L’iris dans la parfumerie et les arômes

Daniel JOULAIN

CECM – 18 novembre 2022
Salon de Provence

Chanel N°19 (H. Robert, 1971)
La clé du N°19 est un iris d'une qualité très particulière choisi par Henri Robert. La formule n'en contient que 1%, mais ce produit « est » le N°19 (J. Polge)

Eau de Guerlain (JP Guerlain, 1974) : 0,5% « d'absolue » d'iris

28 La Pausa de Chanel (J. Polge, 2007) : 6,6% de « beurre » d'iris

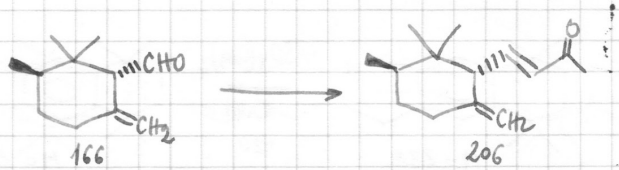
Rhizomes : macération.
Spiritueux, dont le gin

Huile essentielle (beurre), résinoïdes, absolue
Arômes naturels WONF – fruits rouges etc.

24

Mercredi 4 Août 1976

Préparation de la γ-IRONE



166 → 206

On ajoute sous N_2, (RMN CORRECTE)

71 g du prétiral brut obtenu page 20 soit environ: 0,34 mole

en solution dans ~~200~~ 150 cm³ de glyme sec (distillé sur CaH2 juste avant)

à une suspension agitée à reflux de 216 g de phosphorane bien sec

[0,68 mole, 2 équivalents] dans 1000 cm³ de glyme sec.

On agite mécaniquement à reflux pendant ~~48~~ 46 heures. → (1060 cm³ recyclables)

On distille le glyme qui est ainsi recyclé, (en 1 heure ½ (atteint vers 180 Torr)) 706 puis 4 x 200 cm³

reprend le résidu dans 1500 cm³ de pentane bouillant et refroidit à 5°. On filtre, et lave le filtre au pentane glacé (2 fois). On concentre sous P.R. → 68,5 g de huile jaune foncé (théorie 70 g)

On conserve à 4° jusqu'à la distillation.

CPV du brut, voir ci-contre :

Distillation: (Lundi 9/8/76)

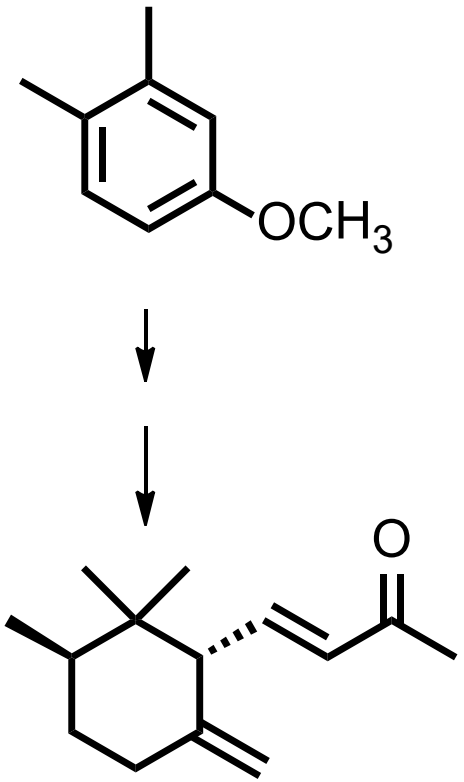
1) $Eb_{0,5}$: 50-67° 12,9 g jaune très pâle

2) $Eb_{0,5}$: 68-81° ~~8,8 g~~ 25,1 g jaune clair

3) $Eb_{0,5}$: 82- ~~8,5 g~~ 8,9 g jaune orangé.

Résidu: 17,3 g noir

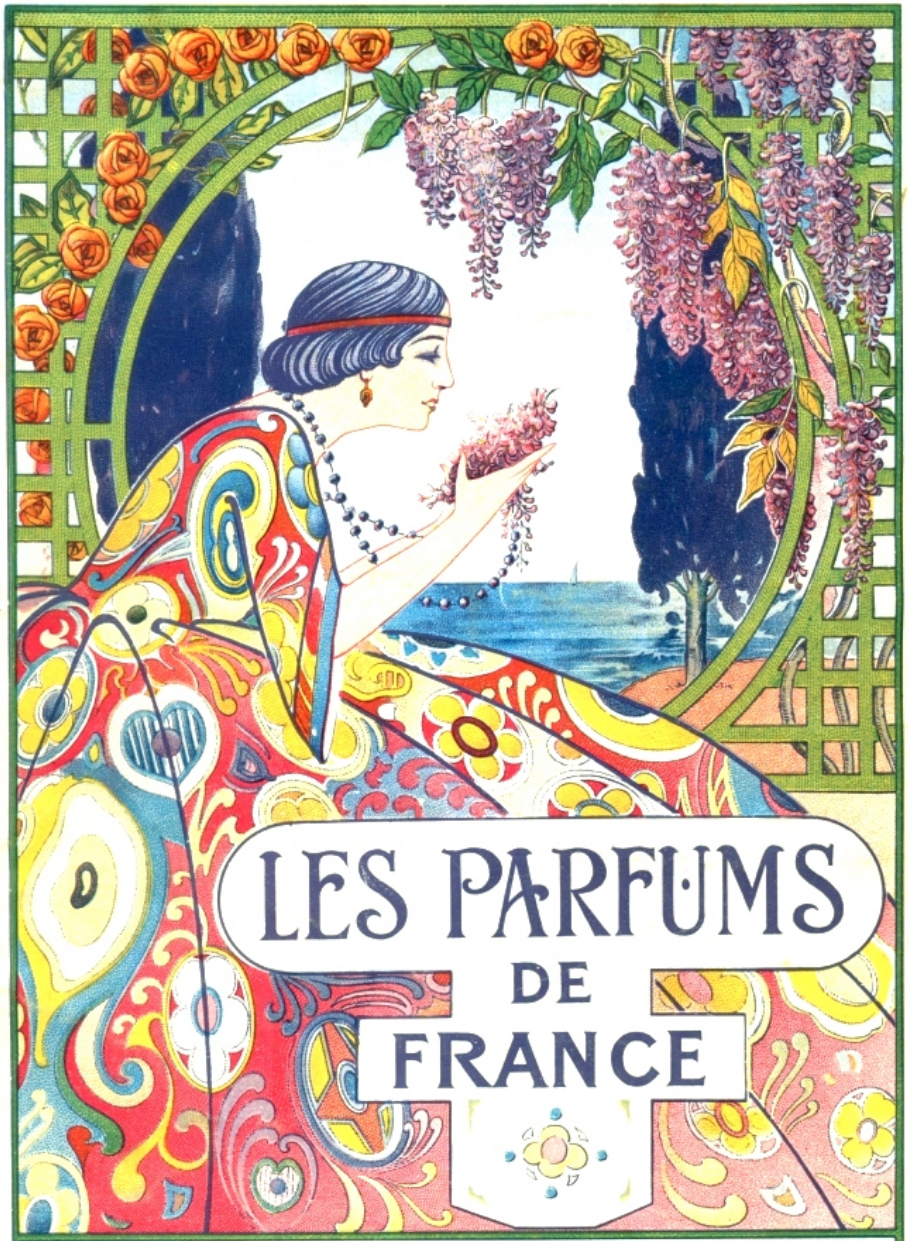
(Suite page 25)



(Robertet)
Bull. Soc. Chim. 1979

(Firmenich)
Helv. Chim. Acta, 1984

N° 35 PRIX : 5 Francs Janvier 1926

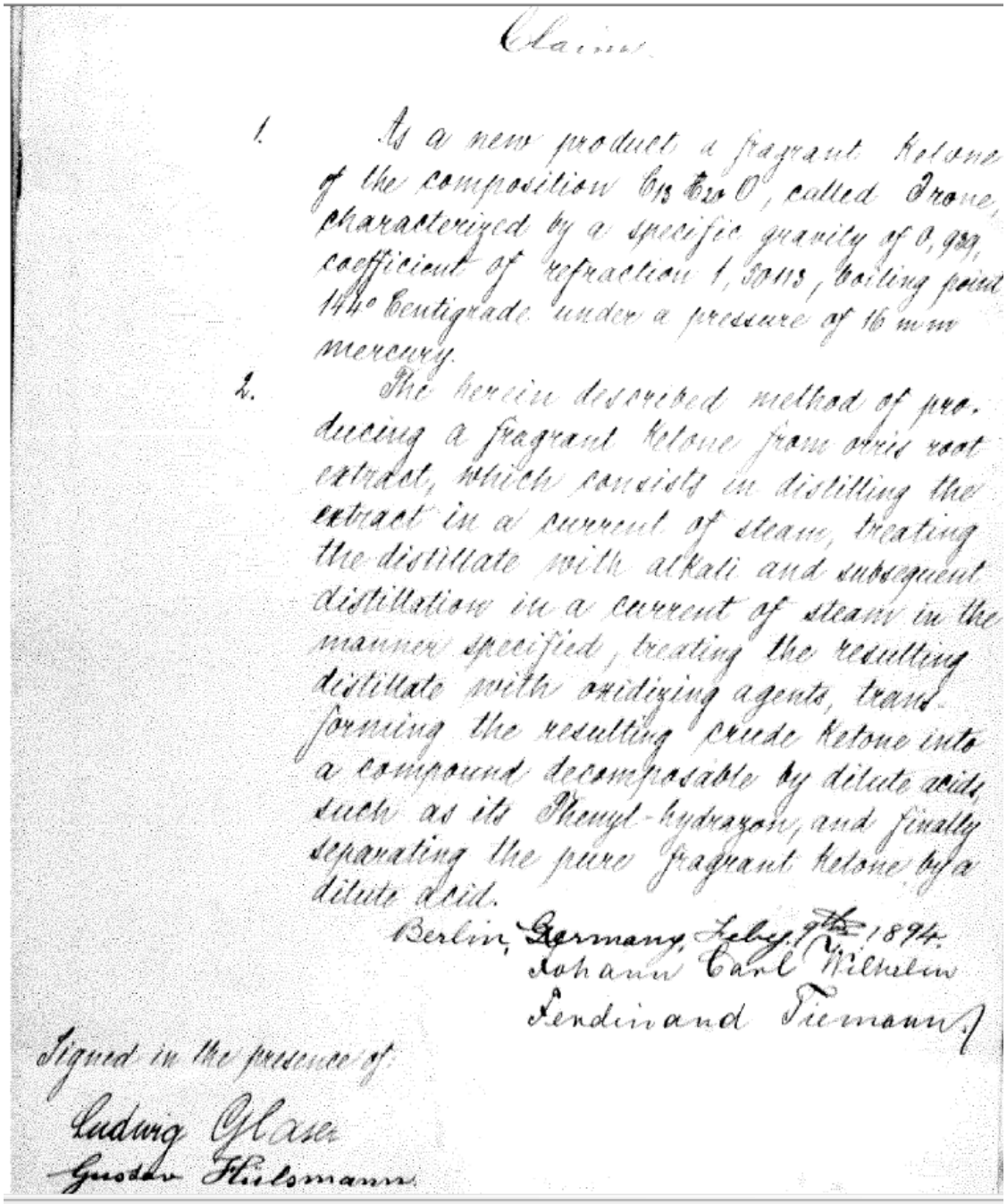


LES PARFUMS DE FRANCE

Administration et Rédaction
Avenue Chiris

GRASSE

Rhizomes d’iris
(*Iris pallida* L.



Claims.

1. As a new product a fragrant ketone of the composition $C_{13}H_{22}O$, called Irone, characterized by a specific gravity of 0,927, coefficient of refraction 1,5013, boiling point 144° Centigrade under a pressure of 16 m/m mercury.

2. The herein described method of producing a fragrant ketone from orris root extract, which consists in distilling the extract in a current of steam, treating the distillate with alkali and subsequent distillation in a current of steam in the manner specified, treating the resulting distillate with oxidizing agents, transforming the resulting crude ketone into a compound decomposable by dilute acids, such as its Phenyl-hydrazone, and finally separating the pure fragrant ketone by a dilute acid.

Berlin, Germany, Feby. 9th 1894.

Johann Carl Wilhelm
Ferdinand Tiemann

Signed in the presence of:

Ludwig Glaser
Gustav Fürstmann

Brevet Canadien CA 45624
Publié le 24 mars 1894
Déposé le 9 février 1894
par Haarmann & Reimer

Inventeur:
Wilhelm Ferdinand Tiemann

Revendications

1 As a new product of fragrant ketone of the composition **$C_{13}H_{20}O$** called Irone characterized by a specific gravity of 0,989, coefficient of refraction of 1,50113, boiling point 144° centigrade under a pressure of 16 mm mercury.

2 The herein described method of producing a fragrant ketone from orris root extract, consists in distilling the extract in a current of steam, treating the distillate with alkali and subsequent distillate in a current of steam in the manner specified, treating the resulting distillate with oxidizing agent, transforming the resulting crude ketone into a compound decomposable by dilute acids such as its phenylhydrazone, and finally separating the pure fragrant ketone by dilute acid.

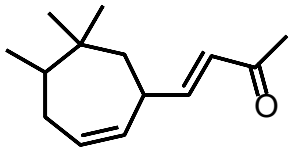
L'erreur de F. Tiemann et P. Krüger*, Ber. Dtsch. Chem. Ges.*, 1893*, <u>26</u>*, 2675

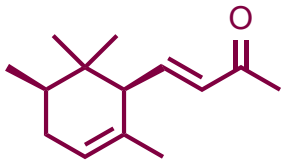
~~**$C_{13}H_{20}O$**~~ **$C_{14}H_{22}O$**

1893 : Tiemann détermine une formule brute **$C_{13}H_{20}O$**

1913 : Ruzicka exprime des doutes au sujet de la formule brute

1933 : Ruzicka établit la formule brute **$C_{14}H_{22}O$**





14/07/1947 : Naves établit la structure chimique

01/09/1947 : Naves présente ses travaux à l'assemblée de la Société Chimique Suisse

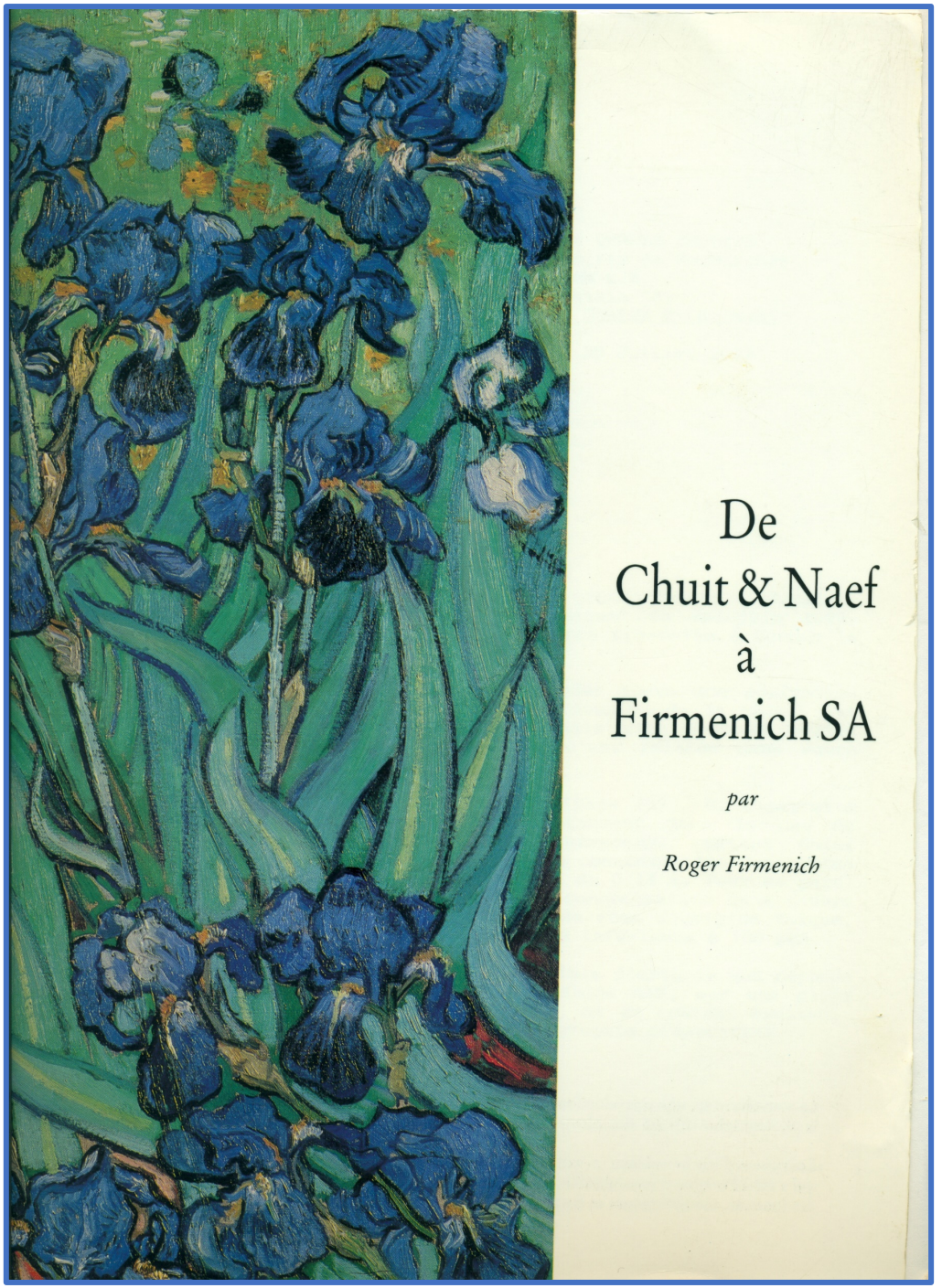
03/09/1947 : Ruzicka établit la structure chimique; **plis cachetés du 28/06/1946**

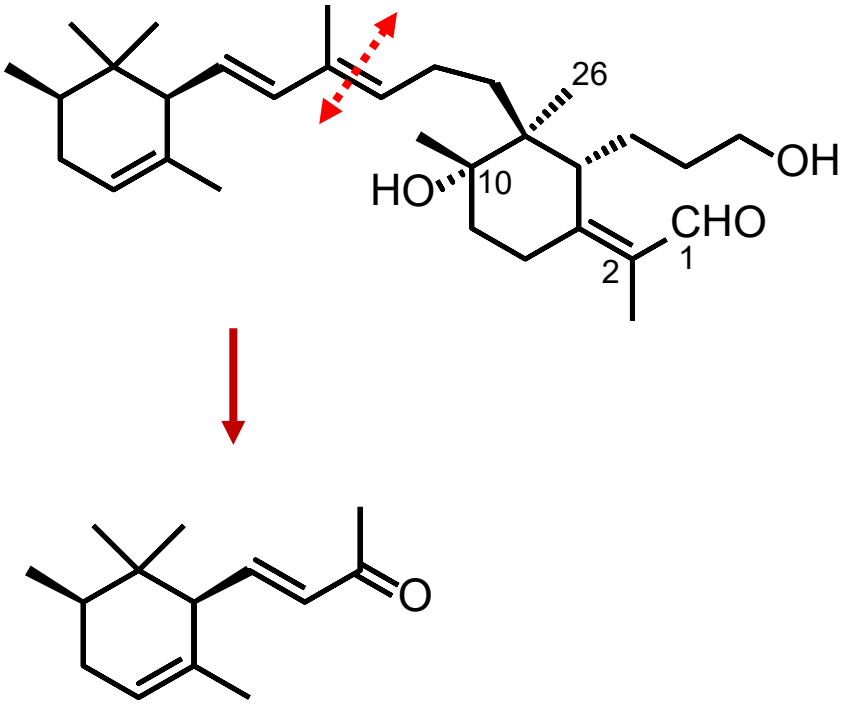
15/10/1947 : Naves revendique l'antériorité ; **plis cachetés du 10/06/1943**

01/12/1947 : Naves enfonce son clou!

Mémoires de Roger Firmenich (1989)

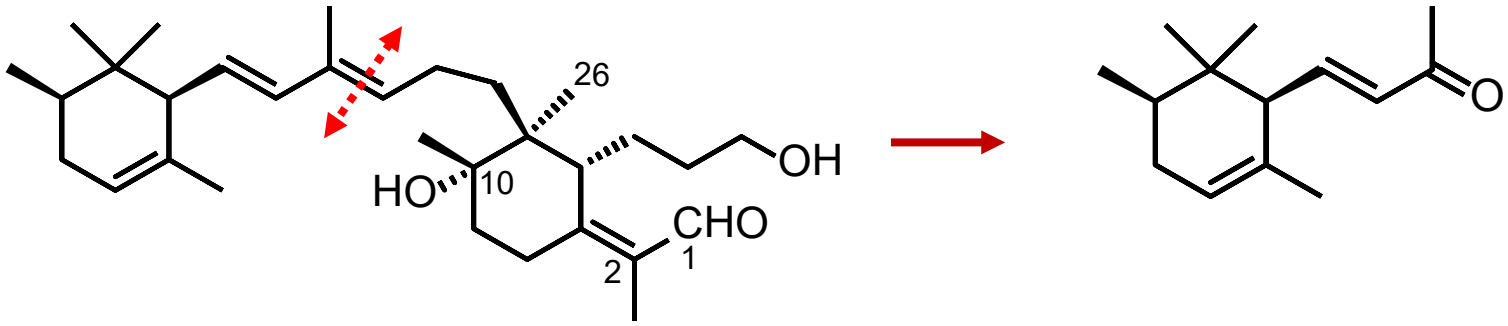
Les racines d'iris fournissent un extrait, le beurre d'iris, dont l'élément olfactif spécifique est l'irone, qui a été à l'origine d'innombrables travaux scientifiques dès 1890. Ils ont conduit à la découverte des ionones, méthylionones et corps similaires si importants dans l'industrie aromatique.





Franz-Josef Marner
Grasse
Jeudi 24 Avril 1986 à 14H30

F.-J. Marner, L. Jaenicke et coll. , *Journal of Organic Chemistry*, 1982



KMnO4 etc. (Elf/Sanofi - 1987)

Entérobactéries (Givaudan-Roure - 1988)

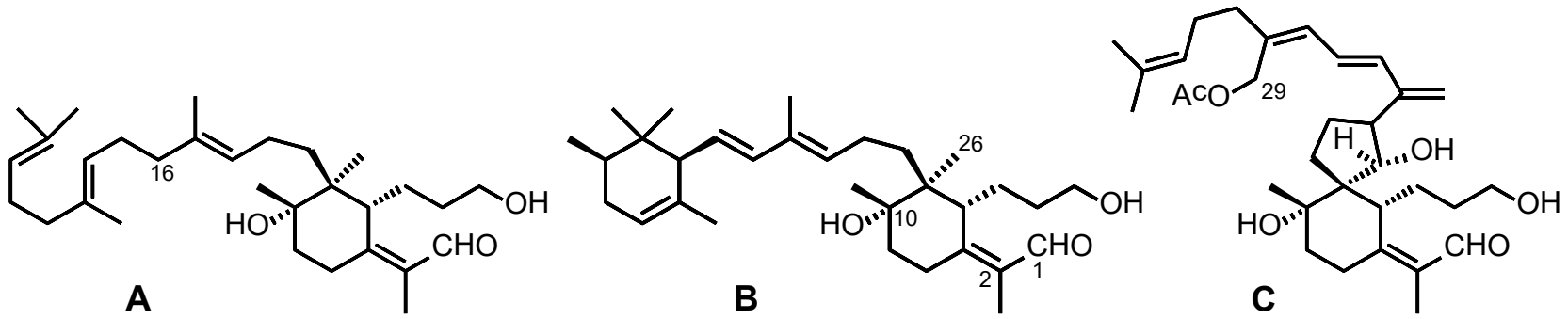
Lipoxygénases (Elf/Sanofi - 1990)

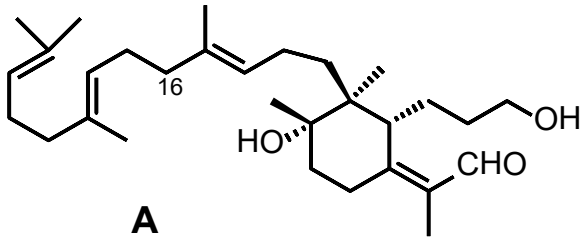
Champignons filamenteux (Elf/Sanofi - 1990)

Nitrites en milieu acide (Givaudan-Roure - 1997)

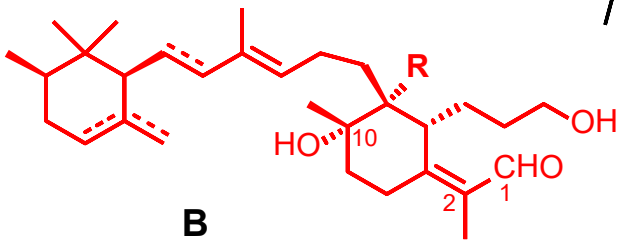
Incubation à 50°C en atmosphère humide (Firmenich - 2007)

autres (>2010)

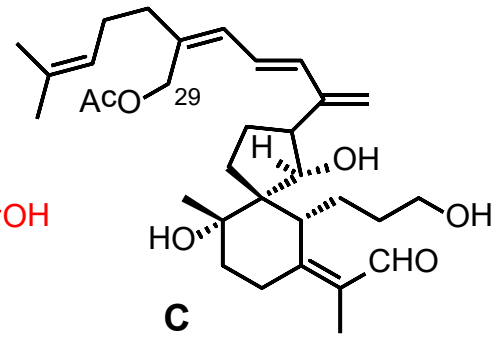

16
HO
OH
CHO
A
26
HO
10
OH
CHO
2
1
B
AcO
29
H
OH
HO
OH
CHO
C



A



B



C

R = CH_3 : irigermanals

R = CH_2OH : iriflorental (γ)

iripallidal (α)

Techniques d'extraction, de raffinage etc.

Extraction en phase solide (Danisco/Cultor – 1999)

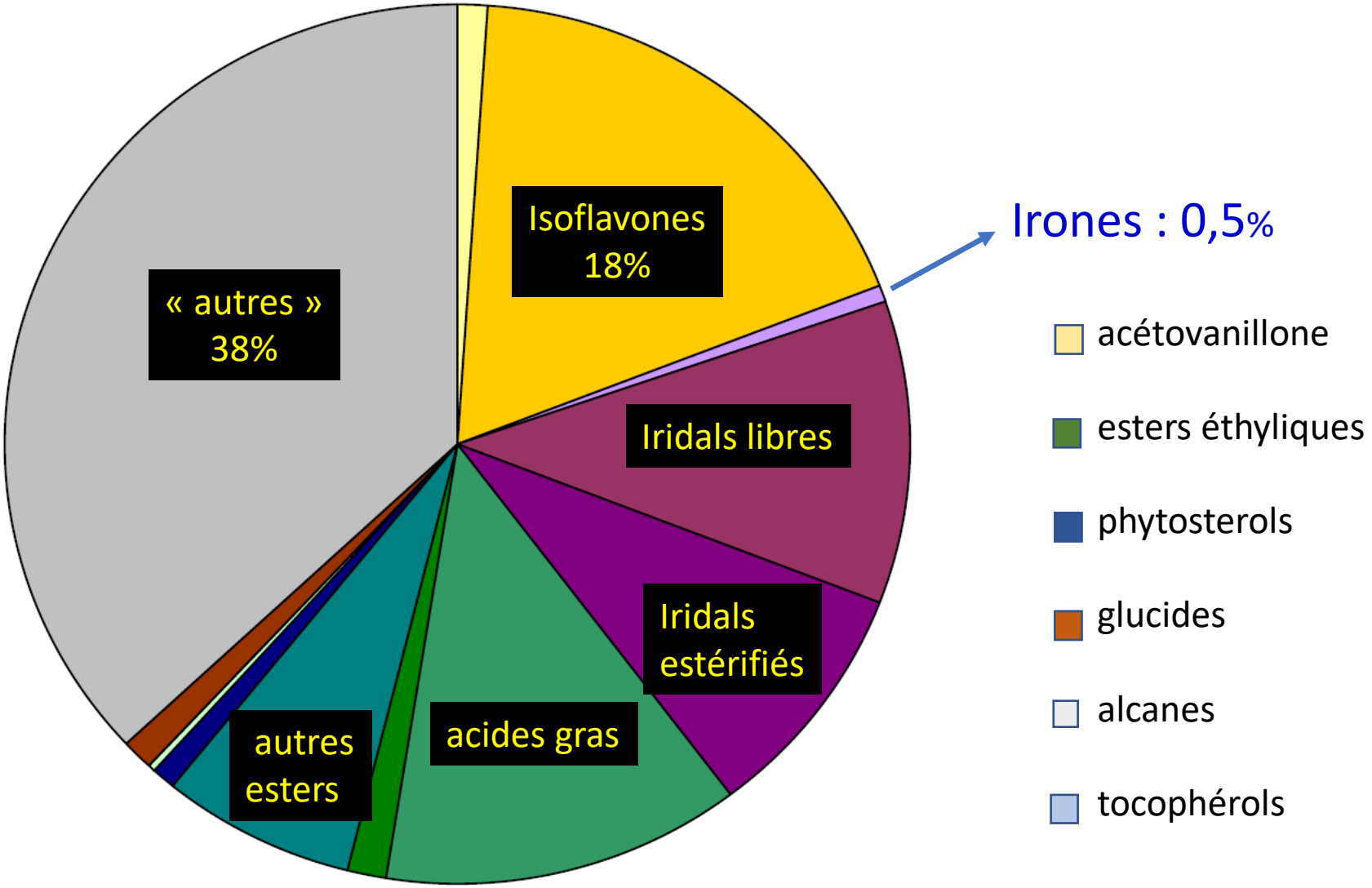
Liquides ioniques (Univ. Regensburg – 2015)

Lactate d'éthyle et CCC (Univ. Bordeaux/Sayous – 2016)

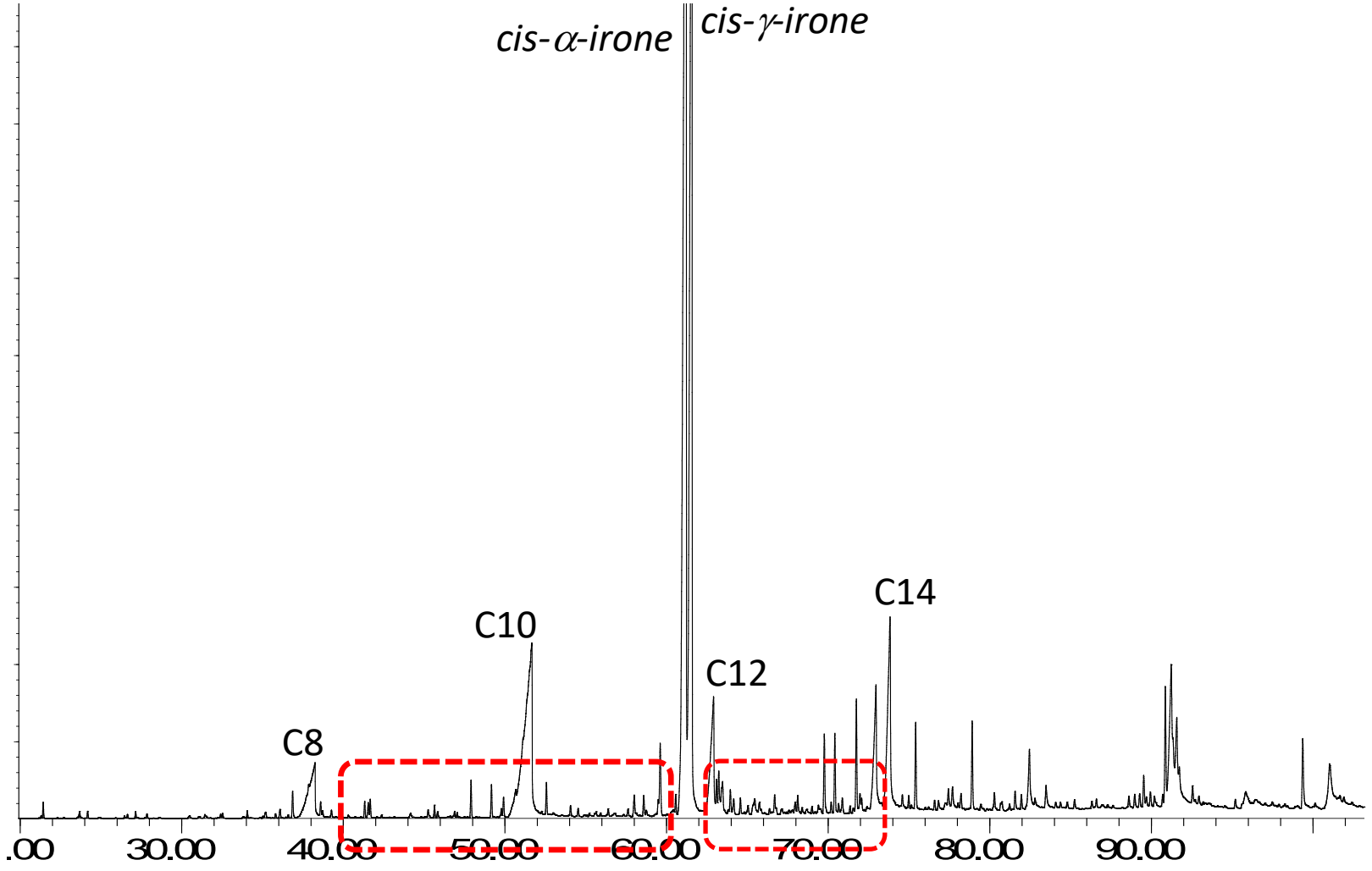
Extraction « évaporative » (NES Technologies – 2020)

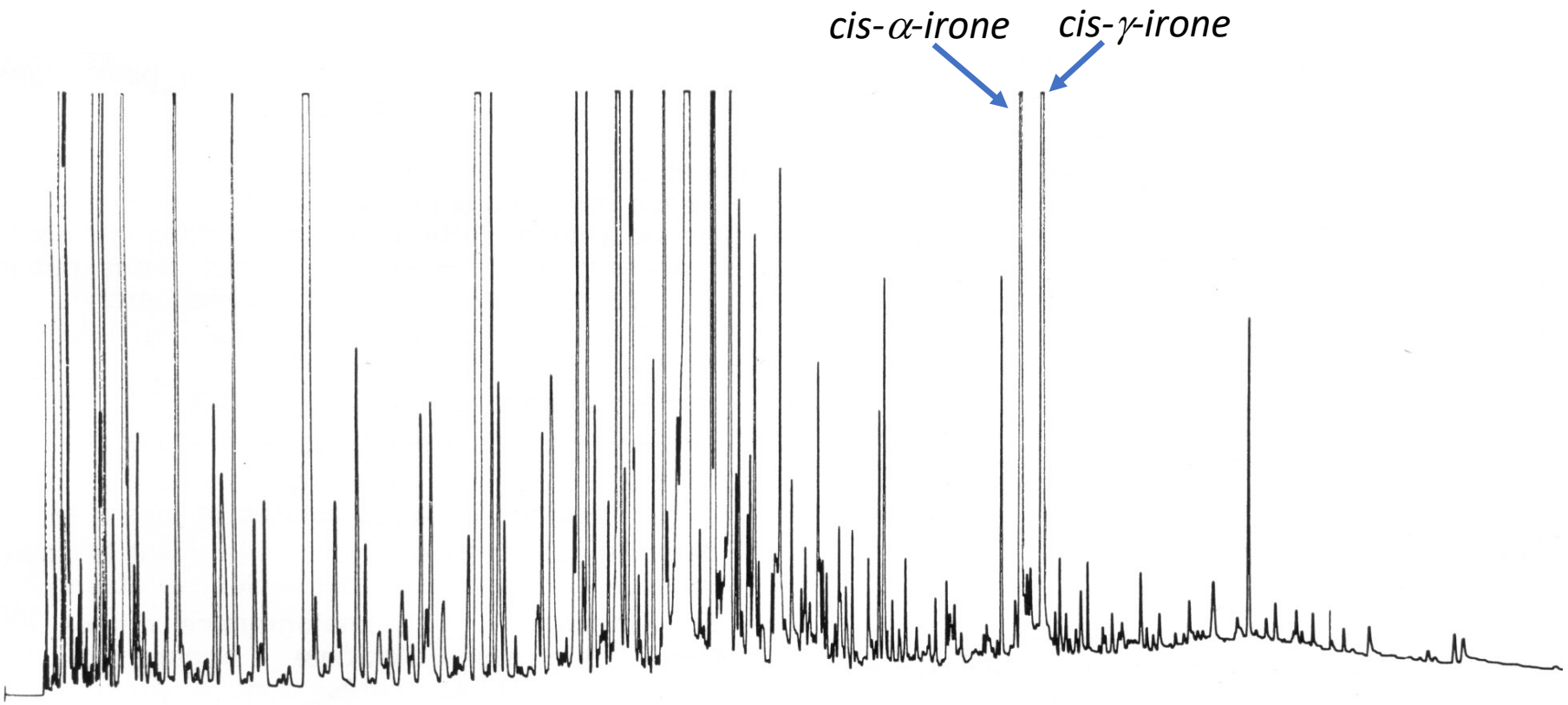
Résinoide de rhizomes d'*Iris germanica*

selon B. Roger, thèse - 2010



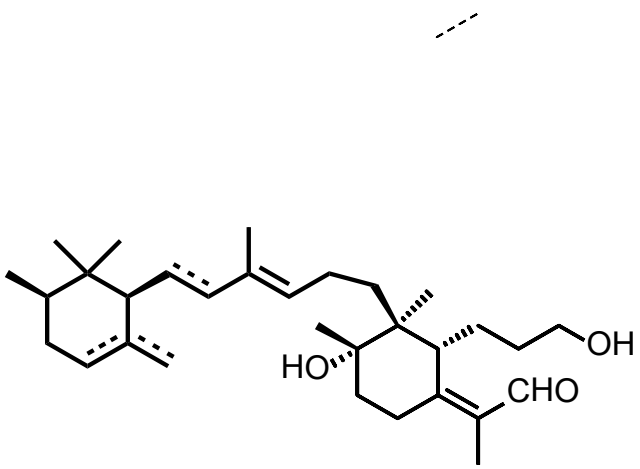
Irone enrichie DM (*Iris pallida*)

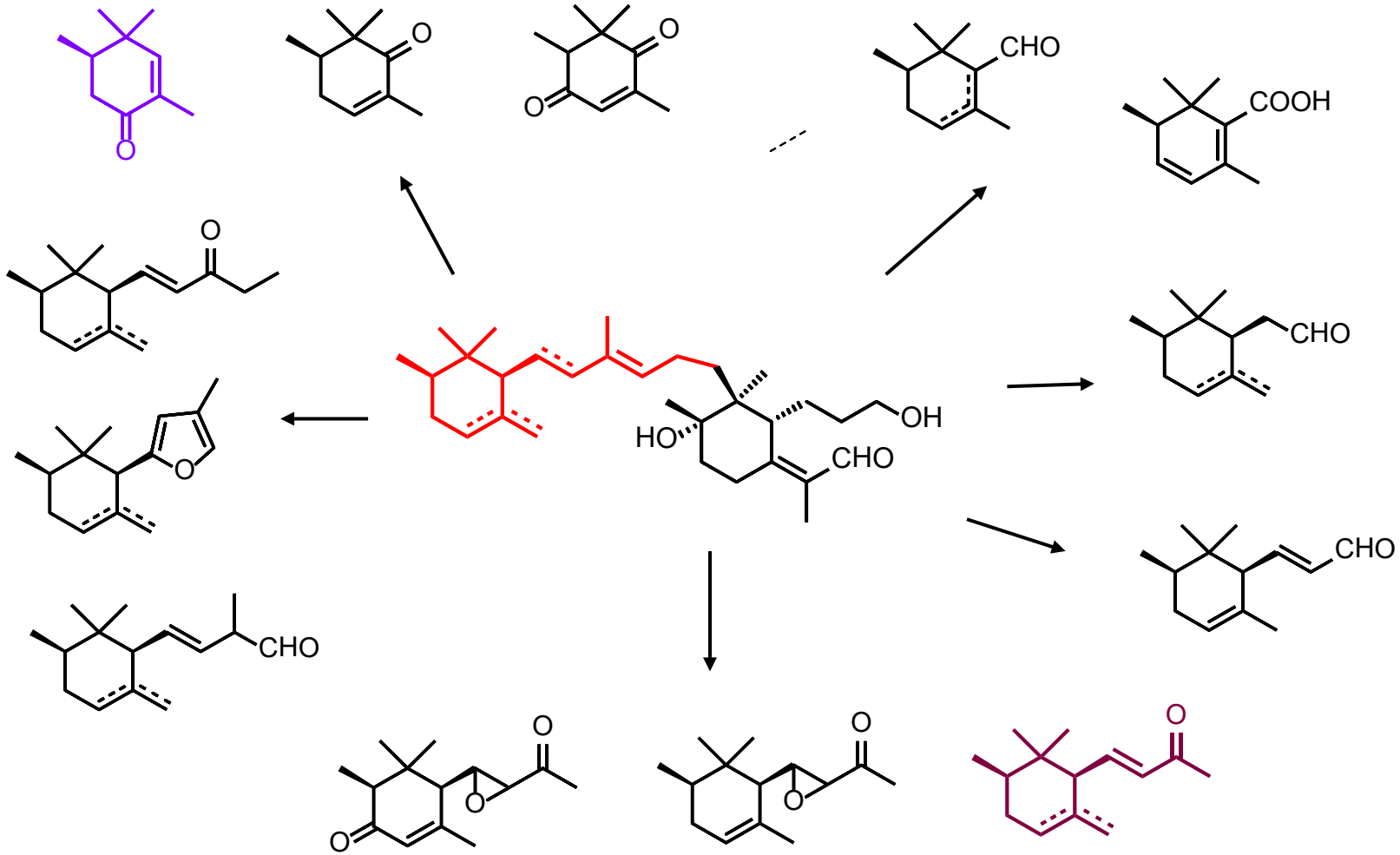


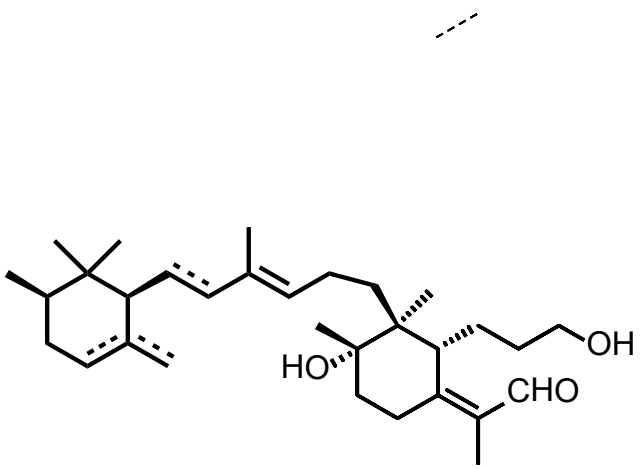


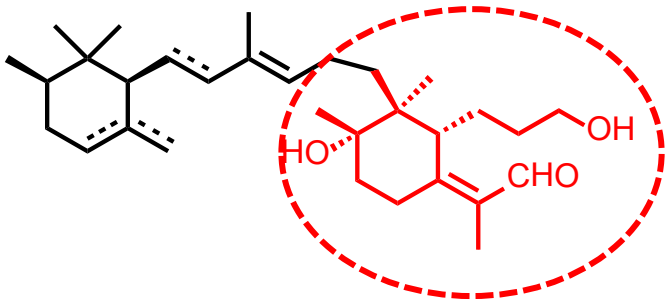
(1979)

Colonne de verre WCOT 70 m x 0,35 mm recouverte de UCON 50 HB-2000
40° C isotherme pendant 25 min puis 2°C/min jusqu'à 190°C, détection FID
Rivista Ital. E.P.P.O.S. 1981, **LXIII** (3, maggio), 141


HO
OH
CHO

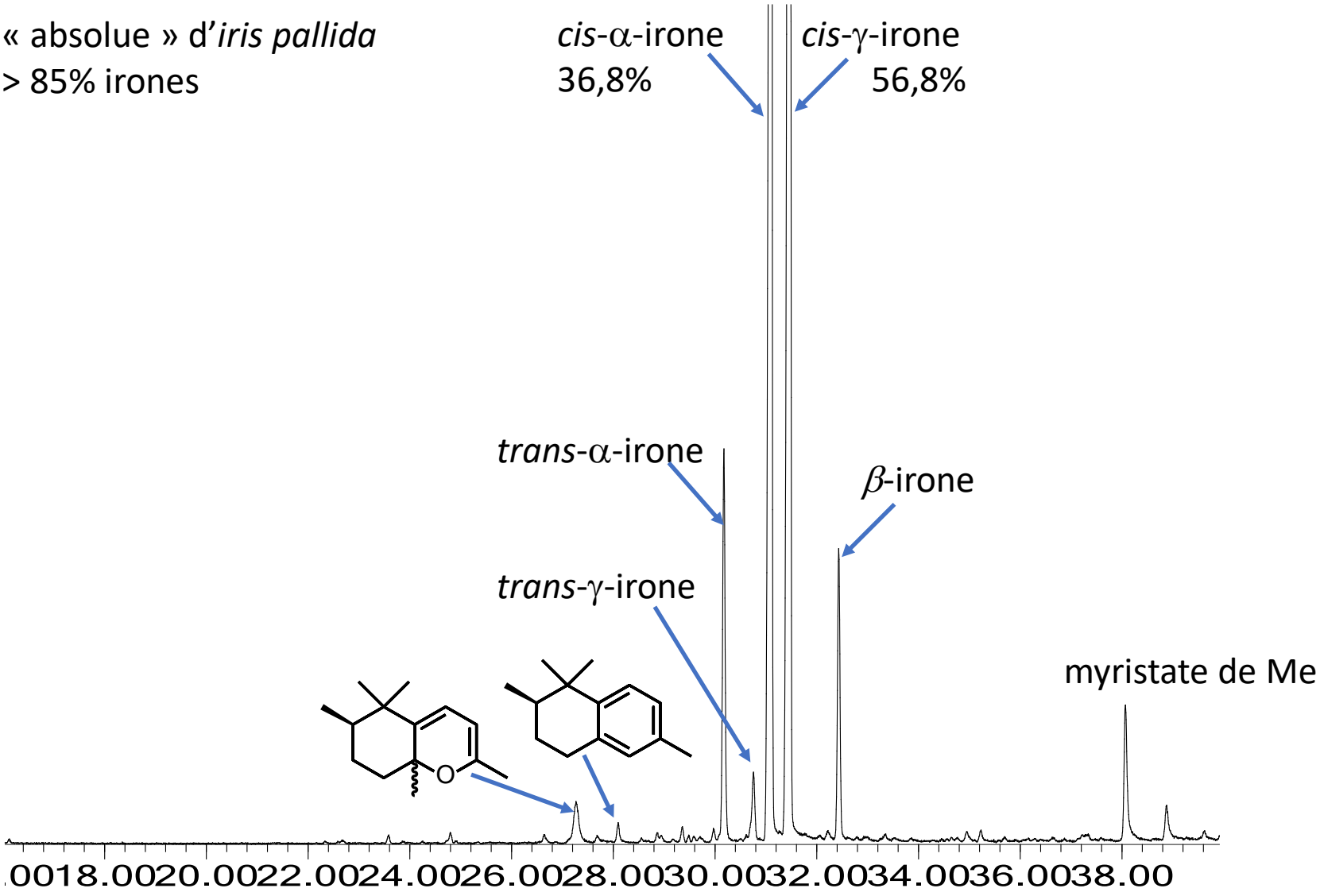

O
O
O
CHO
COOH
O
CHO
O
HO
OH
CHO
CHO
CHO
O
O
O
O


HO
OH
CHO


HO
OH
CHO

?

« absolue » d'*iris pallida*
> 85% irones



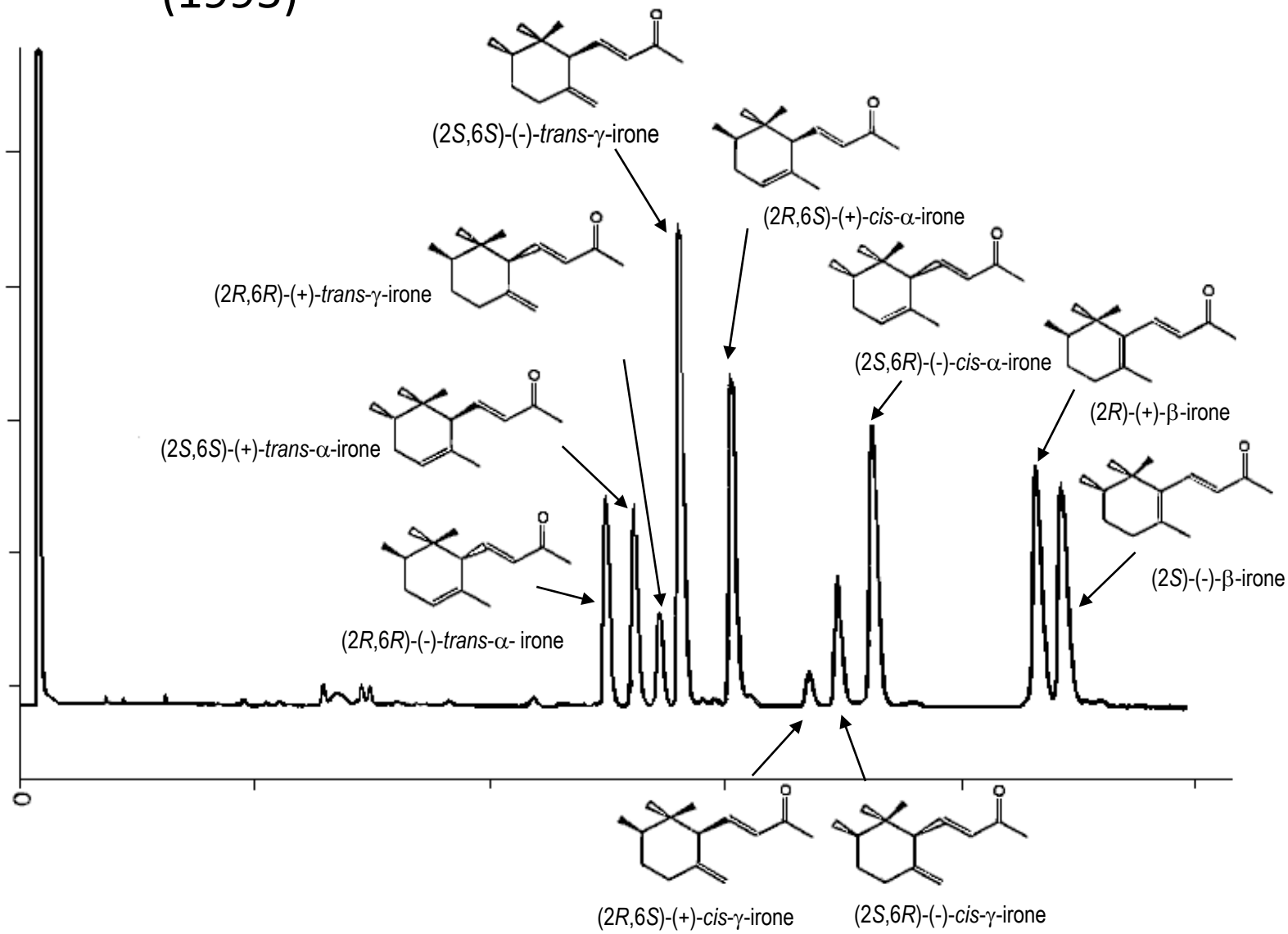
par Laurent et Jean CRABALONA
(Laboratoires R.E.A.C., Grasse)

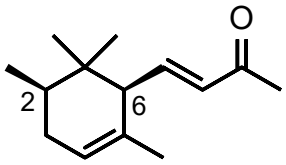
IRONES LEVOGYRES NATURELLES*

Leur présence prédominante dans la " portion à irones " de l'huile essentielle de rhizomes d'iris du Maroc (Iris germanica L.)

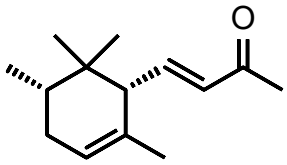

Grasse
GROUPE SCOLAIRE
JEAN CRABALONA

(1995)

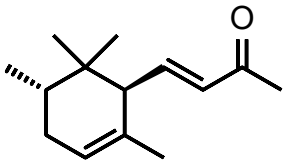

(2S,6S)-(-)-trans-γ-irone
(2R,6S)-(+)-cis-α-irone
(2R,6R)-(+)-trans-γ-irone
(2S,6R)-(-)-cis-α-irone
(2R)-(+)-β-irone
(2S,6S)-(+)-trans-α-irone
(2S)-(-)-β-irone
(2R,6R)-(-)-trans-α- irone
(2R,6S)-(+)-cis-γ-irone
(2S,6R)-(-)-cis-γ-irone



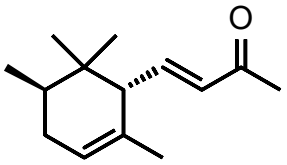
(+)-(2*R*,6*S*)-***cis***-α



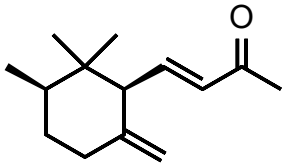
(-)-(2*S*,6*R*)-***cis***-α



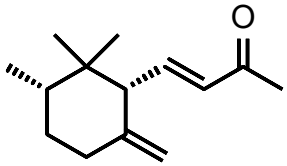
(+)-(2*S*,6*S*)-***trans***-α



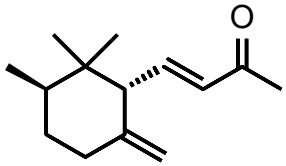
(-)-(2*R*,6*R*)-***trans***-α



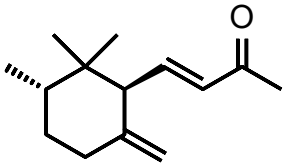
(+)-(2*R*,6*S*)-***cis***-γ



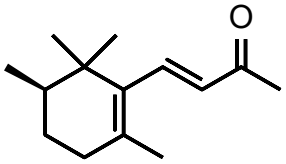
(-)-(2*S*,6*R*)-***cis***-γ



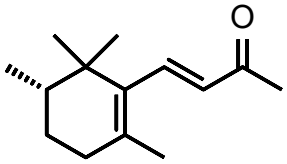
(+)-(2*R*,6*R*)-***trans***-γ



(-)-(2*S*,6*S*)-***trans***-γ

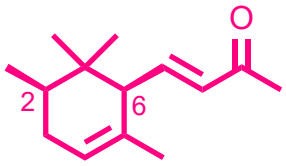


(+)-(2*R*)-β

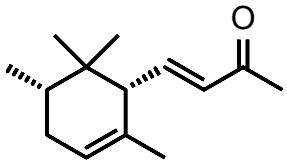


(-)-(2*S*)-β

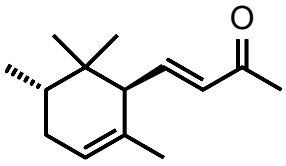
Galfré et coll, 1993



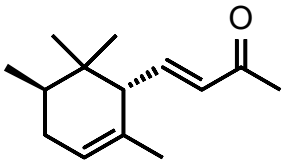
(+)-(2*R*,6*S*)-***cis***-α-



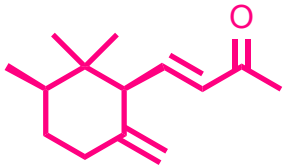
(-)-(2*S*,6*R*)-***cis***-α-



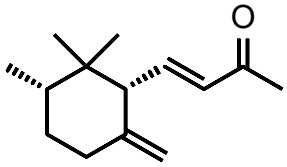
(+)-(2*S*,6*S*)-***trans***-α-



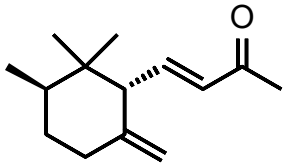
(-)-(2*R*,6*R*)-***trans***-α-



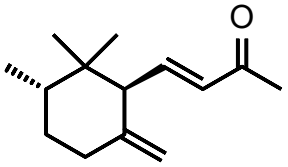
(+)-(2*R*,6*S*)-***cis***-γ-



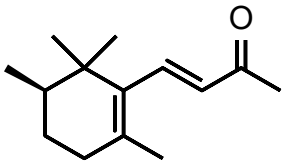
(-)-(2*S*,6*R*)-***cis***-γ-



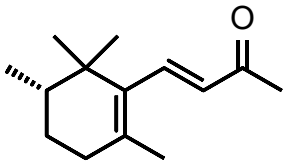
(+)-(2*R*,6*R*)-***trans***-γ-



(-)-(2*S*,6*S*)-***trans***-γ-



(+)-(2*R*)-β-



(-)-(2*S*)-β

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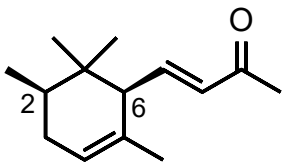
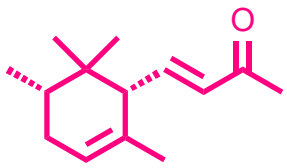
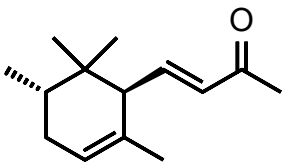


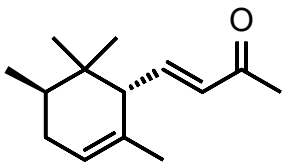
(+)-(2*R*,6*S*)-***cis***-α-



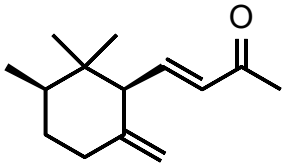
(-)-(2*S*,6*R*)-***cis***-α-



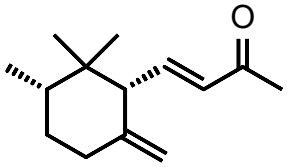
(+)-(2*S*,6*S*)-***trans***-α-



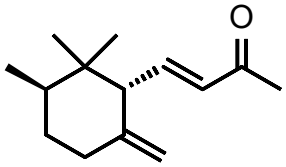
(-)-(2*R*,6*R*)-***trans***-α-



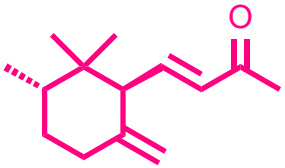
(+)-(2*R*,6*S*)-***cis***-γ-



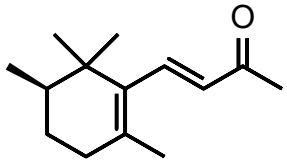
(-)-(2*S*,6*R*)-***cis***-γ-



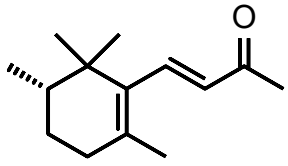
(+)-(2*R*,6*R*)-***trans***-γ-



(-)-(2*S*,6*S*)-***trans***-γ-



(+)-(2*R*)-β-



(-)-(2*S*)-β

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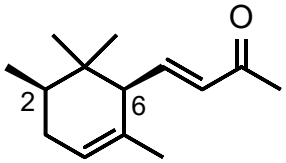
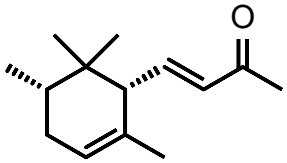
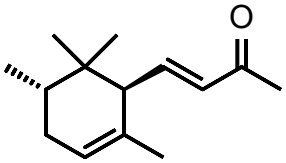


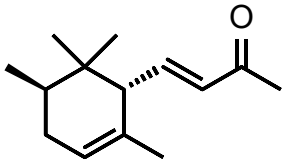
(+)-(2*R*'6*S*)-
cis-α-



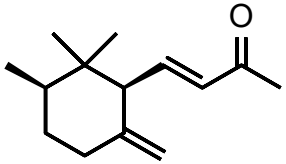
(-)-(2*S*'6*R*)-
cis-α-



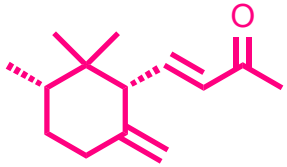
(+)-(2*S*'6*S*)-
trans-α-



(-)-(2*R*'6*R*)-
trans-α-

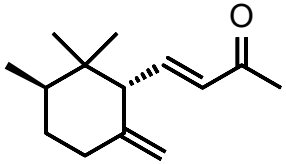


(+)-(2*R*'6*S*)-
cis-γ-

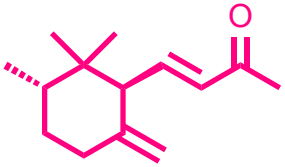


(-)-(2*S*'6*R*)-
cis-γ-

0,75 ng/l air

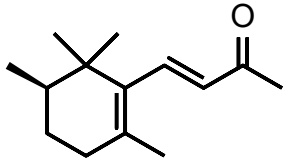


(+)-(2*R*'6*R*)-
trans-γ-

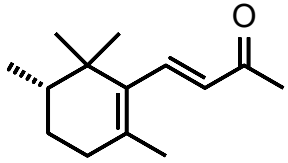


(-)-(2*S*'6*S*)-
trans-γ-

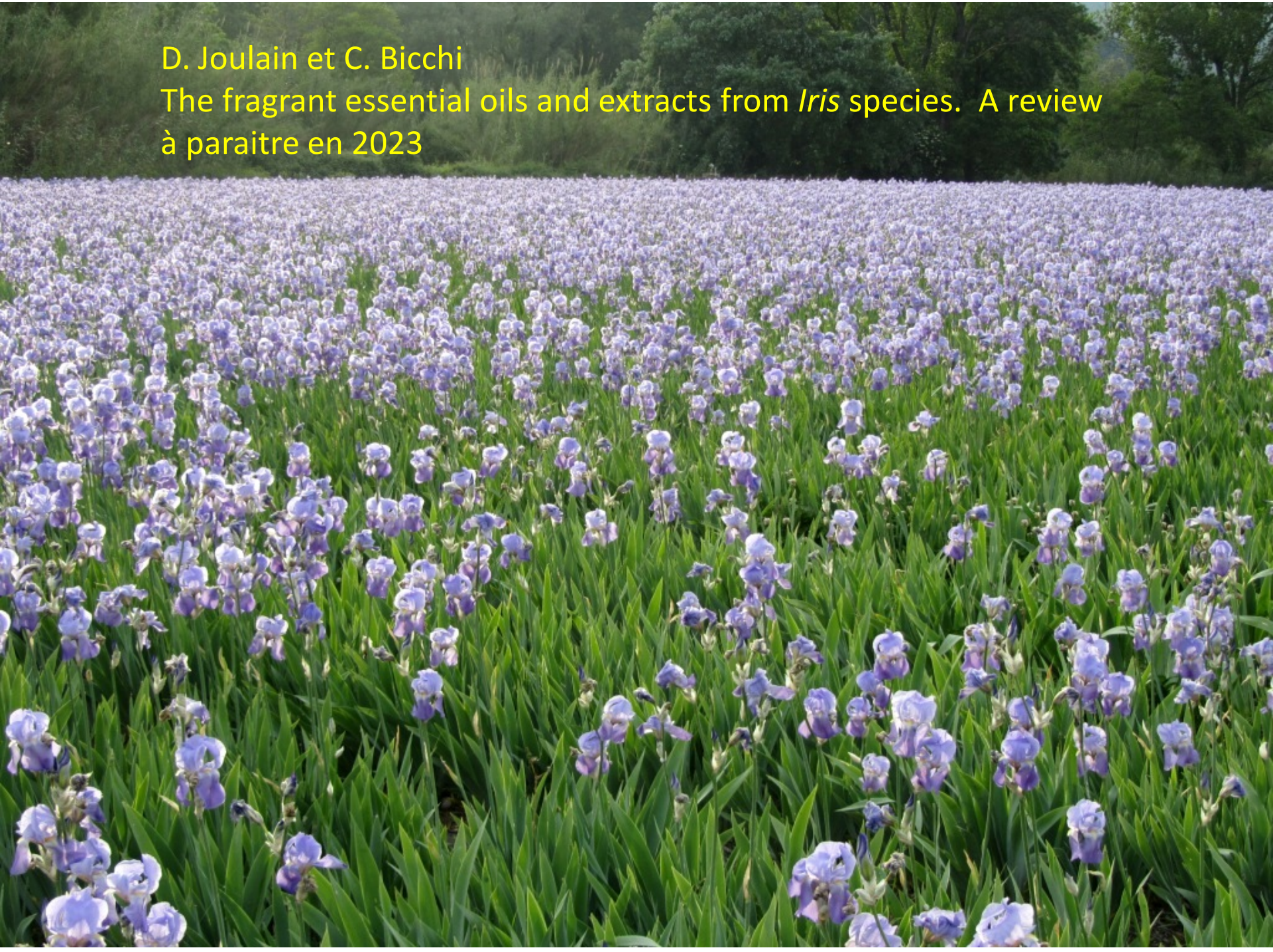
26,4 ng/l air



(+)-(2*R*)-β-



(-)-(2*S*)-β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à paraitre en 2023