The chemistry and biogenesis of the C13-norisoprenoids in wine

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Summary

• General presentation of C13-norisoprenoids: from carotenoids to norisoprenoids
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• Biosynthesis of the main C13-norisoprenoids
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• Sensory impact of the main C13-norisoprenoids on wine
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 (FERET, 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 \(\beta\)-carotene and lutein.
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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**.

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)

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- cultural practices
- vintage
- grape variety

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Carotenoid degradation → Norisoprenoids

General presentation of C13-norisoprenoids: from carotenoids to norisoprenoids

Mendes-Pinto, 2009
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Carotenoid degradation $\rightarrow$ Norisoprenoids

Mendes-Pinto, 2009
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Biosynthesis of the main C13-norisoprenoids

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 throughout berry maturation (The hangtime project - UCDavis 2006-2009)

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<tr>
<th>Harvest</th>
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Flavors: metallic, mushroom, fat, green, burned rubber

Higher Alcohols and Aldehydes

Flavors: floral, citrus

C6 Alcohols and Aldehydes

C13 norisoprenoids

Terpenes

Flavors: fruity, honey, violet

Flavors: fresh veggie, grass

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Biosynthesis of β-damascenone
Biosynthesis of the main C13-norisoprenoids

Biosynthesis of \( \beta \)-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.
Biosynthesis of β-Ionone

By enzymatic cleavage

(Mendes-Pinto, 2009)
Biosynthesis of the main C13-norisoprenoids

Biosynthesis of β-Ionone

By enzymatic cleavage

By photooxydation

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Biosynthesis of the main C13-norisoprenoids

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

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


11. La Grappe d’Autan n°97 Nov 2013


Literature on β-damascenone:


