Cabernet Sauvignon: the "green" herbaceous character

Cabernet Sauvignon seems to have a tendency to produce strong "green" herbaceous characters. Herbaceousness can be caused by 1. Methoxy**pyrazine**, 2. Certain unripe monomeric, dimeric and trimeric phenolics or 3. Polyunsaturated fatty acid derivatives, such as hexanal.

Pyrazines (1,4-diazines) are nitrogen-containing heterocyclic compounds that are quite widely distributed in nature in both the animal and plant kingdoms. The food industry is the area in which these compounds have been the most extensively studied. They are considered to be the heterocyclic compounds most widely represented in food aromas. They can be classified into three groups depending on their origins: those formed by heat treatment, those formed by micro-organisms and **those present in the natural state in plants**. Amongst the methoxypyrazines in the last category, the most important ones are 3-isopropyl2-methoxy-pyrazine (IPMP), sec-butyl2-methoxy-3-pyrazine (s-BMP) and **3-isobutyl-2-methoxy-pyrazine (IBMP). IBMP** was identified for the first time in green, or bell, pepper. Its detection threshold in **water** is estimated to be 2 ng/L (equivalent to two berries in a million tons of grapes), and is considered to be responsible for the characteristic aroma of green peppers. It was subsequently identified in several raw vegetables such as chili peppers, beans, broad beans, lettuce, spinach, etc. In 1975, **IBMP** was identified for the first time in Cabernet Sauvignon grapes (Vitis vinifera L. cv. Cabernet Sauvignon). It was thought to be responsible for the green pepper aroma that is characteristic of this variety. In 1982, a study identified **IBMP** in Sauvignon blanc grapes (Vitis vinifera L. cv. Sauvignon blanc). Since 1985, its contribution to the vegetal and green pepper aromas of Cabernet Sauvignon, Merlot and Sauvignon blanc wines has been demonstrated many times. As such, 2-methoxy-3-isobutylpyrazine would seem to be the key compound involved in the green pepper aroma of Cabernet Sauvignon, Sauvignon blanc and some Merlot wines. With these varietals, the **IBMP** concentration significantly exceeds the detection threshold. French studies of Cabernet Sauvignon and Cabernet Franc production in 1991 and 1992 in Bordeaux and the Valley of the Loire showed that the detection threshold for the green pepper aroma in the **wine** was 15 ng/L. These studies showed that IBMP was the main contributor to this vegetal aroma.

This compound is present in grapes, it has no known precursor and its concentration decreases during ripening under the influence of light. Consequently, a high concentration in grapes at harvest is associated with a lack of ripeness and has a negative impact on wine aroma quality. Winemakers and oenologists commonly associate such aroma characteristics in grapes with low anthocyanin content and with mediocre "tannin quality". Cabernet Sauvignon vines can grow rapidly and as a result of shoot growth may lead to shading of grape bunches. The thick grape skins are full of color and phenolics with a high seed-to-pulp ratio of 1:12 (Semillon is 1:25, by comparison). The berries are also small and attention must be paid to seed and skin maturity.

The winemaker will find that clarified musts of Sauvignon blanc contain one-half the levels of IBMP as unsettled musts. Part of the IBPM seems to interact with grape solids and is thus eliminated. In Sauvignon blanc, within 24 hours of maceration (skin contact), prior to start of fermentation, all of the IBMP found in the resulting wine has already been extracted from the crushed grapes. It has been shown that the IBMP content in Cabernet Sauvignon and Cabernet Franc is not increased by successive punching-downs or by extended maceration.

The IBMP content of press wines can be higher than free run. Bottle aging seems to have no effect on IBMP levels. Grape pulp contains little IBMP. Stems contain a lot.

From veraison to harvest, the IBMP proportionately decreases in the stems and increase in the grape skins. In a study in Bordeaux in 1999, the distribution of IBMP in different components of Cabernet Sauvignon cluster during ripening was (in %):

	Stems	Skins	Seeds	Pulp
Before Veraison	79.2	14.8	5.1	0.9
After Veraison	62.4	34.8	2.5	0.2
At Harvest	53.0	44.9	1.9	0.2

At harvest, the IBMP is found mainly in the stems. Up to harvest the IBMP increases in the basal leaves (the first 3 or 4 leaves from the base). There is an advantage to removing basal leaves prior to harvest. It is important to remove summer laterals in the cluster zones and to leaf thin between fruit set and veraison. This leads to higher sugars, lower IBMP and smaller berries at harvest.

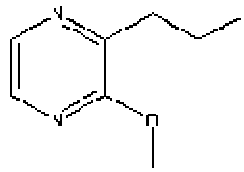
With proper grape ripening conditions, wines can be made without detectable levels of IBMP. IBMP content increase in berries in mid-veraison (late-July to mid-August) and is related to vine vegetative growth. Irrigation can increase vine vigor and resultantly lead to increase in IBMP. The IBMP synthesis seems to occur between fruit set and two to three weeks prior to the onset of veraison. On the primary shoot, the basal leaves have very high levels of IBMP. Products synthesized in the leaves are then transported to the berries. The oldest leaves are the biggest carriers of IBMP.

So, it is in the vineyard that **IBMP** must be controlled. In the vine, the **IBMP** content can be very high in stems and leaves. So, leaves should be kept out and extended cold maceration may cause a problem. The **IBMP** content in berries changes with time; unripe seeds contain **IBMP.** After veraison, the **IBMP** content in seeds declines and may be negligible at harvest. Skin **IBMP** content also declines with ripening, however many factors dictate. It'd been shown that vineyards in cloudy locations or with shaded clusters will have slower decline in levels of **IBMP.** Bunch exposure is important, but sunburned fruit must be avoided. Better drained soils lead to faster decline in **IBMP.** The **IBMP** reaction to water or nitrogen levels in the vineyard is not understood. However, it has been shown that levels of **IBMP** can closely follow levels of malic acid, a very easy item to measure.

As a side, it is known that phenolic compounds can impart bitter, herbaceous flavors in grapes or wine. The phenolics in seeds and skins increase rapidly a couple weeks before veraison. Ripe skins have a high proportion of polymeric phenolics, which either have associated with anthocyanin to become astringent tannin or have bound to polysaccharides or protein, inducing softer mouthfeel. Ripe seeds have few bitter phenolics. They contain tannins which taste like dark toasted bread or coffee beans.

Synonyms: Methoxypyrazine, Pyrazine, 2-methoxy-3-(2-methylpropyl)-; 3-Isobutyl-2-methoxypyrazine; **2-Methoxy-3-isobutylpyrazine**; 2-Methoxy-3(6)-isobutyl-pyrazine; 2-Isobutyl-3-, 5 or 6-methoxy-pyrazine; 2-Isobutyl-3-methoxypyrazine, cont. 20% 2-isobutyl-6-

methoxypyrazine

Structure:  **3-isobutyl2-methoxy-pyrazine (IBMP)**

CAS RN: 24683-00-9	**Formula**: $C_9H_{14}N_2O$
MW: 166.2224	**OAV**: 1.70×10^4

Contribution to coffee: earthy aroma

Other: Flavor constituent in green bell peppers.

IBMP is very water-soluble, so fermentor extraction happens quickly. Maceration period, pressing time and pump over have little influence of final concentration.

Avoiding high **2-methoxy-3-isobutylpyrazine** levels at harvest:

1. High moisture content in soils before and after veraison delays **IBMP** degradation.
2. Sun exposure to the bunches speeds **IBMP** reduction.
3. Removal of leaf shading leaves, done well before veraison, can decrease **IBMP**.
4. North –south row orientation give the best results for sun exposure; morning and late afternoon exposure is preferred.
5. **IBMP** decline after veraison follows malic acid decline. Warm nights may also assist in **IBMP** decline.
6. Unripe seeds have high levels of **IBMP**. Berry sensory analysis before harvest can reveal lack of seed ripeness.
7. Maceration in the fermentor is not important.

Enhancing phenolic maturity:

1. Extremes of water availability may cause imbalance in phenolic development.
2. Inadequate leaf area-to-fruit weight ratios seem to slow phenolic ripening.
3. Berries should be in the optimum range for enzyme activity (15° to 35° C, 60° to 95° F)

Roujou de Boubee, Dominique, "Research on 2-methoxy-3-isobutylpyrazine in grapes and wine." School of Oenology, University of Bordeaux II.

9 December 2004 George Vierra gjvnapa@sbcglobal.net