The chemistry and biogenesis of the C13-norisoprenoids in wine

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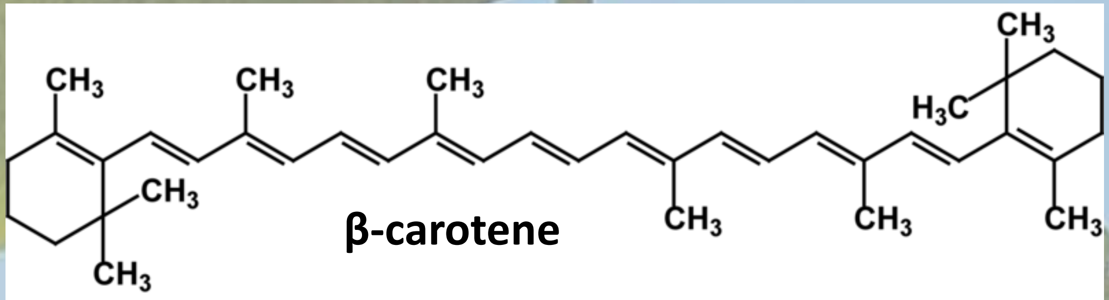
- **Sensory impact of the main C13-norisoprenoids on wine**

Carotenoids

Carotenoids are a family of **40-carbon** yellow or orange photosynthetic pigments. Capable of absorbing light, they have a photoprotective role (Baumes et al., 2002). The plant is able to protect its photosynthetic sites from excessive light radiation (FÉRET, 2009)

In *Vitis vinifera* species, **carotenoids** are present **in the leaves** and in the **grape skins** (Baumes et al., 2002), predominantly (85% of total carotenoids) present as **β-carotene** and **lutein**



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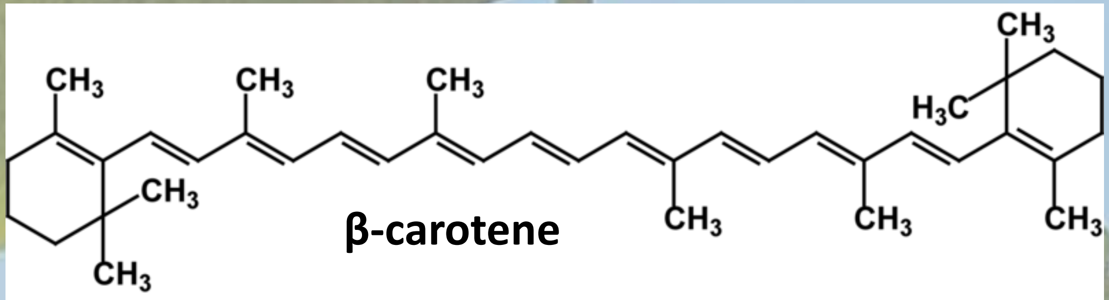

Neoxanthin, violaxanthine, zeaxanthine, lutein-5,6-epoxide, neochrome (Baumes et al., 2002; Mendes Pinto, 2009).

The presence of many conjugated **double bonds** makes this molecules family very unstable but this gives a strong **antioxidant** power. **Carotenoids will degrade into various molecules** that will differ according to their number of carbon atoms and their degree of oxidation (Mendes-Pinto, 2009)

Factors affecting carotenoids levels

With a photosynthetic and **photoprotective role**, the **level of carotenoids** present in the berry is **strongly dependent on its sun exposure** (Mendes-Pinto, 2009)

(Marais, Van Wyk and Rapp, 1991, Baumes et al., 2002, Kwasniewski et al., 2010, Marais et al., 2017, Demmig-Adams, Gilmore and Adams 3rd, 1996, Razungles et al., 1987)

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- **climatic conditions**
- **cultural practices**
- **vintage**
- **grape variety**

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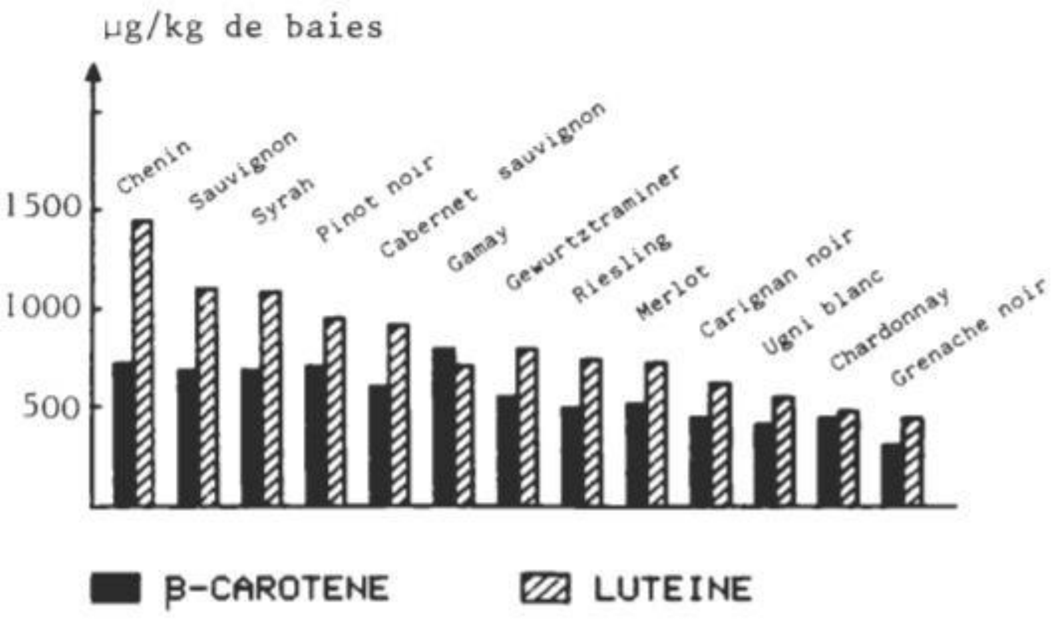
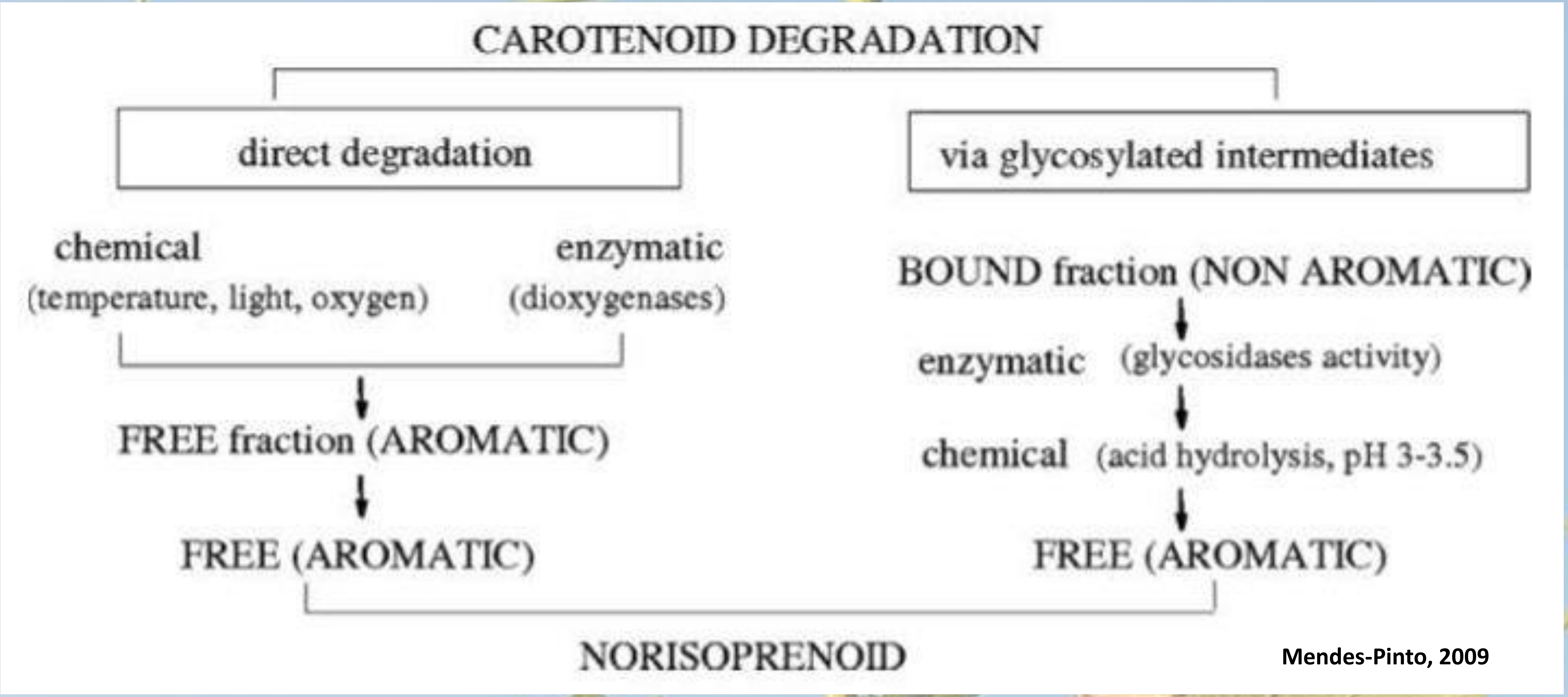


Fig. 1: Teneurs en β-carotène et en lutéine dans les baies de quelques cépages.
Contents of β-carotene and lutein in the berries of different grapevine varieties.

(Marais, Van Wyk and Rapp, 1991, Baumes et al., 2002, Kwasniewski et al., 2010, Marais et al., 2017, Demmig-Adams, Gilmore and Adams 3rd, 1996, Razungles et al., 1987)

Carotenoid degradation → Norisoprenoids



Mendes-Pinto, 2009

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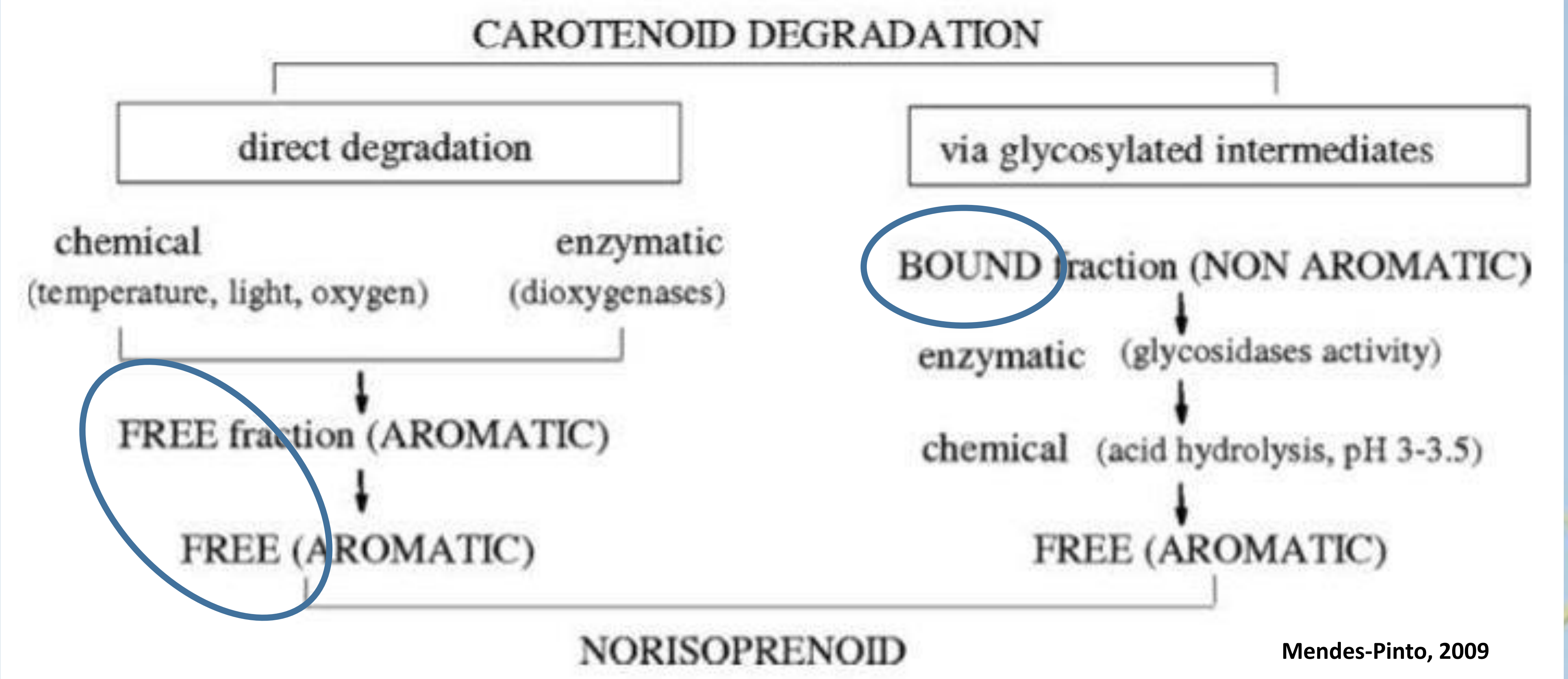

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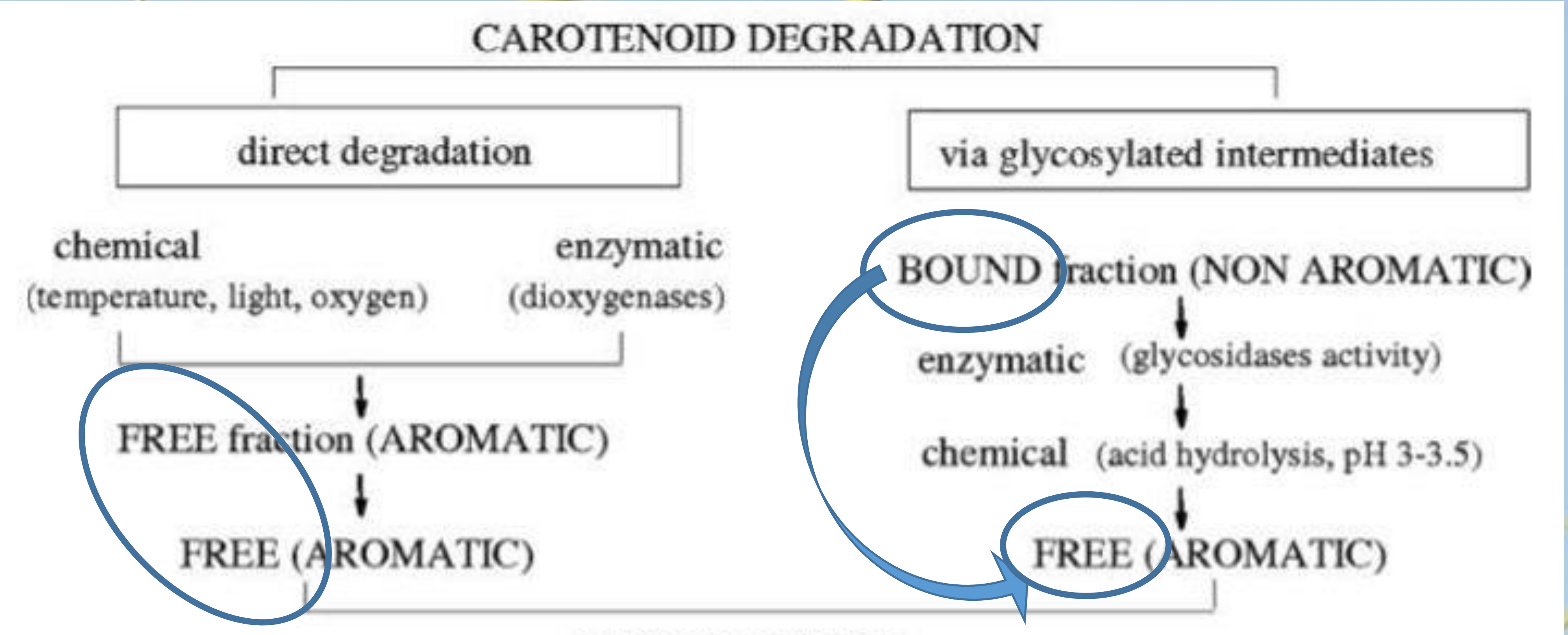

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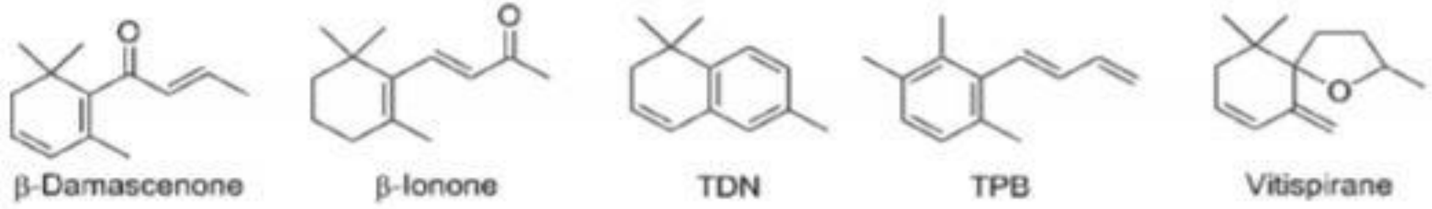
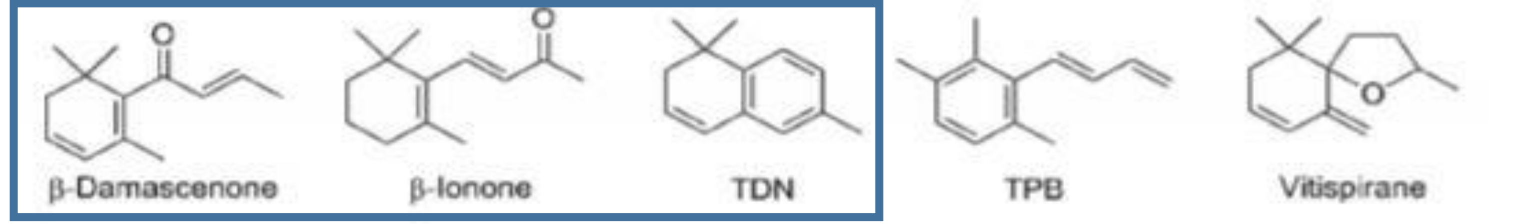
Biosynthesis of the main C13-norisoprenoids



Chemical structures of some important C_{13}-norisoprenoids in grapes



Chemical structures of some important C_{13}-norisoprenoids in grapes

The three C13-norisoprenoids compounds having the major impact on the flavor profile of the wine are:

- **β-damascenone**
- **β-ionone**
- **1,1,6-trimethyl-1,2-dihydronaphthalene (or TDN)**

Expression of nor-isoprenoids throuhout berry maturation (The hangtime project - UCDavis 2006-2009)

	2006 (8/9/06)	2007 (8/1/07)	2008 (8/16/08)
Harvest	Brix (DAV)	Brix (DAV)	Brix (DAV)
H1	22.4 (29)	21.0 (23)	19.9 (21)
H2	23.1 (38)	22.1 (30)	22.6 (29)
H3	24.7 (53)	24.6 (38)	23.2 (41)
H4	26.0 (74)	26.2 (58)	25.0 (63)
H5	27.8 (88)	26.2 (80)	36.6 (84)
H6	30.7 (98)	30.8 (120)	

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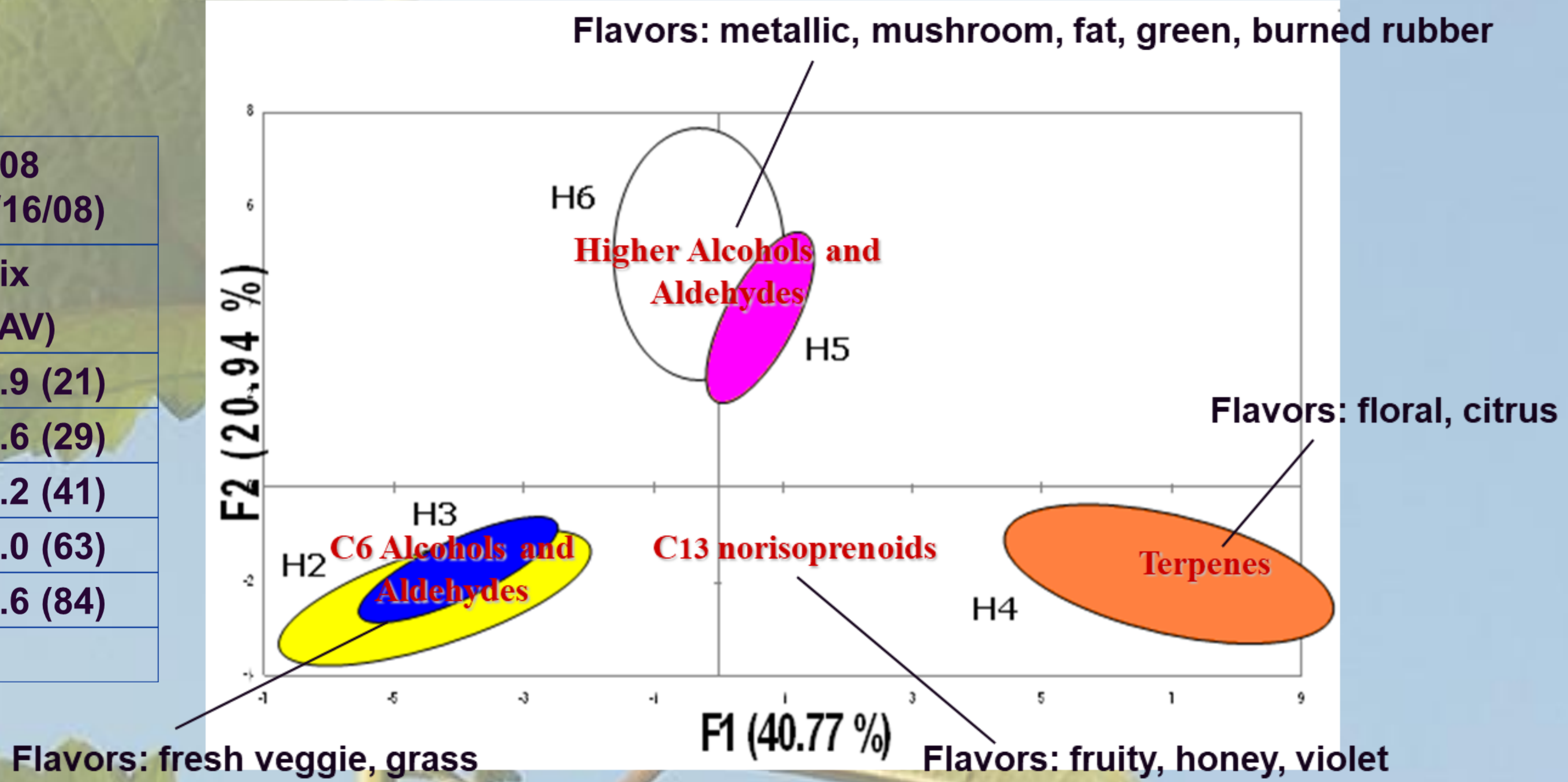

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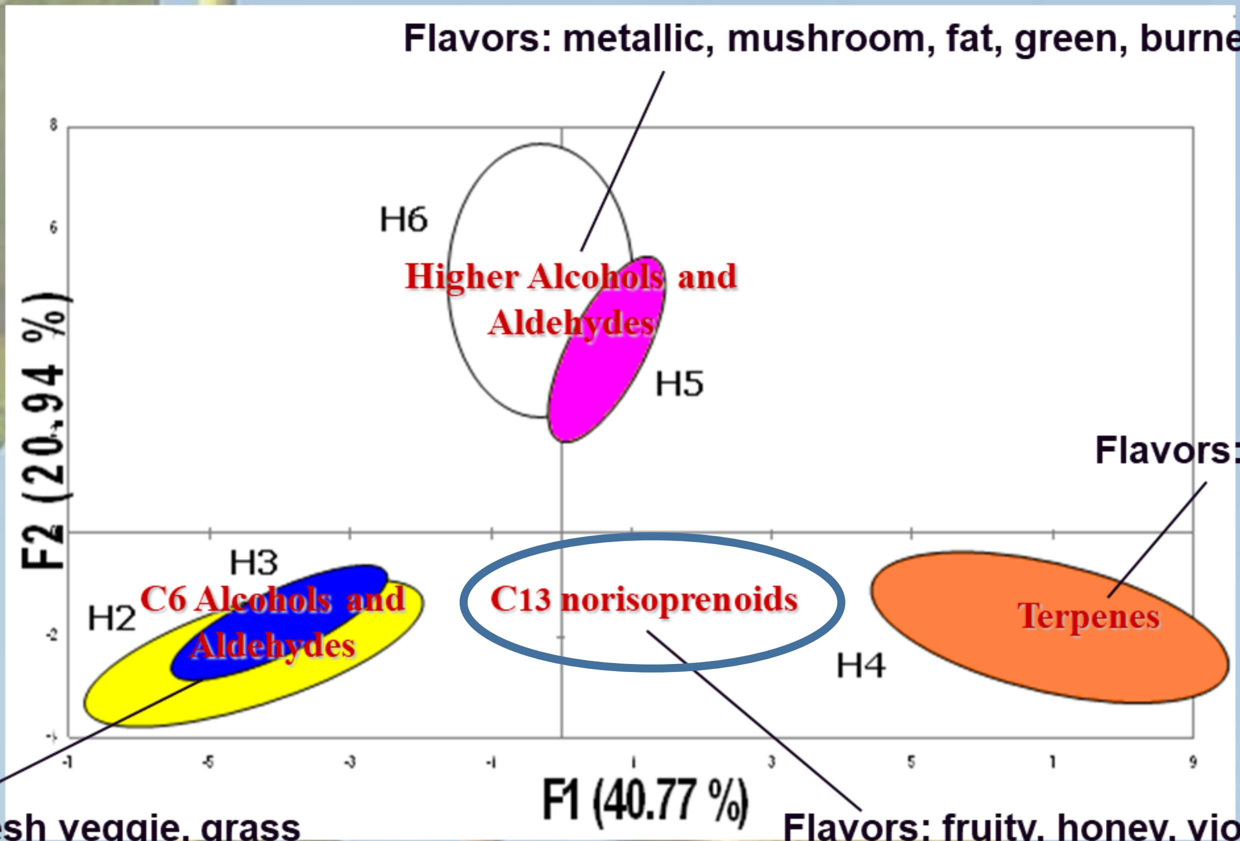
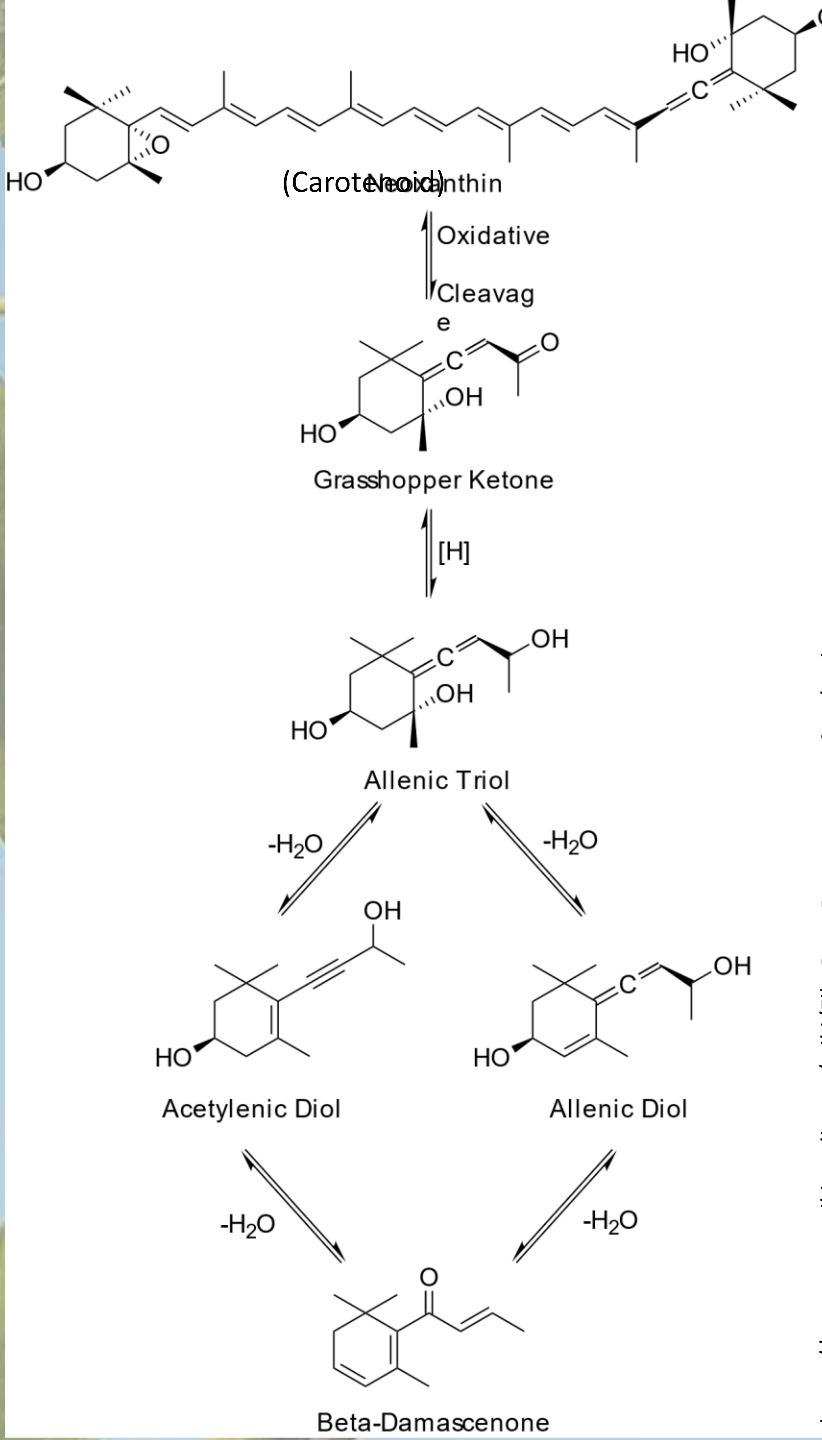
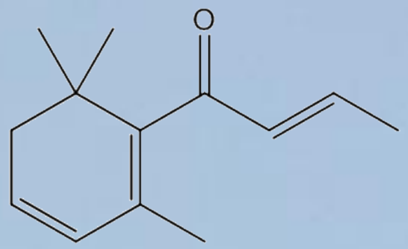


Biosynthesis of β-damascenone

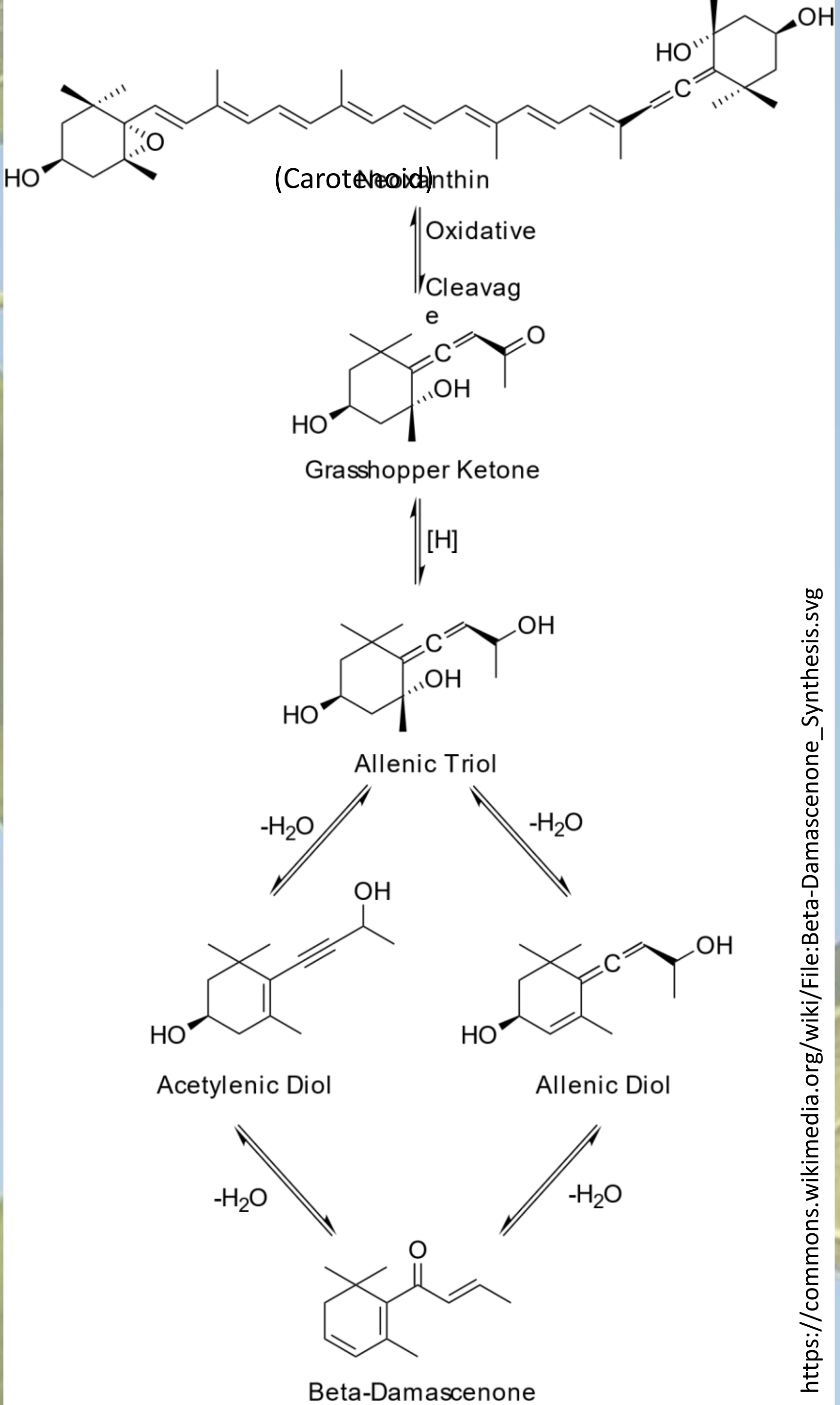


https://commons.wikimedia.org/wiki/File:Beta-Damascenone_Synthesis.svg



Biosynthesis of β-damascenone

Neoxanthin is a carotenoid.
In plants, it is an **intermediate in the biosynthesis of the plant hormone abscisic acid (ABA)**. Among other functions, ABA controls the stomatal closure



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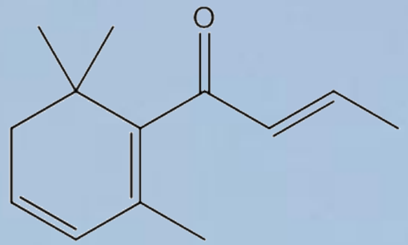
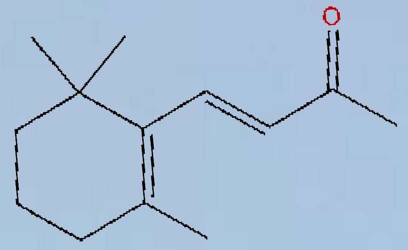
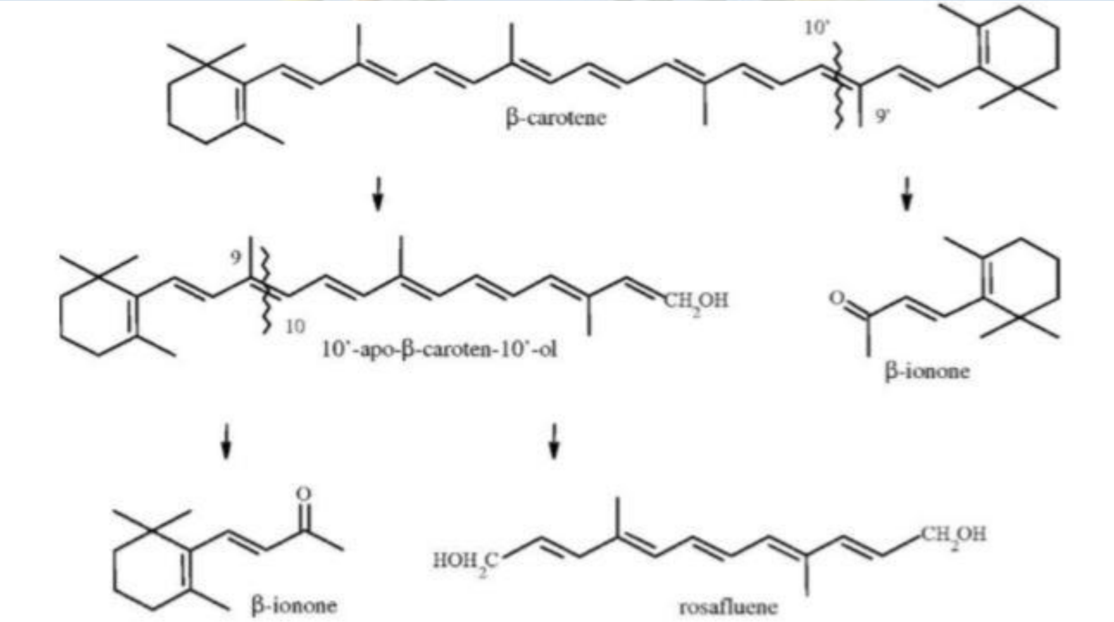




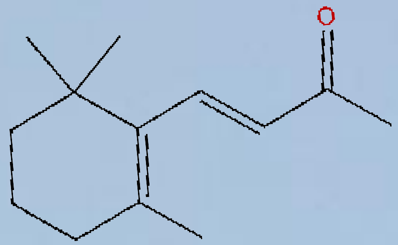
Biosynthesis of β-Ionone

By enzymatic cleavage



(Mendes-Pinto, 2009)

Biosynthesis of β-Ionone



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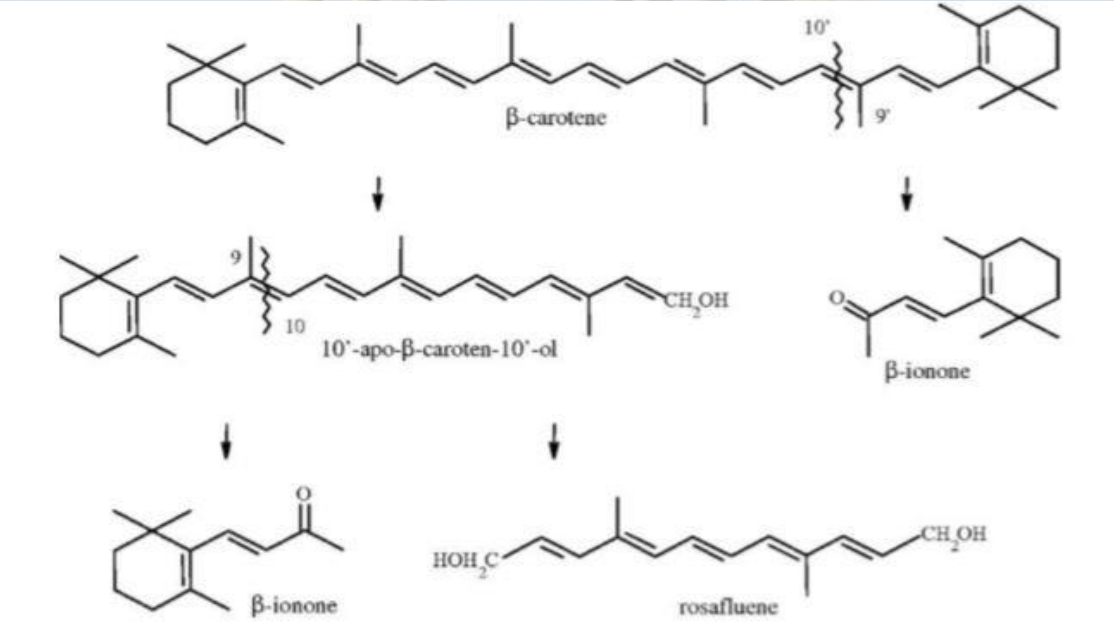
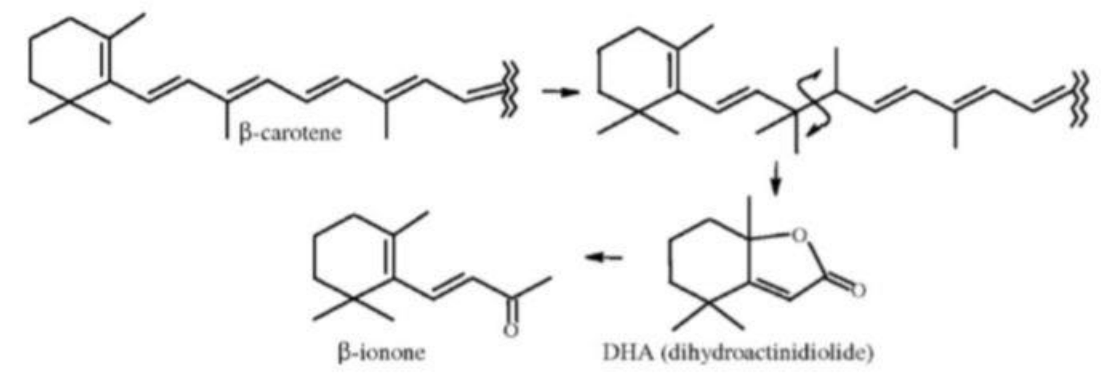


By photooxydation



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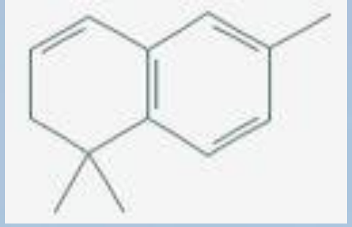
Biosynthesis of TDN



TDN in grapes is considered to be potential **degradation products from β-carotene** and lutein.
The first step of TDN formation is from the photochemical or enzymatic degradation of C-40 carotenoid compounds, which exist in wine around 1-2 mg/L concentrations (Marais et al, 1990).

The increase of **TDN in wine** over time is considered to be results of **acid catalyzed hydrolysis of** carotenoid derived precursors, such as Zeaxanthin, **Riesling acetal** and glycosylated precursors (Daniel et al, 2009)

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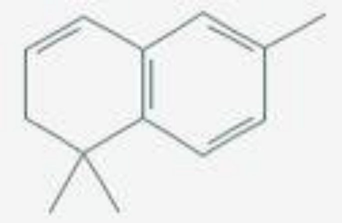

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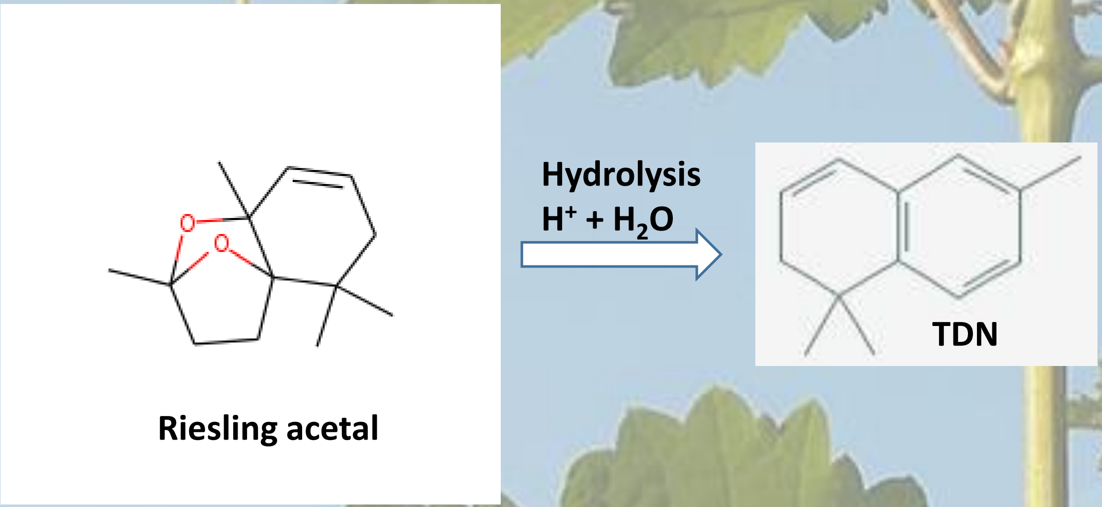
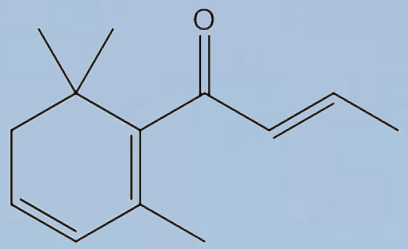


Sensory impact of the main C13-norisoprenoids on wine

Compound	Descriptors	Threshold	Grapes/Wines	Range of conc.
TDN		2µg/L	aged Rieslings and others	up to 50 µg/L
β-Damascenone	  cooked apple, prunes, honey, ripe fruit 	in wine 4-7 µg/L*	several whites and reds	Reds: up to 2 µg/L Whites: 5-10 µg/L
β-Ionone	  Violet Raspberry	90 ng/L	Syrah, Negrette (Pinot Saint George) Pinot noir and others	**up to 340 µg/L (Negrette)

*Kotseridis, Baumes and Skouroumounis, 1999
**La Grappe d'Autan n°97 Nov 2013

β-damascenone: a fruity aroma enhancer



In a study by PINEAU et al., both free and bound β-damascenone were isolated from various **French red wines** revealing **concentrations of 1-2 µg/L** for both free and bound compounds

In hydroalcoholic model solution, **β-damascenone:**

- **enhances the intensity of the fruity notes of a mix of ethyl esters** (ethyl cinnamate and ethyl hexanoate)
- **masks the herbaceous aroma of IBMP (3-isobutyl-2-méthoxypyrazine) vegetal character**

The results suggest that β-damascenone has more an indirect than a direct impact on red wine aroma

Now the question is, “how can we increase the concentration of β-damascenone from the vineyard to the bottle?” Answers in the next two presentations

Impact of β-damascenone on wine aroma profile:

Marco’s representation!

Impact of β-damascenone on wine aroma profile:

Marco’s representation!

β-ionone: a floral/red berry aroma

The β-ionone is associated with a very characteristic **violet, raspberry** and sometimes **woody** aroma (Mendes-Pinto, 2009).

Its **perception threshold in red wines** is **90 ng/L**, which is close to its content in wine (Kotseridis et al., 1999).

β-ionone has been identified in several red varieties:

- **Bordeaux varieties** (Kotseridis 1999)
- **Pinot noir** (Fang and Qian 2005)
- **Syrah**
- **Negrette (Pinot St George)**
- Etc.

TDN: the kerosene aroma of aged Rieslings

1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), is the chemical compound responsible for the **kerosene or petroleum odor typical of Riesling**

The perception **threshold is 2 µg/L**

It exists in highest quantities in **aged Riesling wines**, reaching **as high as 50µg/L** but is also widely prevalent in:

Chardonnay

Sauvignon Blanc

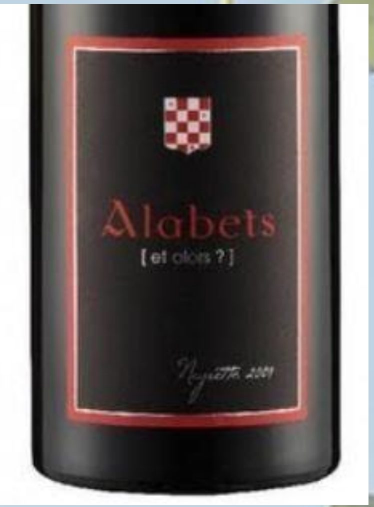
Pinot noir

Cabernet Sauvignon (at levels close to its threshold) with exception of 6.4µg/L in

Cabernet Franc

In berries and wine, it is present in the form of non-aromatic **glycosylated precursors** which will be hydrolysed during the aging of bottled wine

Thus, its concentration in young wines is often below the perception threshold, but increases with age (Sacks et al., 2012)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PINOT NOIR
SÜDTIROL · ALTO ADIGE
KEROSENE
RHEIN
RIESLING

Thanks for your attention!

General literature:

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