Viticulture, enology and marketing for cold-hardy grapes

Pre-fermentation skin contact temperatures and their impact on aroma compounds in white wines made from La Crescent grapes using aroma dilution analysis and simultaneous multidimensional gas chromatography – mass spectrometry - olfactometry

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Background and Rationale: Aroma extract/headspace dilution analysis (AEDA), solid phase microextraction (SPME), and simultaneous multidimensional gas chromatography – mass spectrometry – olfactometry (MD-GCMS-O) was used to determine which aroma(s) are dominant in the wines made from La Crescent berries, in relation to pre-fermentation skin contact temperature. AEDA is a method for characterizing the "strength" or potency of a particular compound in relation to its aroma threshold. Successive dilutions of wine (diluted with model wine) were analyzed until the aroma response from each compound or region of interest is no longer noted at the olfactory detector of the MD-GCMS-O. The persistent compounds detected in the most dilute wine samples were determined to be the major contributor to the aroma profile of the wine. The goal of this study was to determine if pre-fermentation skin contact treatments on La Crescent berries had an impact on wine aroma.

Treatments: Wines were made using a method described in this report (http://northerngrapesproject.org/wp-content/uploads/2016/02/La-Crescent-skin-contact-trials-Year-4.pdf). Pre-fermentation skin contact temperature treatments were applied at 45˚F (Lot B) and 70˚F (Lot A) for 24 hours. Additionally, a control lot was produced with no skin contact treatment (Lot C).

Methods: A 50/30 μm DVB/Carboxen/PDMS fiber (57328-U, Sigma-Aldrich, St. Louis, MO) solid phase microextraction (SPME) fiber was used for all samples to extract and pre-concentrate volatile organic compounds (VOCs) from samples. 4 mL of sample was added to 2 g of sodium chloride in a 10 mL glass amber vial. All prepared samples were collected by headspace extraction with SPME. The SPME procedure was performed automatically using a CTC CombiPAL™ LEAP GC autosampler (LEAP Technologies, Inc., Carrboro, NC, USA) equipped with a heated agitator. For each sample, the automated sequence started by transferring the headspace vial to the agitator, set to 50 ◦C, and the vial was

equilibrated at this temperature for 10 min with 500 rpm agitation. The equilibration was followed by exposing the fiber, which was desorbed in the injection port for 2 min prior to extraction, to the headspace of the vial for 10 min while agitating at 500 rpm. After the exposition period, the fiber was immediately inserted into the 260 ^{0}C GC injector for 2 min for desorption for further separation and analysis.

Multidimensional GC-MS-O (Mocon, Round Rock, TX) was used for all analyses. The system integrates GC-O with conventional GC-MS (Agilent 6890N GC / 5973 MS, Wilmington, DE, USA) as the base platform with the addition of an olfactory port and flame ionization detector (FID). The system was equipped with a non-polar precolumn and polar analytical column in series as well as system automation and data acquisition software (MultiTrax™ V. 10.1 and AromaTrax™ V. 10.1, Mocon and ChemStation™, Agilent). The general run parameters used were as follows: injector, 260 °C; FID, 280 °C, column, 40 °C initial, 3 min hold, 7 °C /min, 240 °C final, 8.43 min hold; carrier gas, He. Mass to charge ratio (m/z) range was set between 33 and 450. Spectra were collected at 6 scans/sec and electron multiplier voltage was set to 2058 V. The MS detector was auto-tuned daily before analysis.

The identity of compounds was verified by matching mass spectrums of unknown compounds with AMDIS (U.S. Department of Commerce, Gaithersburg, MD, USA) MS library search system (NIST 05). Highly trained human panelists sniffed GC separated compounds simultaneously with chemical analyses. Aroma evaluations consisted of qualitative comparisons of the number of separated aroma events recorded in an aromagram. An aromagram was recorded by a panelist utilizing the human nose as a detector. Aroma events resulting from separated compounds eluting from the column were characterized for aroma descriptor with a 32-descriptor panel and aroma intensity with Aromatrax software (Mocon, Round Rock, TX). The olfactory responses of a panelist were recorded using Aromatrax software by applying an aroma tag to a peak or a region of the chromatographic separation. The aroma tag consisted of editable aroma character descriptors, an aroma event time span (aroma duration) and perceived aroma intensity.

Results:

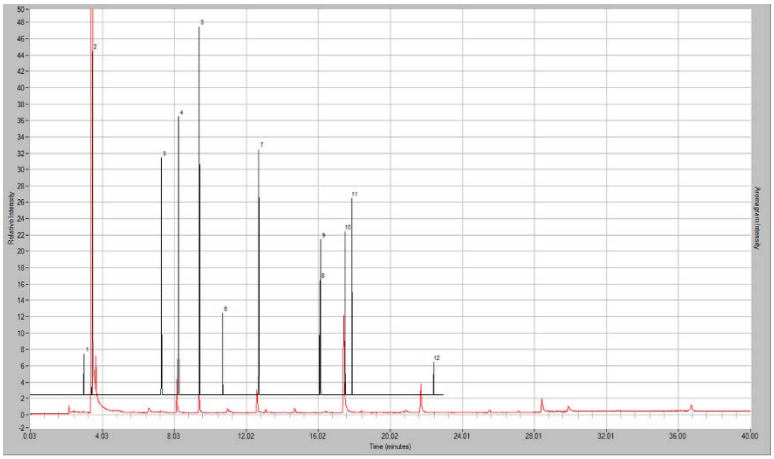

Fig 1. Simultaneous chemical and sensory analysis of wine made from La Crescent grapes, pre-fermentation skin contact temperature of 70 °F for 24 hours (Lot A), and diluted 1:32 in model wine. Aroma analysis by human nose (black signal) detected aroma compounds described as (1) sweaty, (2) alcoholic, (3) banana, (4) body odor, (5) banana, (6) unknown, unpleasant, (7) strawberry, (8) fruity, (9) and (10) sickly sweet, (11) wine, and (12) unknown, unpleasant. Mass spectral identification of these aroma compounds using probability match to NIST05 mass spectral library are (1) sulfur dioxide, (2) ethanol, (3) ethyl butyrate, (4) isoamyl alcohol, (5) isoamyl acetate, (6) not detected (ND) by mass spectrometer (MS), (7) ethyl hexanoate, (8) ND by MS, (9) ethyl sorbate, (10) ethyl octanoate, (11) and (12) ND by MS. The height of each aroma peak indicates the relative intensity of the aroma. The 4 aroma compounds in La Crescent wines after 70 °F pre-fermentation with skin contact were isoamyl acetate, isoamyl alcohol, ethyl hexanoate, and ethyl butyrate, ranked by most intense aroma. Please note that ethanol was found in all samples.

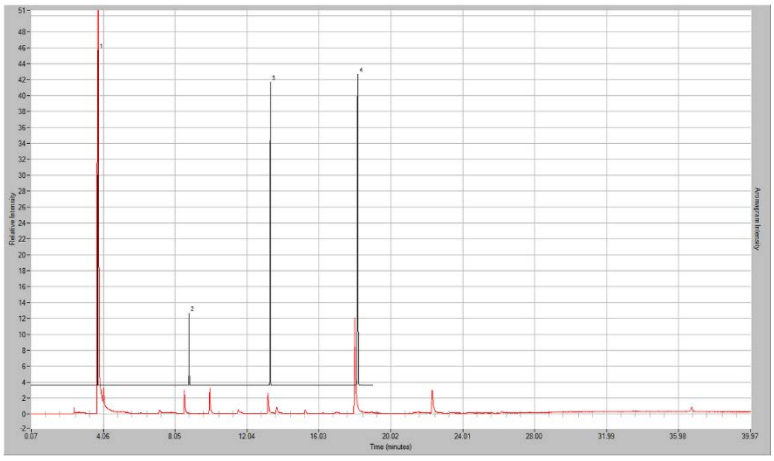

Fig 2. Simultaneous chemical and sensory analysis of wine made from La Crescent grapes, pre-fermentation skin contact temperature of 45 °F for 24 hours (Lot B), and diluted 1:32 in model wine. Aroma analysis by human nose (black signal) detected aroma compounds described as (1) alcoholic, (2) unknown, unpleasant, (3) pleasant, tree fruit, and (4) fruity, pleasant. Mass spectral identification of these aroma compounds using probability match to NIST05 mass spectral library are (1) ethanol, (2) isoamyl alcohol, (3) ethyl hexanoate, and (4) ethyl octanoate. The height of each aroma peak indicates the relative intensity of the aroma. The 3 aroma compounds in La Crescent wines after 45 °F pre-fermentation with skin contact were ethyl octanoate, ethyl hexanoate, and isoamyl alcohol, ranked by most intense aroma. Please note that ethanol was found in all samples.

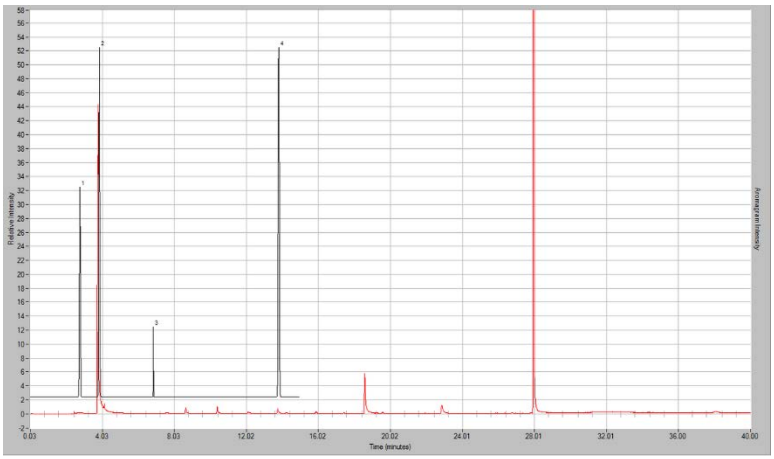

Fig 3. Simultaneous chemical and sensory analysis of wine made La Crescent grapes, no pre-fermentation skin contact treatment (Lot C), and diluted 1:32 in model wine. Aroma analysis by human nose (black signal) detected aroma compounds described as (1) sewer, unpleasant, (2) alcoholic, and (3) and (4) fruity, pleasant. Mass spectral identification of these compounds using probability match to NIST05 mass spectral library are (1) sulfur dioxide, (2) ethanol, (3) ND by MS, and (4) ethyl hexanoate. The height of each aroma peak indicates the relative intensity of the aroma. The aroma compounds in La Crescent with no pre-fermentation with skin contact treatment were ethyl hexanoate, sulfur dioxide, and an unknown compound, ranked by most intense aroma. Please note that ethanol was found in all samples.

What the results mean:

- 20 total aroma events were detected in the headspace of undiluted wine made from La Crescent berries with pre-fermentation skin contact temperature of 70 °F (Lot A). Top 4 compounds contributing most to the overall aroma of La Crescent wine from Lot A were (1) isoamyl acetate, (2) isoamyl alcohol, (3) ethyl hexanoate, and (4) ethyl butyrate, described by human panelist as (1) banana, (2) body odor, (3) strawberry, and (4) banana.
- 26 total aroma events were detected in the headspace of undiluted wine made from La Crescent berries with pre-fermentation skin contact temperature of 45 °F (Lot B). Top 3 compounds contributing most to the overall aroma of La Crescent wine from Lot B were (1) ethyl octanoate, (2) ethyl hexanoate, and (3) isoamyl alcohol, described by human panelist as (1) fruity, pleasant, (2) tree fruit, pleasant, and (3) unknown, unpleasant.
- 14 total aroma events were detected in the headspace of undiluted wine made from La Crescent berries with no pre-fermentation skin contact treatment (Lot C). Compounds contributing most to the overall aroma of the control La Crescent wine were (1) ethyl hexanoate, (2) sulfur dioxide, and (3) an unknown compound, described by human panelist as (1) fruity, pleasant, (2) sewer, unpleasant, and (3) fruity, pleasant.
- Statistical analysis for significant difference in aroma compounds due to pre-fermentation skin contact temperature is currently being investigated and will be reported in year 5.
- Isoamyl alcohol has previously been described as whiskey, malt, burnt (Acree 2004)
- Isoamyl acetate has previously been described as banana (Acree 2004)
- Ethyl butyrate has previously been described as apple (Acree 2004)
- Ethyl hexanoate has previously been described as apple peel and fruit (Acree 2004)
- Ethyl octanoate has previously been described as fruit and fat (Acree 2004)
- Ethyl decanoate has previously been described as grape (Acree 2004)

References:

Acree, T.E., Arn, H. Flavornet and human odor space [Internet]. Geneva, NY: Cornell University; [2004; cited 2016 January 3]. Available: http://flavornet.org/flavornet.html