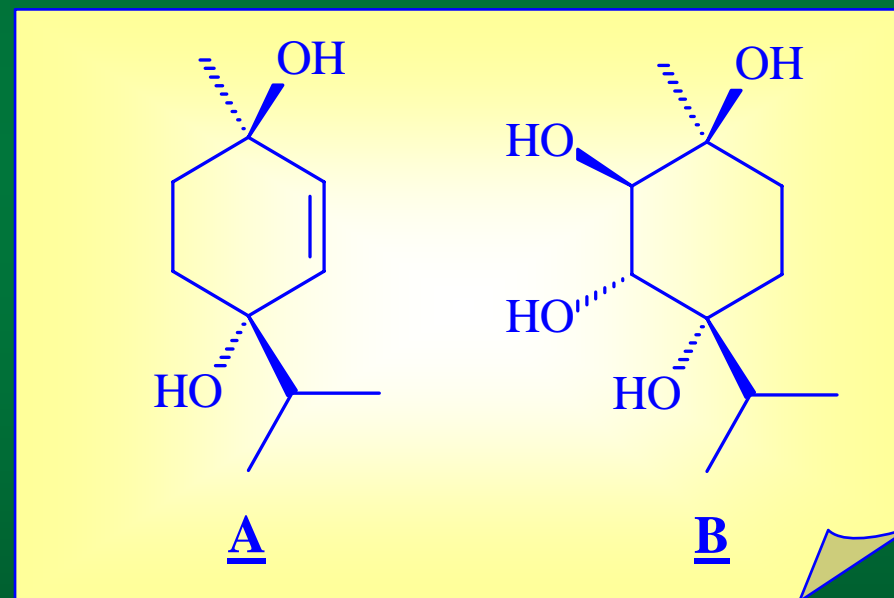
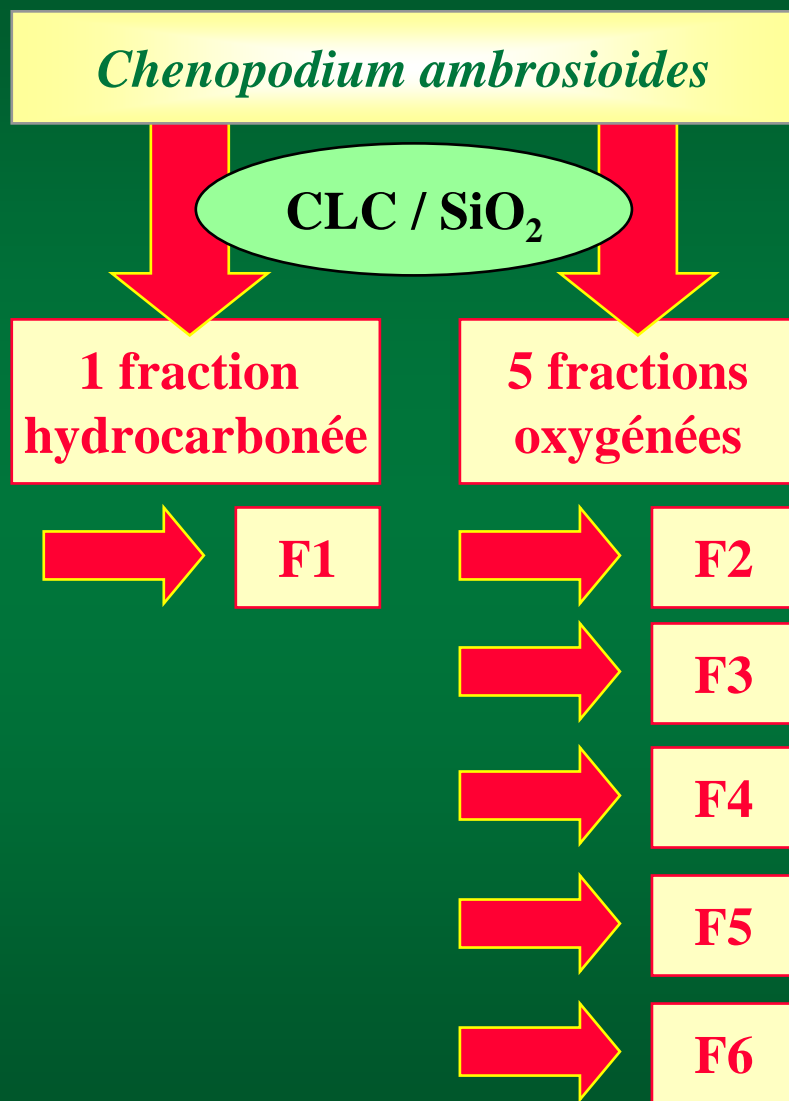
L'huile essentielle de *Chenopodium ambrosioides*



L'huile essentielle de *Chenopodium ambrosioides*

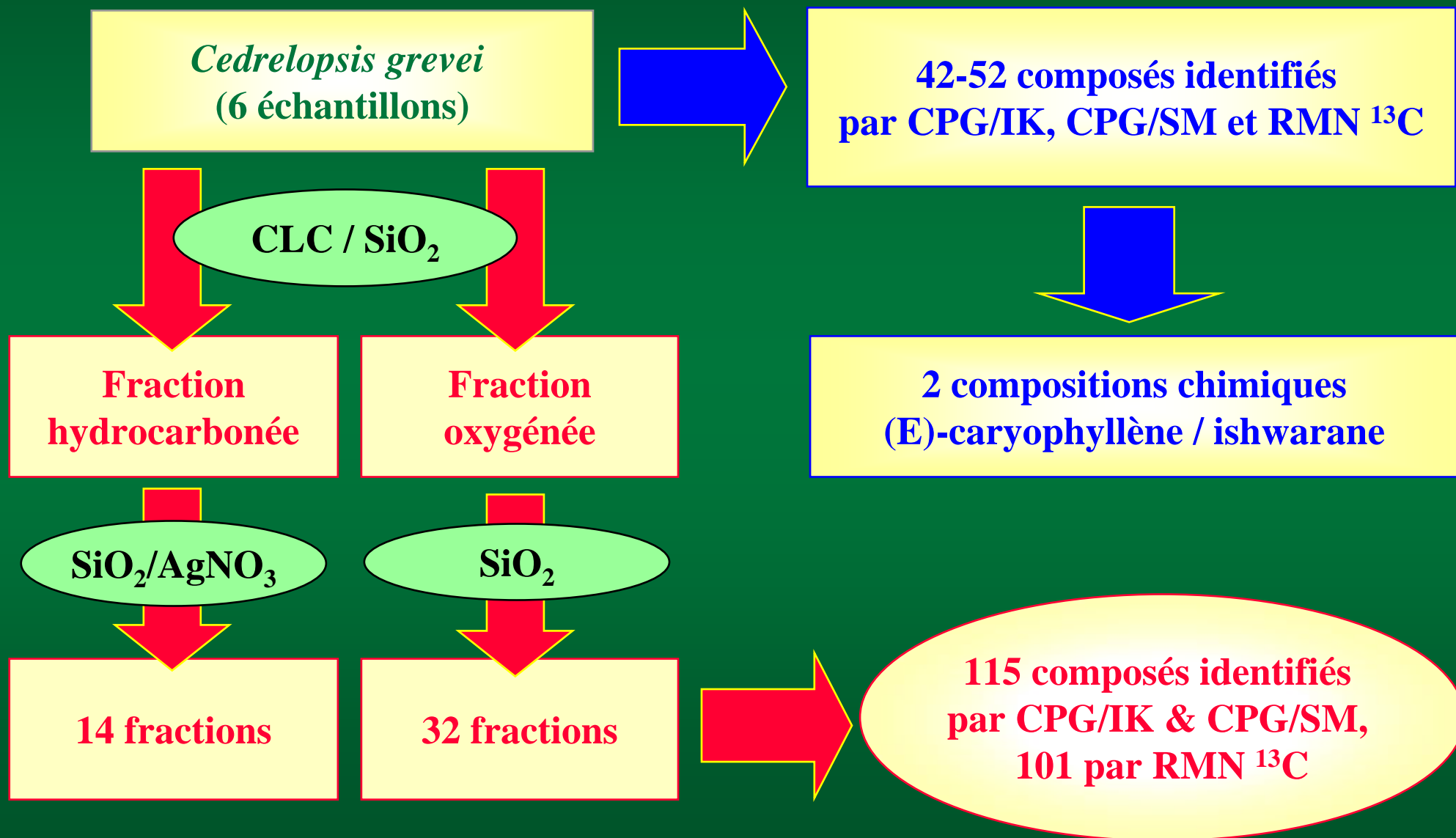


L'huile essentielle de *Chenopodium ambrosioides*



1,4-dihydroxy-p-menth-2-ène (A)
1,2,3,4-tetrahydroxy-p-menthane (B)

L'huile essentielle d'écorce de *Cedrelopsis grevei*



Cedrelopsis grevei

14 Fractions hydrocarbonées

Identification de 53 composés hydrocarbonés

Bibliothèques "Arômes" & "Terpènes"

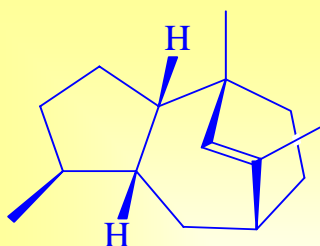
48 composés hydrocarbonés

Bibliothèques littéraires

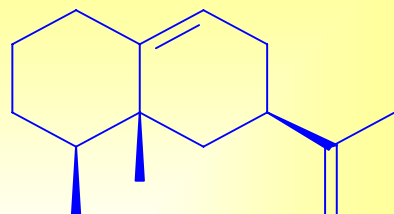
4 composés hydrocarbonés :
rotundène, 4,5-di-épi-aristolochène,
cadalène et trans-calaménène

Reconstruction du spectre de RMN

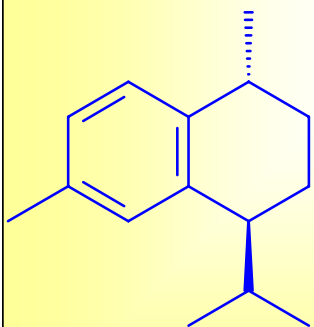
1 composé hydrocarboné :
 β -curcumène



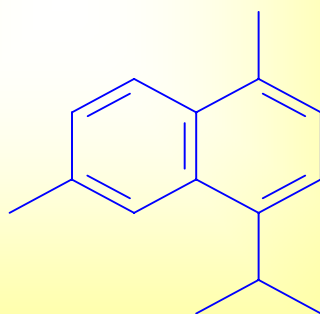
rotundène



4,5-di-épi-aristolochène



trans-calaménène

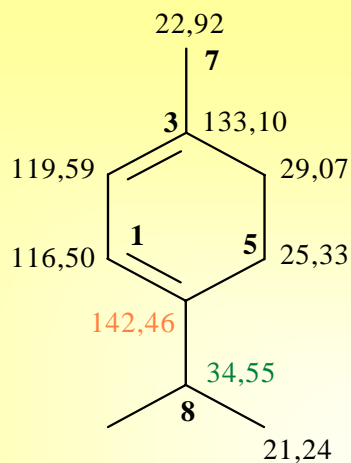


cadalène

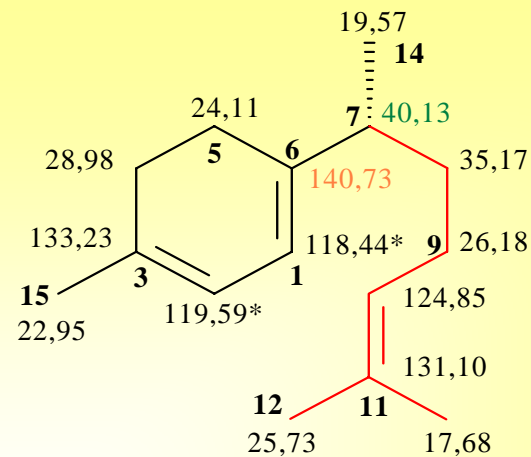
Cedrelopsis grevei

β -curcumène

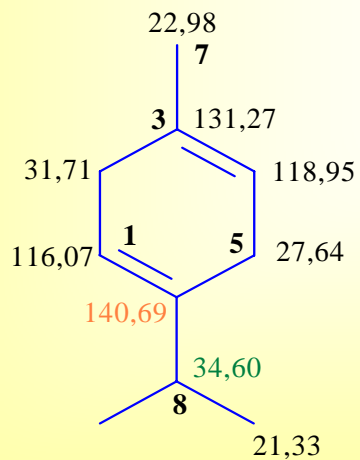
14 Fractions hydrocarbonées



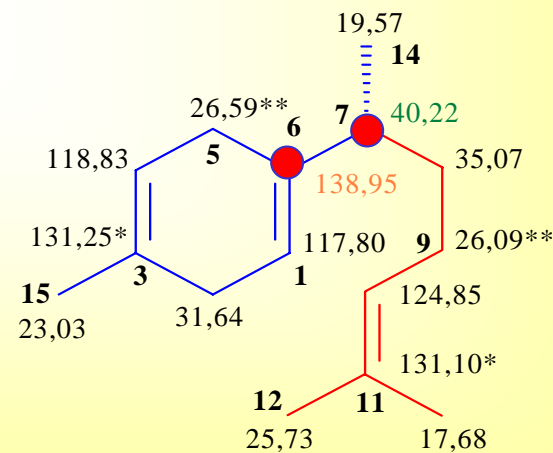
α -terpinène



γ -curcumène

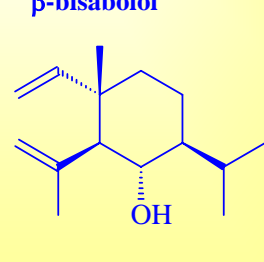
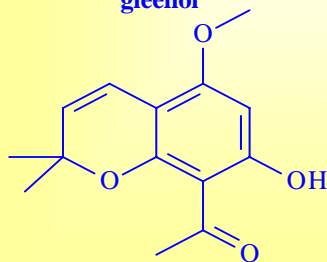
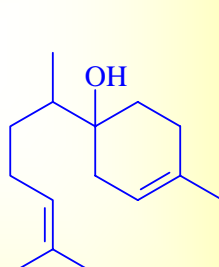
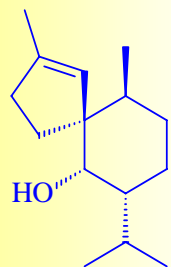
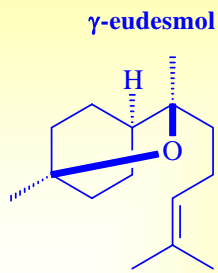
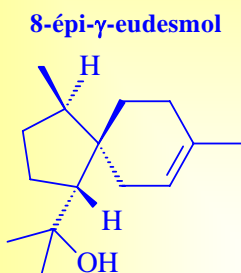
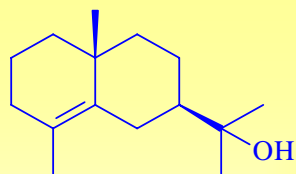
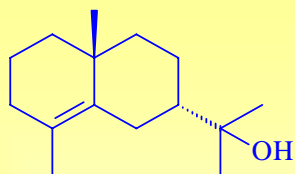


γ -terpinène



β -curcumène

Identification de 62 composés oxygénés



Bibliothèques "Arômes" & "Terpènes"

49 composés oxygénés

Bibliothèques littéraires

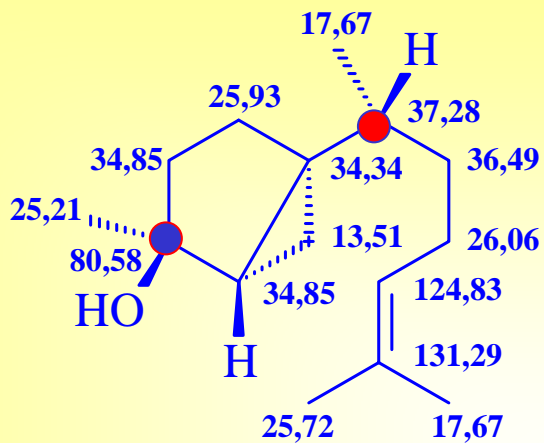
12 composés oxygénés :

8-épi-γ-eudesmol, γ-eudesmol, sesquicinéole, α-acorénol, gleenol, β-bisabolol, 6-épi-shyobunol, alloévodionol et 4 hydrates du sesquisabinène

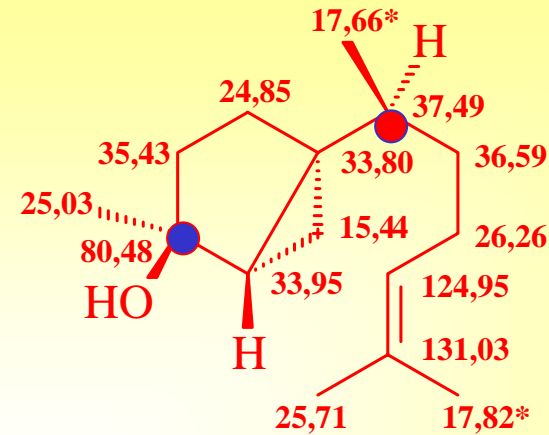
Composé non décrit en SM & RMN ¹³C

1 composé oxygéné :

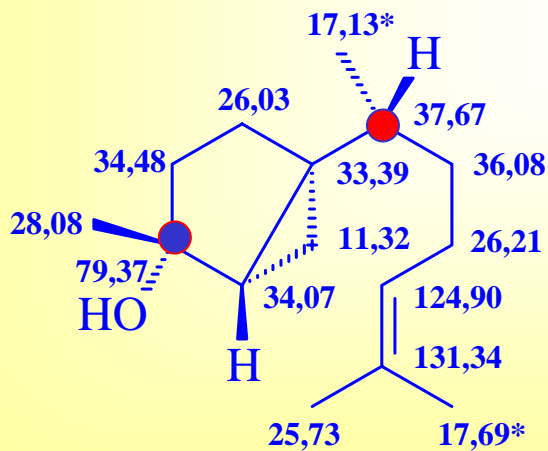
4-épi-cis-dihydroagarofurane



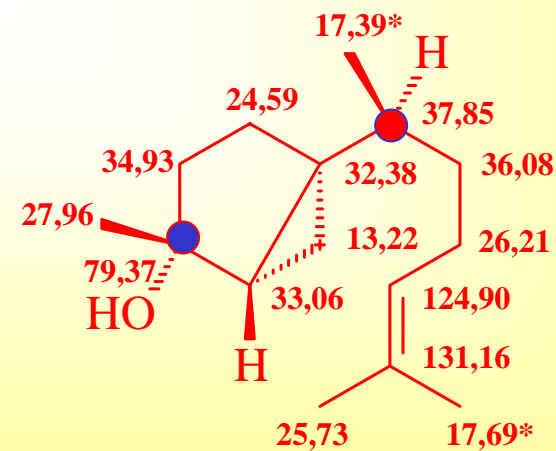
hydrate de trans-sesquibabinène



hydrate de 7-épi-trans-sesquibabinène



hydrate de cis-sesquibabinène

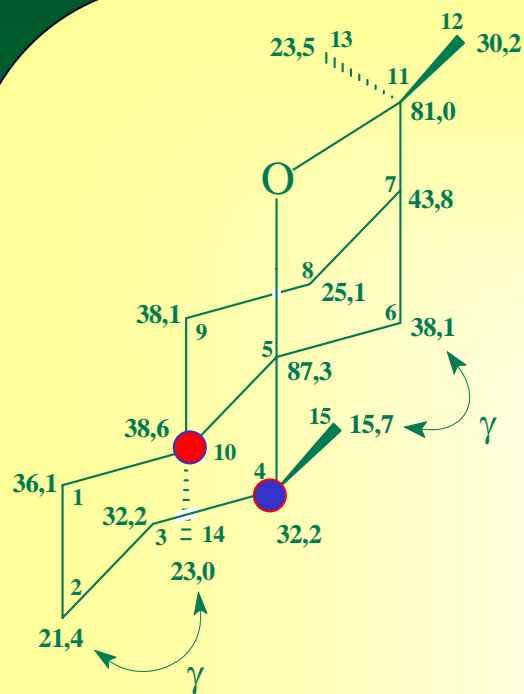


hydrate de 7-épi-cis-sesquibabinène

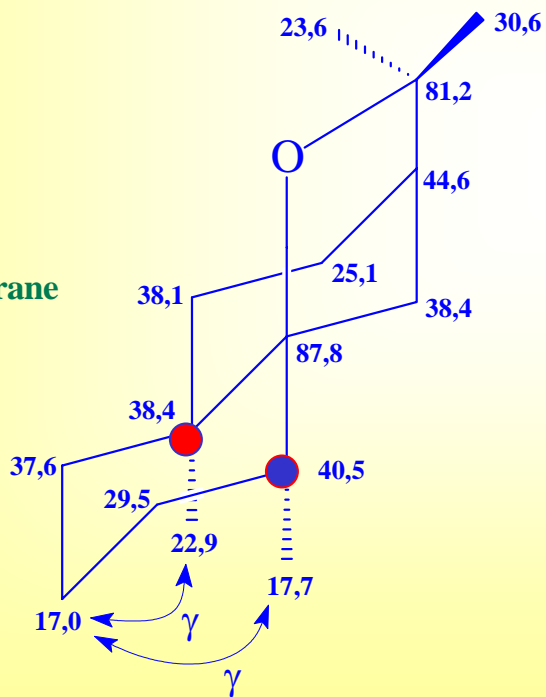
Cedrelopsis grevei

4-épi-cis-dihydroagarofurane

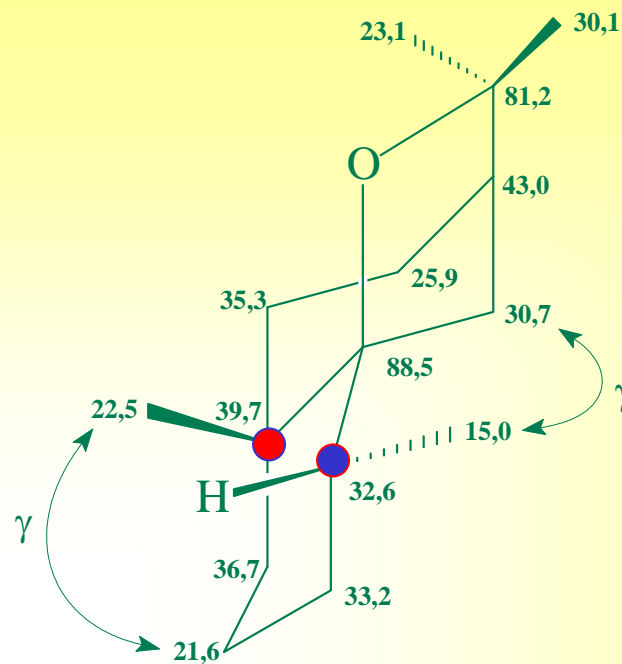
32 Fractions oxygénées



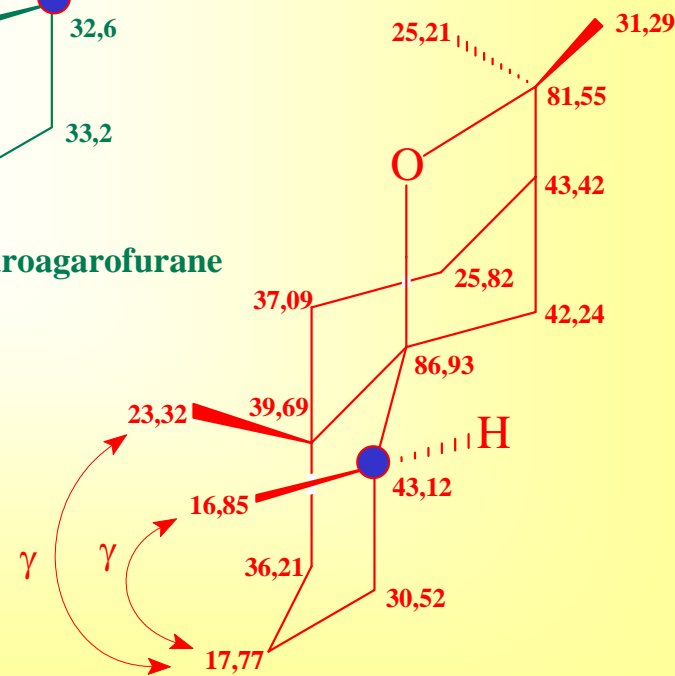
isodihydroagarofurane



trans-dihydroagarofurane

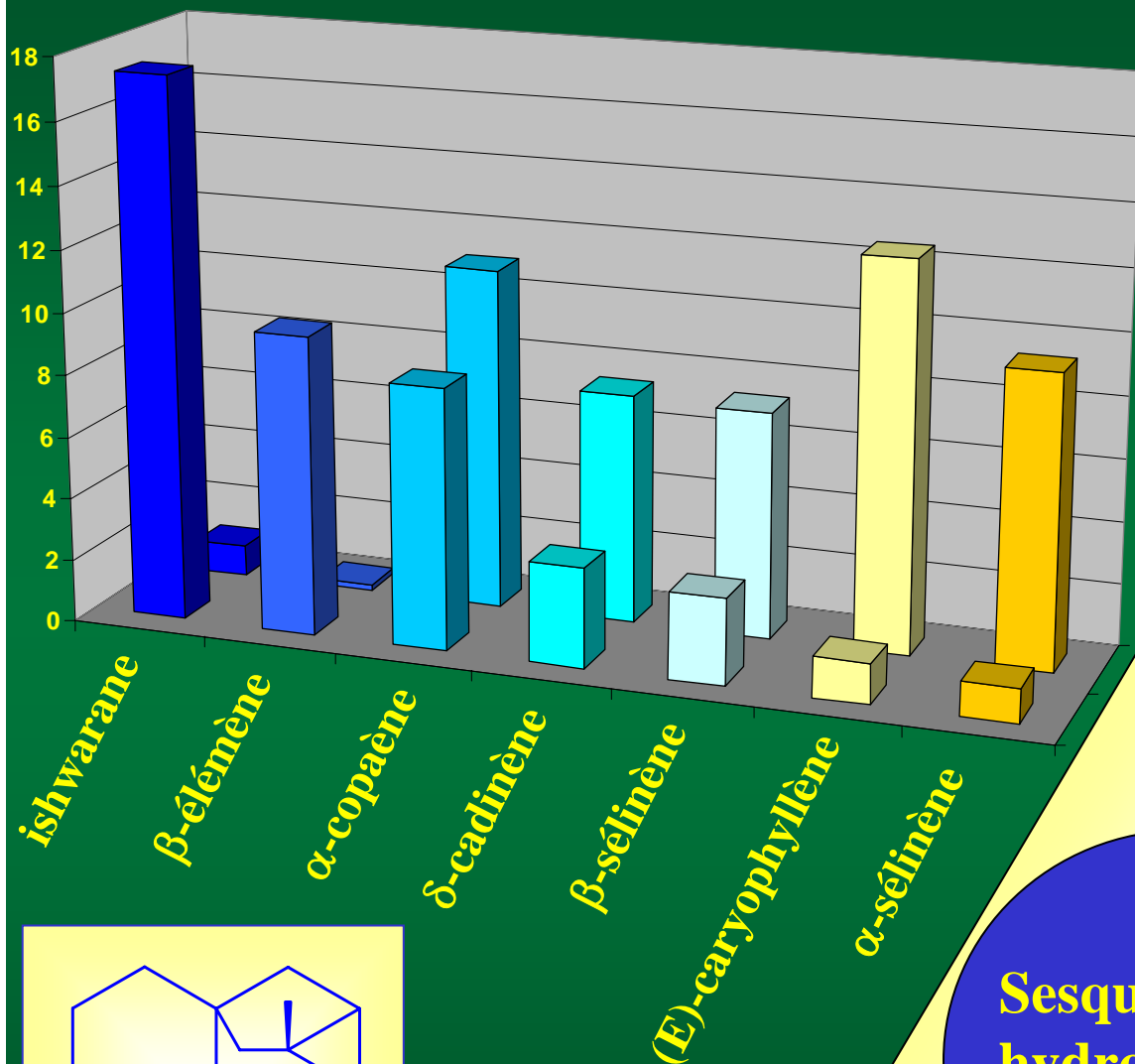


cis-dihydroagarofurane

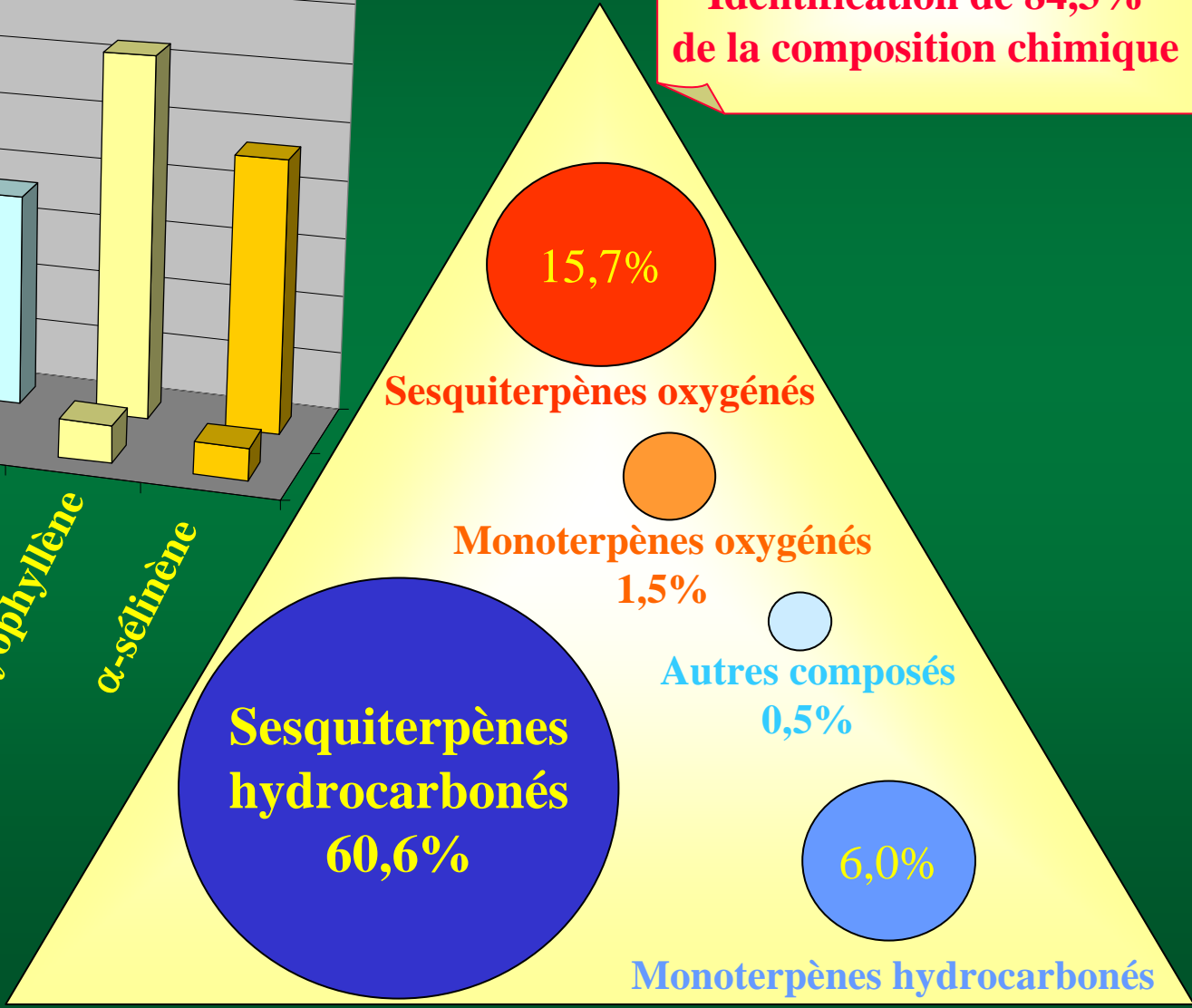
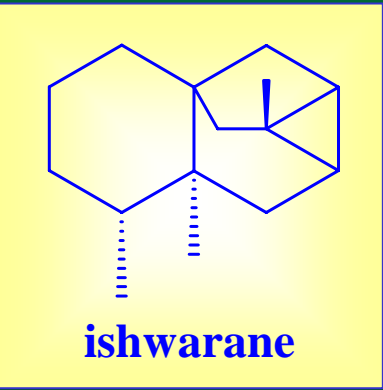


4-épi-cis-dihydroagarofurane

L'huile essentielle d'écorce de *Cedrelopsis grevei*



115 composés identifiés
Identification de 84,3%
de la composition chimique



Helichrysum de Madagascar

H. selaginifolium
H. cordifolium
H. hypnoides
Helichrysum sp.

H. gymnocephalum

H. bracteiferum

H. faradifani



Échantillon
C.N.A.R.P.



Échantillon
C.N.A.R.P.



Échantillon
C.N.A.R.P.



Échantillons
C.N.A.R.P.



Échantillon
commercial



Échantillon
commercial



Échantillon
commercial



CPG/IK, CPG/SM
& RMN ¹³C

CLC / SiO₂

CLC / SiO₂

CLC / SiO₂

Fraction
hydrocarbonée

Fraction
oxygénée

Fraction
hydrocarbonée

Fraction
oxygénée

Fraction
hydrocarbonée

Fraction
oxygénée

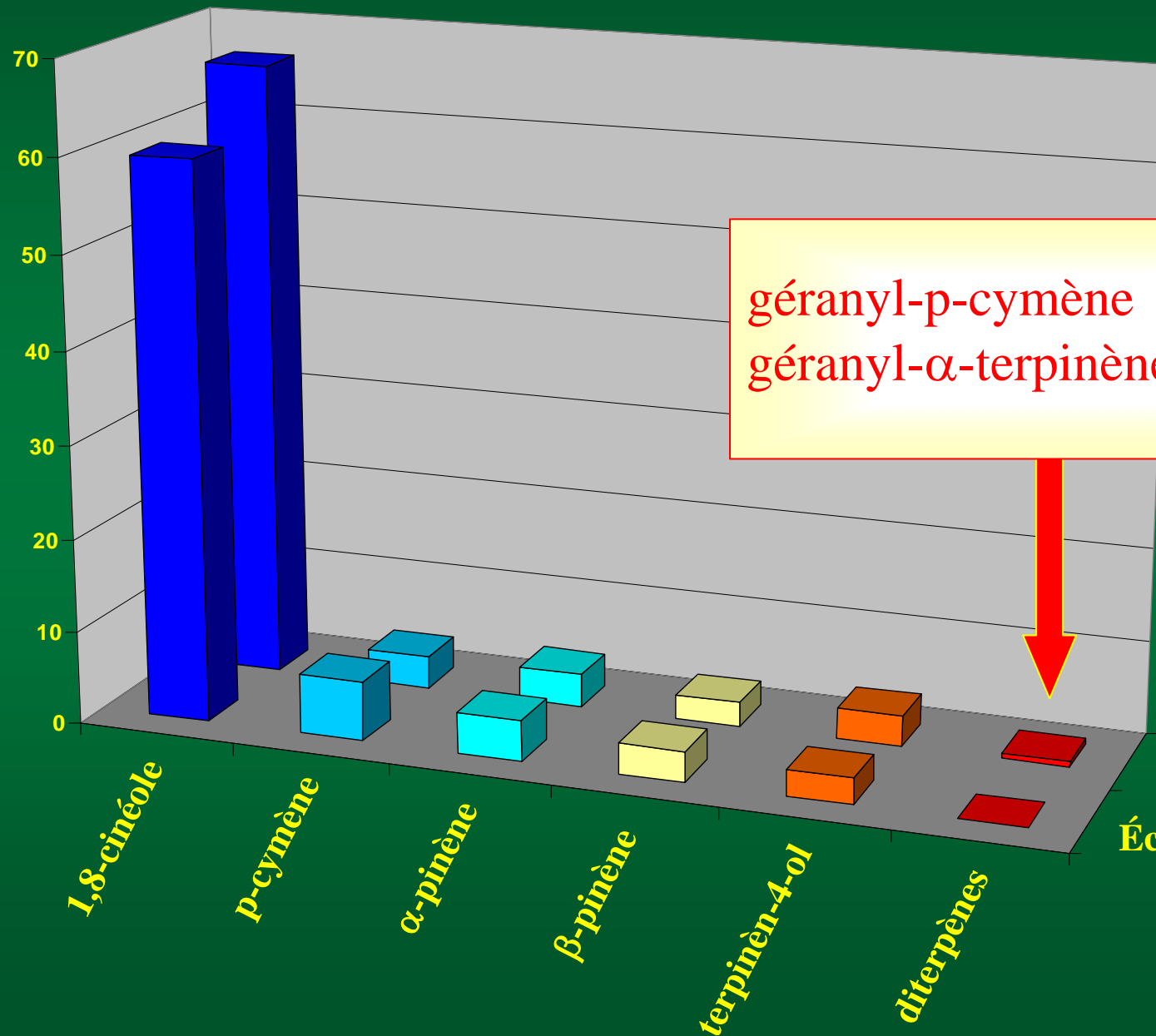
CPG/IK, CPG/SM
& RMN ¹³C

CPG/IK, CPG/SM
& RMN ¹³C

CPG/IK, CPG/SM
& RMN ¹³C

Helichrysum de Madagascar

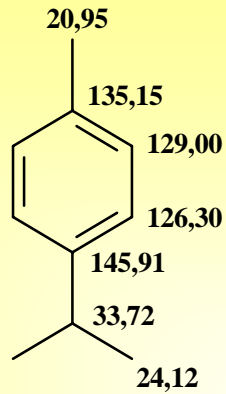
H. gymnocephalum



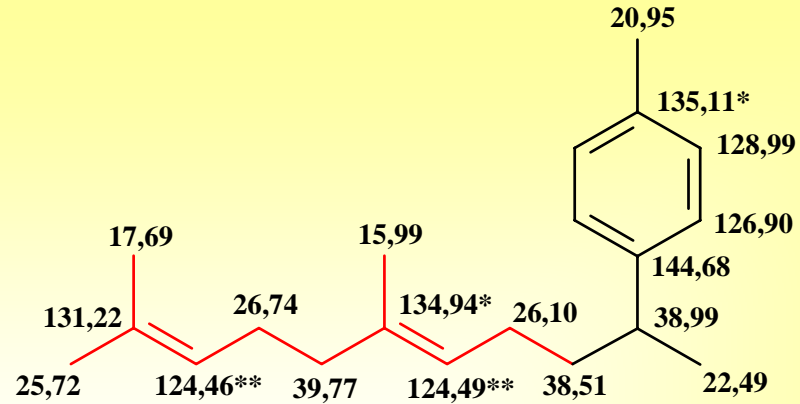
Échantillon commercial
Échantillon C.N.A.R.P.

Helichrysum de Madagascar

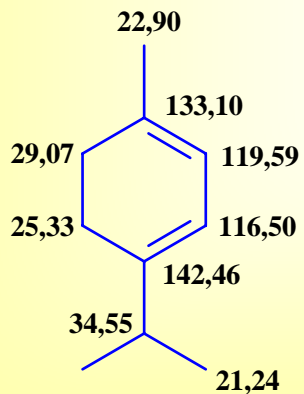
H. gymnocephalum



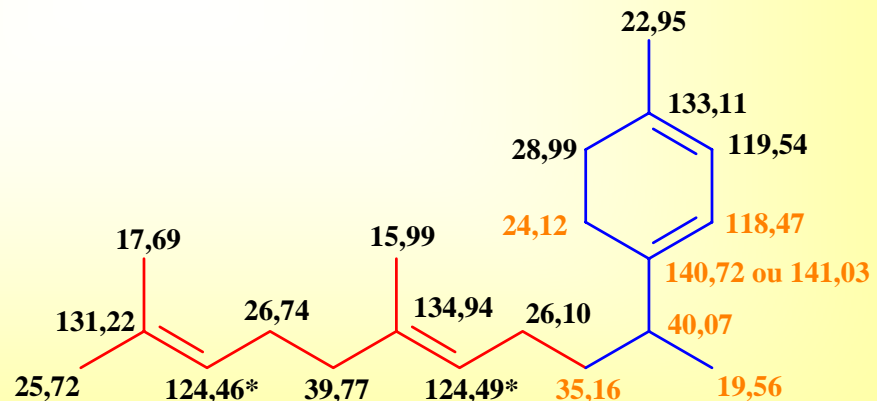
p-cymène



géranyl-p-cymène



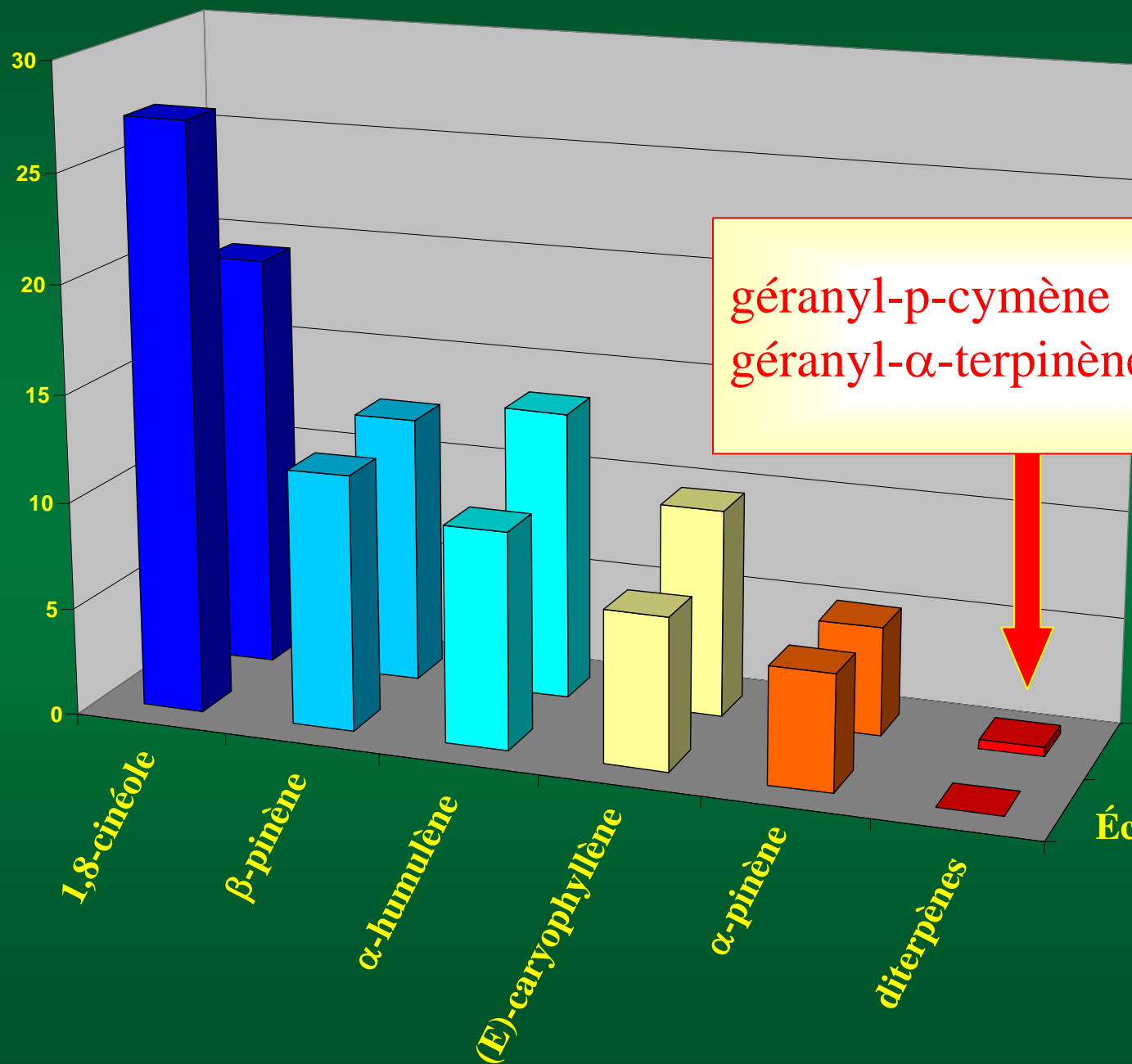
α-terpinène



géranyl-α-terpinène

Helichrysum de Madagascar

H. bracteiferum

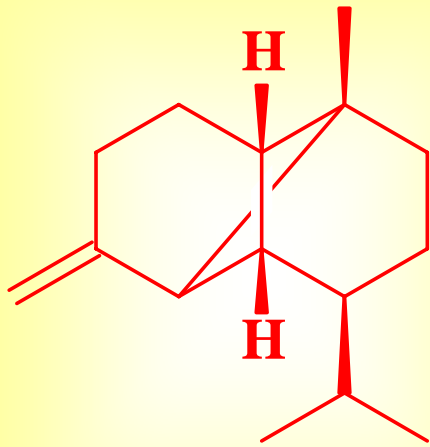


géranyl-p-cymène 0,1%
géranyl-α-terpinène 0,3%

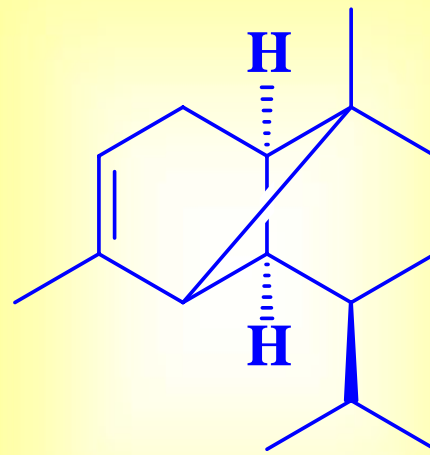
Échantillon commercial
Échantillon C.N.A.R.P.

Helichrysum de Madagascar

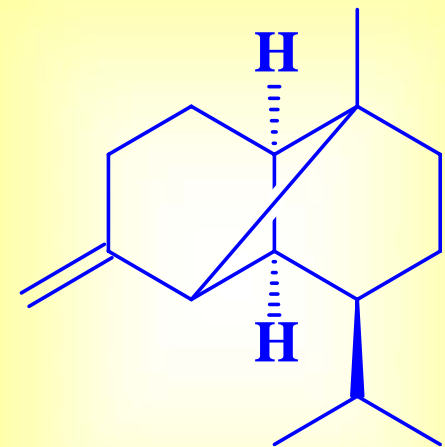
H. bracteiferum



β -copaène



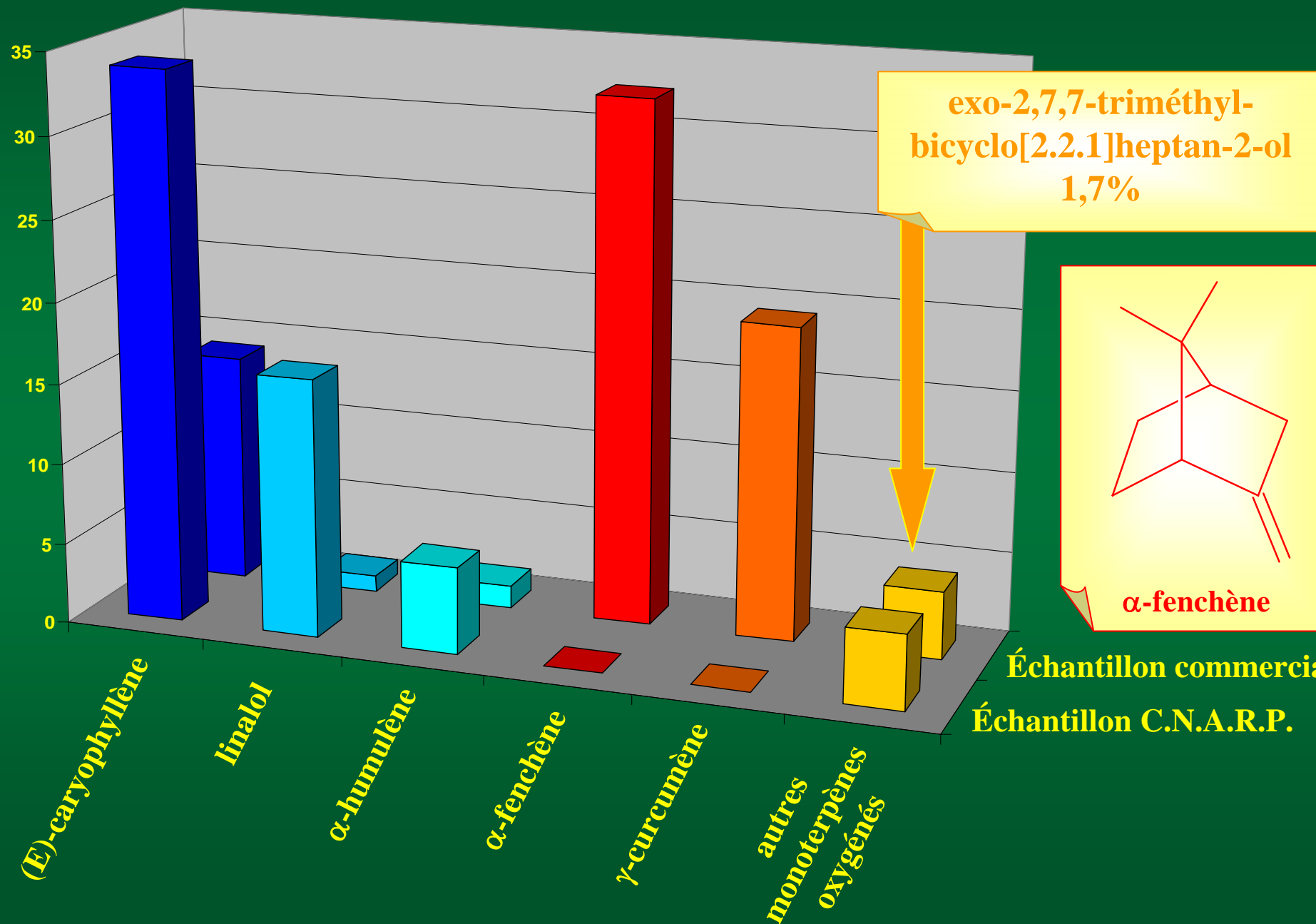
α -ylangène



β -ylangène

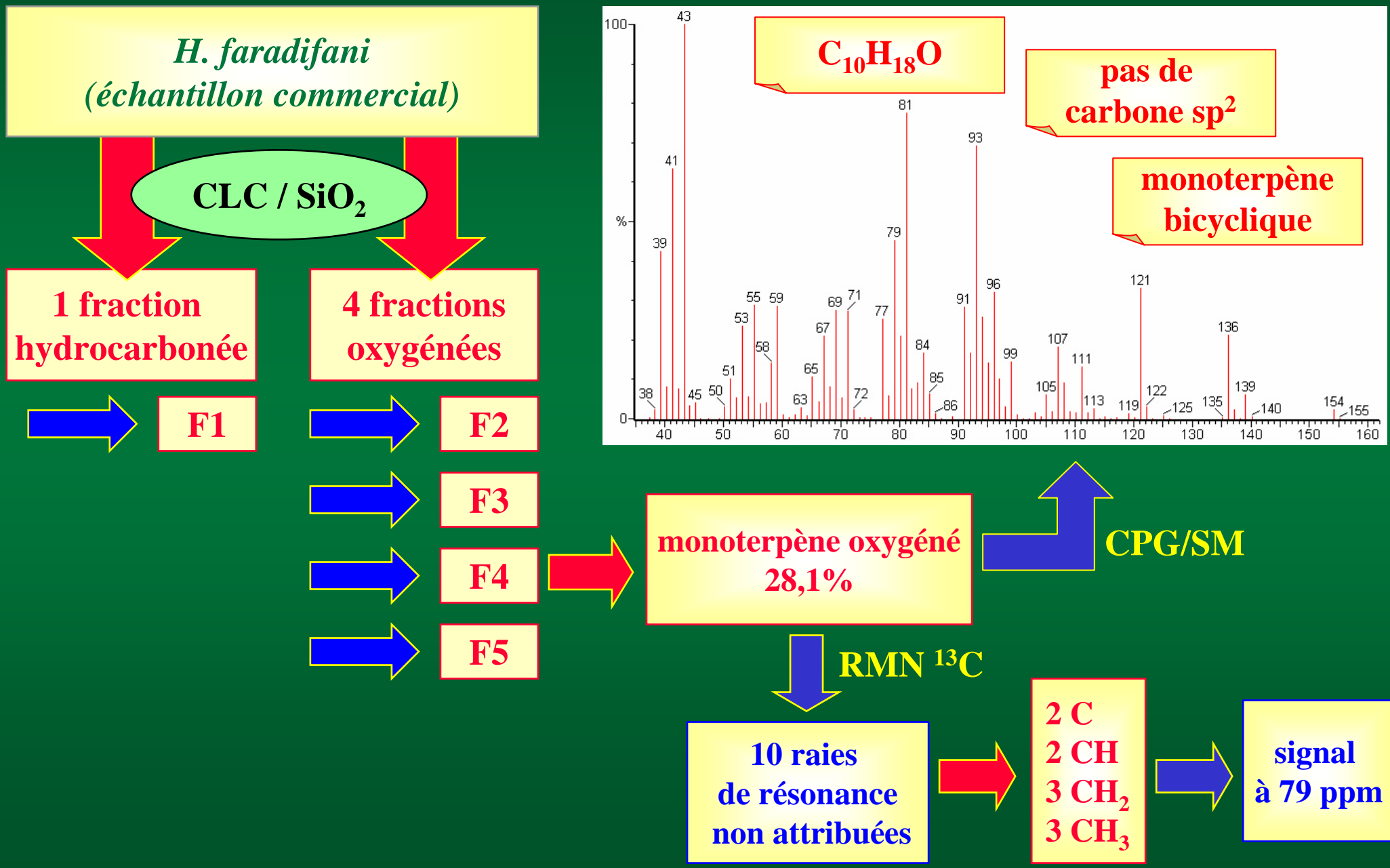
Helichrysum de Madagascar

H. faradifani



Helichrysum de Madagascar

H. faradifani



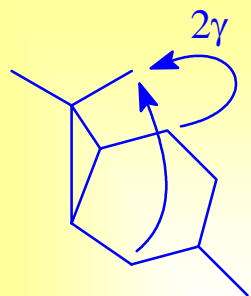
Helichrysum de Madagascar

H. faradifani

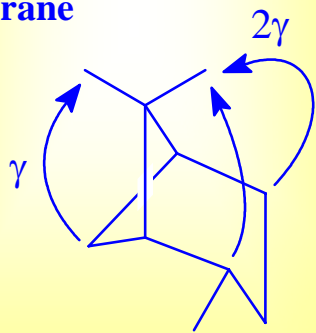
2 méthyles
23,02 ppm & 23,68 ppm



pas de squelette carane,
pinane, etc...

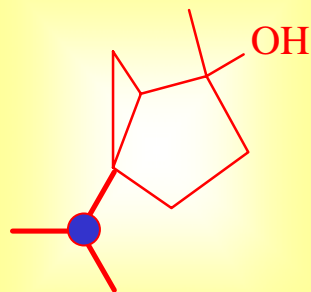


carane

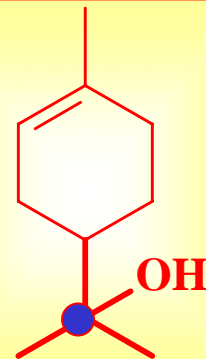


pinane

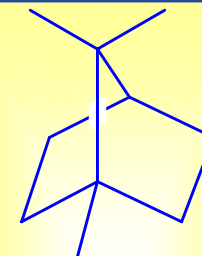
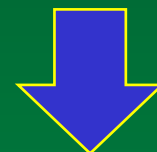
pas de méthyle
résonant aux
environs
de 30 ppm



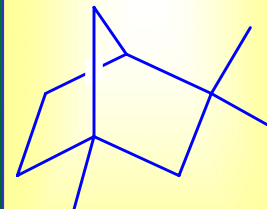
pas de motif
isopropanolique



pas de
squelette
camphane
et fenchane

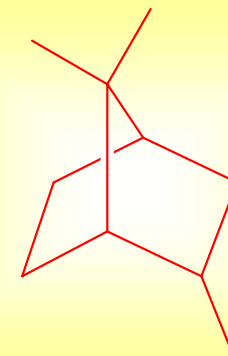


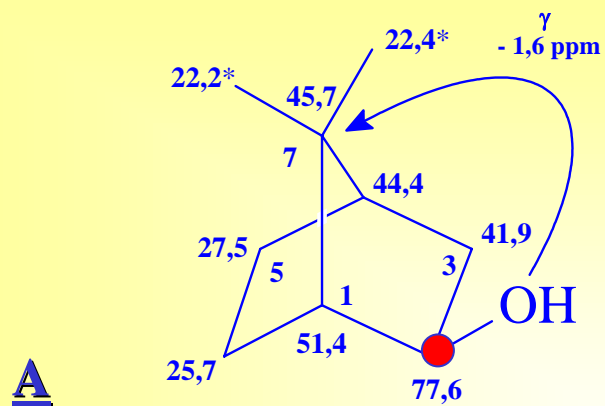
camphane



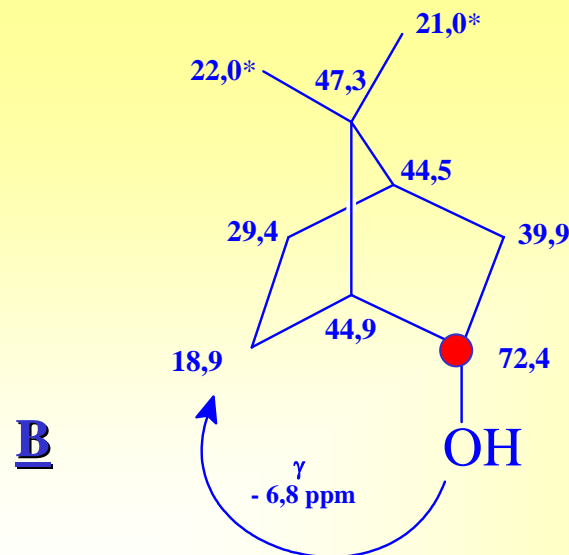
fenchane

structure de type
triméthyl-2,7,7-
bicyclo[2.2.1]heptanique

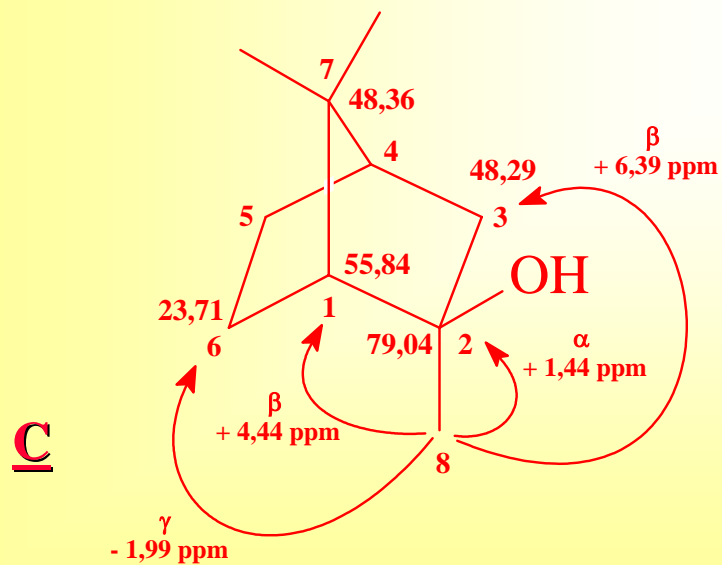




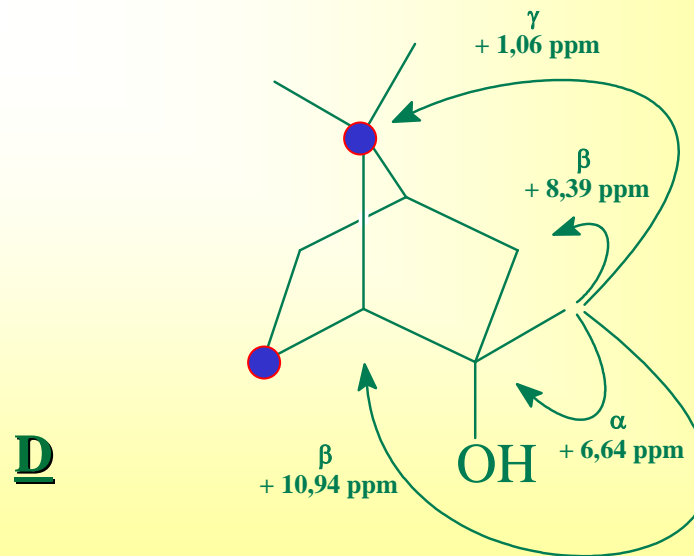
exo-7,7-diméthylbicyclo[2.2.1]heptan-2-ol



endo-7,7-diméthylbicyclo[2.2.1]heptan-2-ol



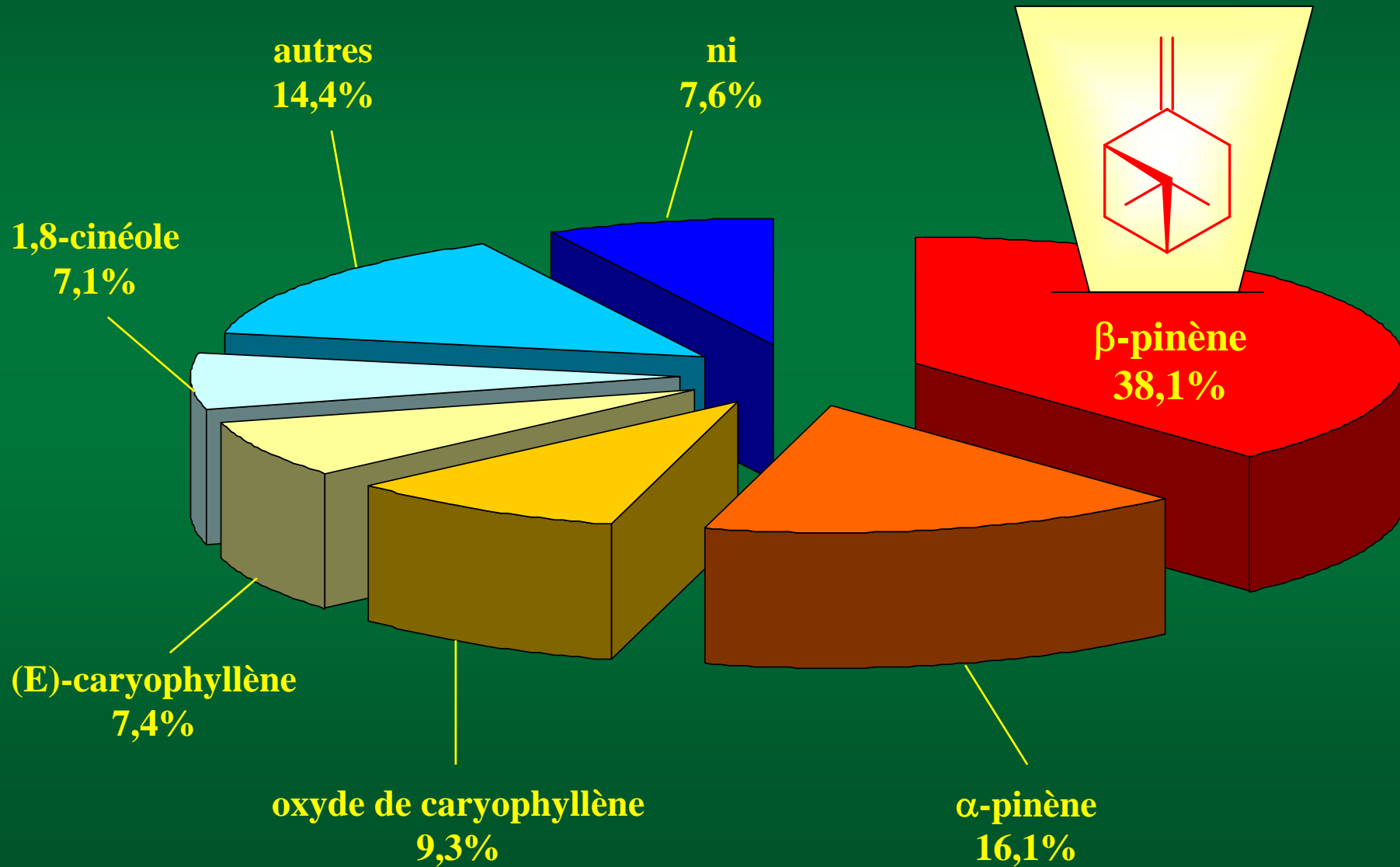
exo-2,7,7-triméthylbicyclo[2.2.1]heptan-2-ol



endo-2,7,7-triméthylbicyclo[2.2.1]heptan-2-ol

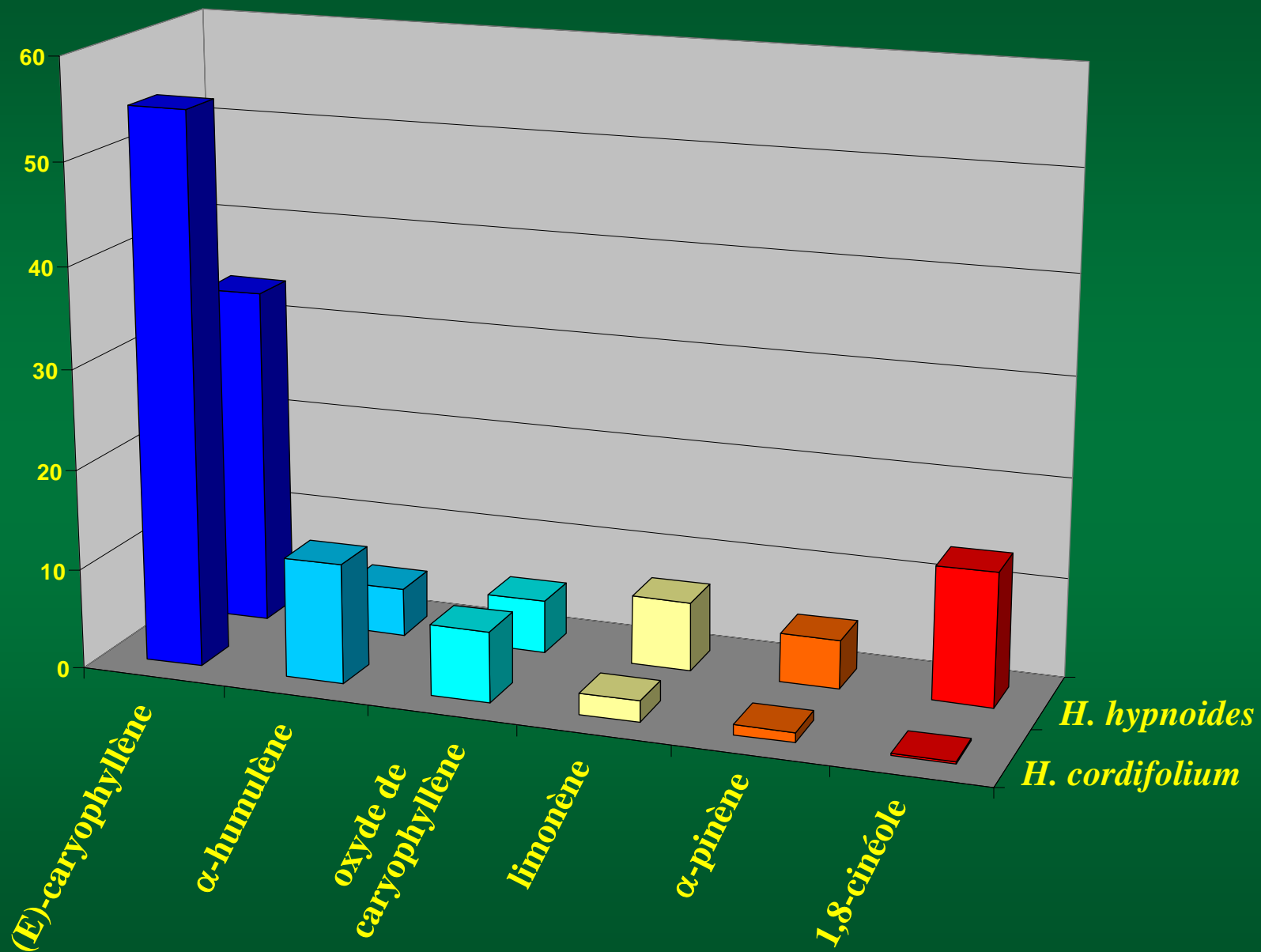
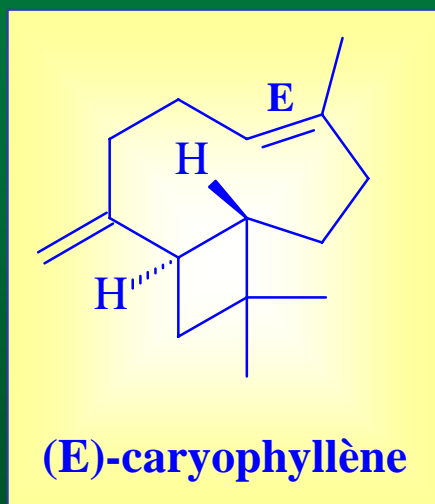
Helichrysum de Madagascar

H. selaginifolium

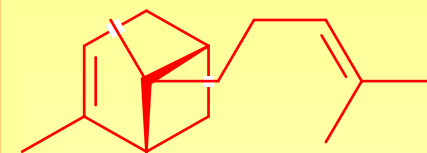
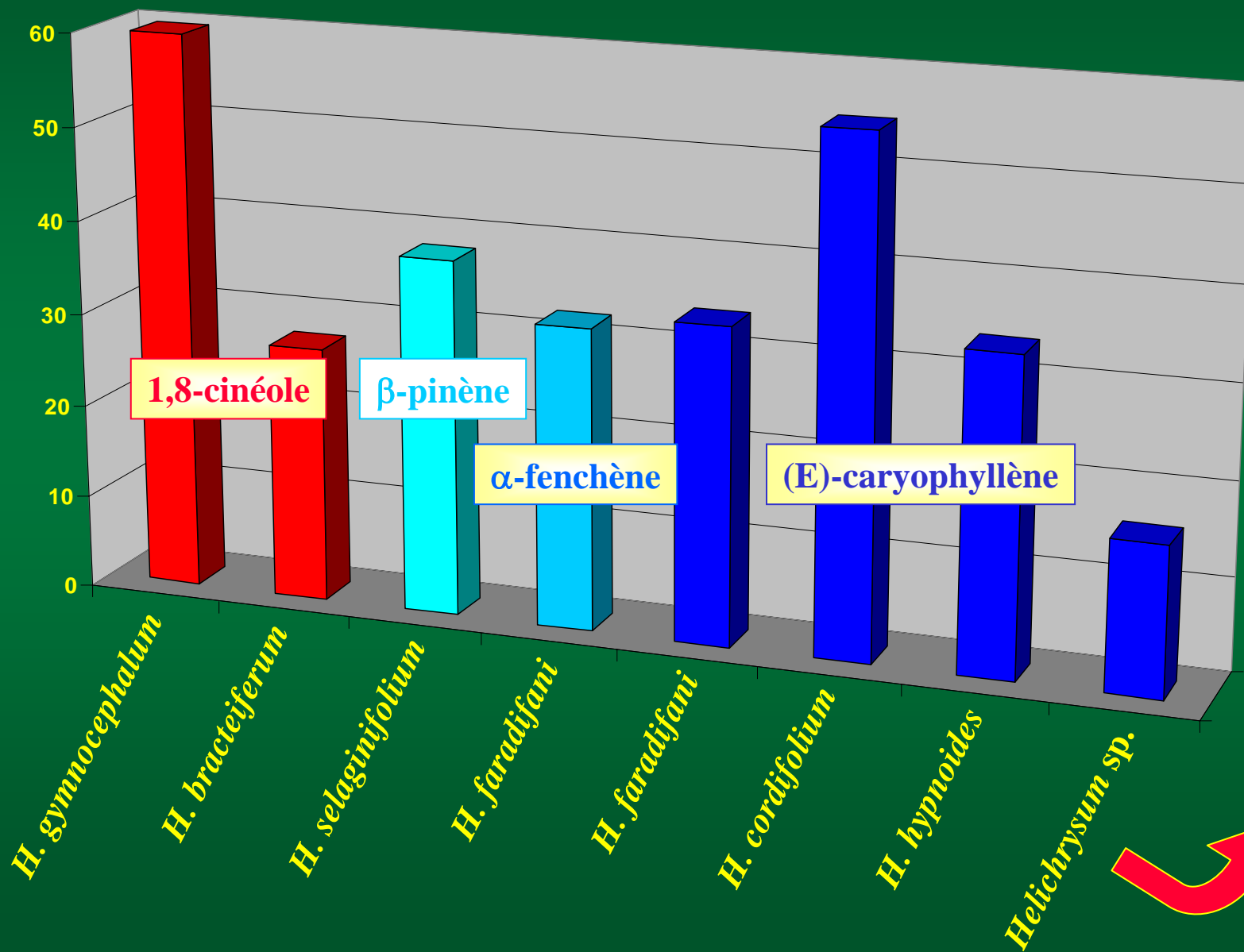


Helichrysum de Madagascar

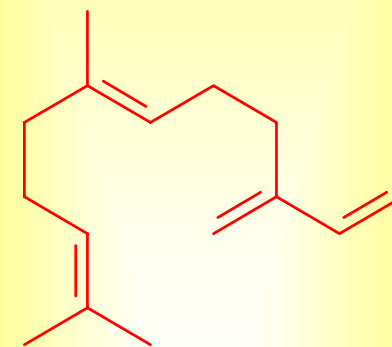
H. cordifolium & hypnoides



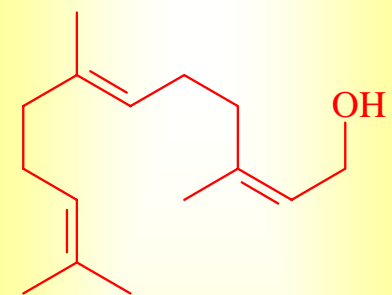
Helichrysum de Madagascar



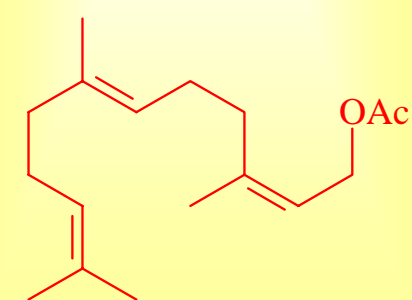
trans- α -bergamotène



(E)- β -farnésène



2Z,6E-farnésol



acétate de 2Z,6E-farnésyle

Cinnamomum camphora



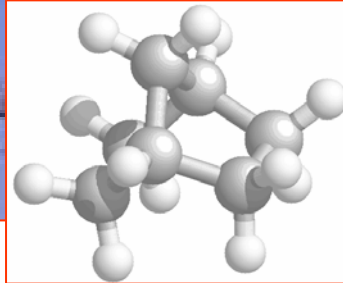
Cupressus lusitanicus



Tagetes bipinata



CONCLUSION



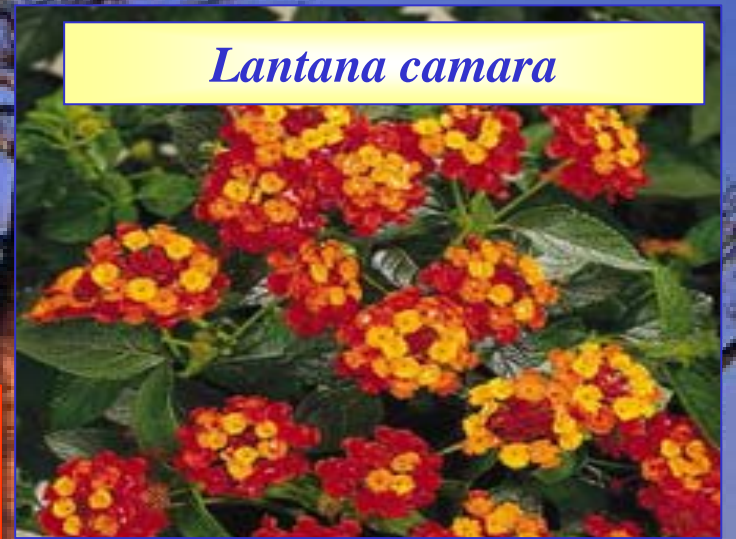
*RMN*¹³*C*
CPG/SM



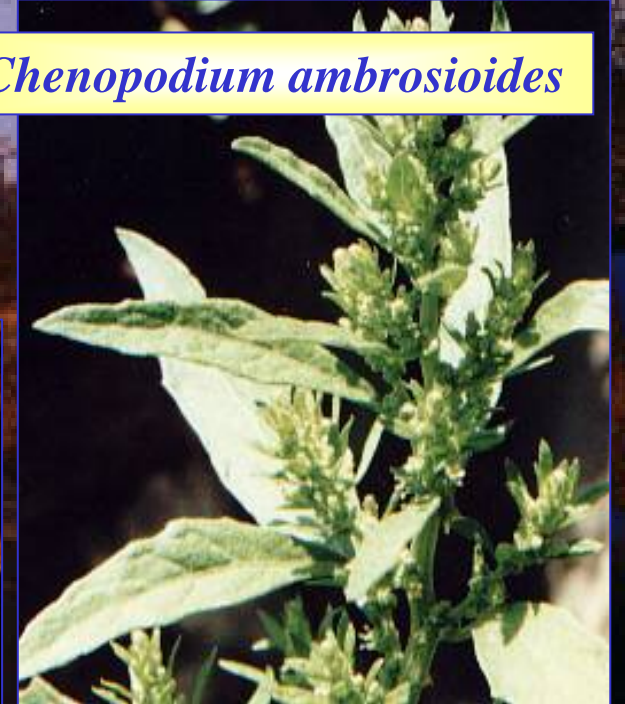
Eucalyptus citriodora



Lantana camara



Chenopodium ambrosioides



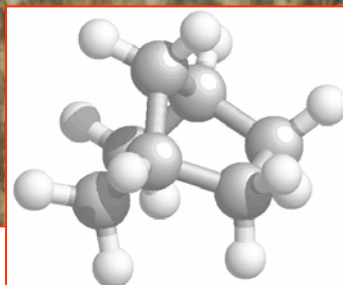
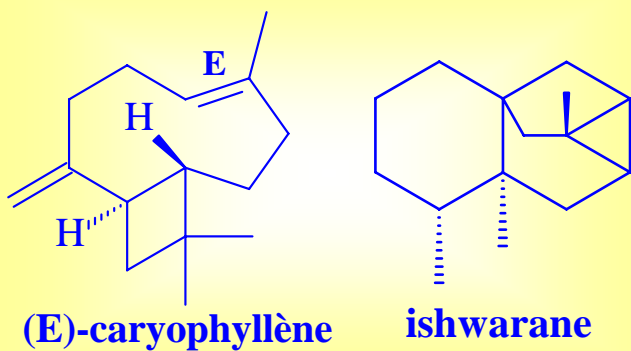
CONCLUSION

Cedrelopsis grevei

6 échantillons étudiés



42-52 composés identifiés
sans fractionnement



*RMN*¹³*C*
CPG/SM



115 composés identifiés
après fractionnement



36 sesquiterpènes
hydrocarbonés
38 sesquiterpènes oxygénés



Bibliothèques littéraires

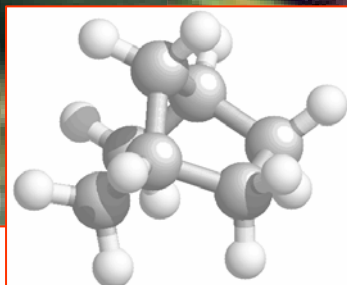
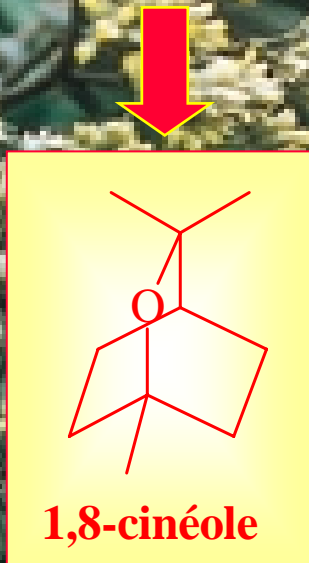
Par reconstruction

4-épi-cis-dihydroagarofurane

CONCLUSION

Helichrysum gymnocephalum

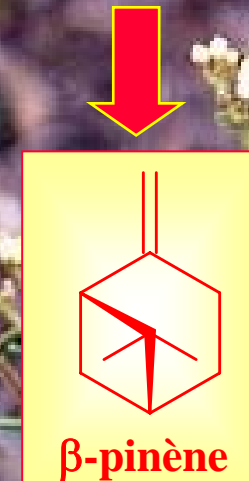
H. bracteiferum



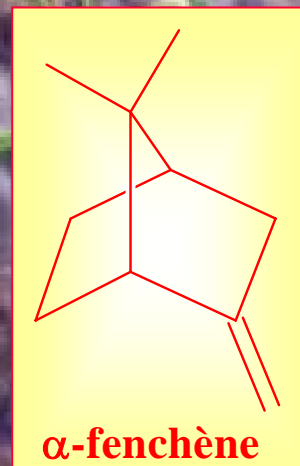
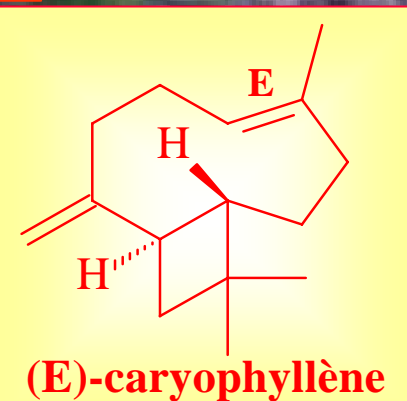
RMN ¹³C
CPG/SM



H. selaginifolium



H. faradifani



H. cordifolium

H. hypnoides

Helichrysum sp.

