

Research Note

3-hexen-1-ol isomers in Müller-Thurgau wines: A "varietal" characteristic affected by must sulfiting time

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S u m m a r y : Must sulfiting time can be responsible for differences in the (3E)/(3Z)-hexen-1-ol ratio of wines produced on a semi-industrial and industrial scale. However, as the (3E) isomer is normally higher than the (3Z) isomer, the ratio could be used, with some caution, as a contributing parameter to verifying the varietal origin of some wines, in particular of Müller-Thurgau. After hexanol, (3E)-hexen-1-ol seems to be the main C₆-alcohol in Müller-Thurgau wines from Trentino (Italy).

Introduction: The content of (3E)-hexen-1-ol has been shown to belong to the most important analytical parameters to discriminate monovarietal wines of Riesling, Müller-Thurgau, Kerner, Scheurebe, Ehrenfelser and Bacchus (RAPP *et al.* 1993). The levels of this compound and of its (3Z) isomer were considered also as possible varietal characteristics because they were sufficiently stable (RAPP 1989) and remained unaffected by the metabolic activity of yeasts (JOSLIN and OUGH 1978; DI STEFANO and CIOLFI 1982; HERRAIZ *et al.* 1990). Both (3E)- and (3Z)-hexen-1-ol were found among the significant aroma parameters discriminating Venetian white wines (MORET *et al.* 1984).

High levels of 1-hexanol and, in particular, of (3E)-hexen-1-ol exceeding the corresponding (3Z) isomer were observed in an investigation of Müller-Thurgau wines (vintages 1993 and 1994) from Trentino (northeastern Italy), produced without pomace overpressing (NICOLINI *et al.* 1995 a and b). The (3E)/(3Z)-hexen-1-ol ratio was shown to be affected by the vinification scale, with higher values in wines of the experimental winery of the Institute compared to wines of the industry (VERSINI *et al.* 1995). The short time (10-15 min) between grape crushing and must sulfiting in the experimental winery was considered to be one of the possible causes. Investigations on the effect of SO₂ on the content of C₆-compounds have already been reported (CORDONNIER and BAYONOVE 1977; JOSLIN and OUGH 1978; HERRAIZ *et al.* 1990; GOMEZ *et al.* 1993), but possible variations of (3E)-hexen-1-ol have not been frequently considered (HERRAIZ *et al.* 1990).

Materials and methods: Three blocks (50 kg each) of Müller-Thurgau grapes from the same vineyard were picked at ca. 18.2 °Brix and each of them was divided into 4 lots; each lot was crushed and pressed (2.5 bar 18 °C grape temperature).

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The experiment consisted of 2 treatments ("S" = 50 mg SO₂/kg grapes; "S+A" = 50 mg SO₂/kg grapes + 50 mg ascorbic acid/kg grapes) which were performed at two times: "ANTE" = addition of S or S+A while the must was running down the press; "POST" = addition at racking after settling.

The settling (12 h at 14 °C) of all musts was carried out with bentonite (50 g/hl), then they were racked, inoculated with selected yeasts (30 g/hl) and fermented at 22 °C. The wines were analysed 1 month after fermentation, cold stabilization, sulfiting and racking. Analyses were performed by an already reported method (HRGC after adsorption on XAD-2 and elution with organic solvents: GUNATA *et al.* 1985; VERSINI *et al.* 1993).

The data of the content of C₆-compounds and must yield (%) after pressing were submitted to ANOVA (variance sources: treatments, times, blocks, times x treatments; SAS software).

Results and discussion: No significance was observed for the variable "must yield". The factor „time“ proved to be significant for all 3 C₆-compounds, including 1-hexanol (Tab.1). The early addition (ANTE) of SO₂ or SO₂ + ascorbic acid resulted in lower contents of 1-hexanol and higher levels of 3-hexen-1-ols, particularly the (3E) isomer. The content of (3E)-hexen-1-ol is always higher than that of the corresponding (3Z) form, whatever the time or treatment (Tab. 2).

Table 1

Content of C₆-alcohols (µg/l) in Müller-Thurgau wines as affected by must sulfiting time; 6 observations each. (ANTE, POST: see Materials and methods)

| | ANTE | POST | Pr > F |
|-----------------|----------|------|--------|
| | settling | | |
| 1-hexanol | 1385 | 2438 | 0.0001 |
| (3E)-hexen-1-ol | 131.8 | 46.5 | 0.0001 |
| (3Z)-hexen-1-ol | 27.7 | 18.1 | 0.0010 |

Table 2

Content of 3-hexen-1-ol isomers (µg/l) in Müller-Thurgau wines as affected by must treatment with additives (S = sulfur dioxide, 50 mg/kg; S+A = S + ascorbic acid, 50 mg/kg) and must sulfiting time. (ANTE, POST: see Materials and methods)

| | (3E)-hexen-1-ol | | (3Z)-hexen-1-ol | |
|---------------|-----------------|-------|-----------------|------|
| | S | S+A | S | S+A |
| ANTE settling | 145.3 | 118.4 | 28.0 | 27.4 |
| POST settling | 46.4 | 46.6 | 18.7 | 17.5 |

The factor „treatment“ (S; S+A), but also the interaction „treatment x time“, were significant (Pr > F 0.0055 and 0.0051, respectively) only for (3E)-hexen-1-ol; thus ascorbic acid applied in combination with SO₂ gives dif-

ferent results and is effective in reducing the (3E) isomer content if used before must settling, and not after it (Tab. 2). SO₂ could directly combine (3E)-hexenal or stop the isomerization (3E)-hexenal to (2E)-hexenal, so that the (3E) form could accumulate in the medium. Later on, it may be reduced to the relevant alcohol by yeasts or other reducing systems. Although significant, the relative and absolute modifications due to the factor „time“ for (3Z)-hexen-1-ol proved to be much less important than for the (3E) form and 1-hexanol.

No significant difference was observed for the (2E)-hexen-1-ol (<1 µg/l) and (2Z)-hexen-1-ol (2.1–5.1 µg/l) contents. These two compounds - assessed in 19 different Müller-Thurgau wines of the 1994 vintage, both commercial and experimental - ranged from the detection limit (about 1 µg/l) to 36.7 µg/l, and from 6.4 to 18.7 µg/l respectively for (2E) and (2Z). Thus, in the light of previous papers (NICOLINI *et al.* 1995 a; VERSINI *et al.* 1995), (3E)-hexen-1-ol seems to be the main C₆-alcohol in Müller-Thurgau wines from Trentino (Italy), after 1-hexanol.

Conclusion: The time between pomace pressing and the addition of antioxidation agents to the must affects the content of free 1-hexanol and 3-hexen-1-ols, in particular the (E) isomer, in wines. Changes in the (3E)/(3Z)-hexen-1-ol ratio have already been observed in relation to different skin contact conditions (NICOLINI *et al.* 1995 b). The present investigation supports the hypothesis that the differences observed between Müller-Thurgau wines produced on a semi-industrial scale at the Institute's experimental winery and on industrial scale can, at least partially, be attributed to the must sulfiting time.

Whatever the must sulfiting time, the (3E)-hexen-1-ol content in wine was higher than the (3Z) form. The (3E)/(3Z) ratio >1 can be a parameter which contributes to verifying the wine variety and the origin of grapes (NICOLINI *et al.* 1995 a).

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