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# Sensory Threshold of 1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN) and Concentrations in Young Riesling and Non-Riesling Wines

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**ABSTRACT:** 1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN) is well-known to contribute "petrol" aromas to aged Riesling wines, but its prevalence and contribution to young Riesling or non-Riesling wines is not well understood. TDN concentrations were measured in 1−3-year-old varietal wines produced from Cabernet franc ($n$ = 14 wines), Chardonnay (17), Cabernet Sauvignon (4), Gewurztraminer (4), Merlot (9), Pinot gris (6), Pinot noir (9), Riesling (28), or Sauvignon blanc (6). TDN concentrations in the Riesling wines, 6.4 ± 3.8 $\mu$g/L, were significantly higher than in all other varietals, 1.3 ± 0.8 $\mu$g/L. The odor detection thresholds for TDN were then determined in both model wine and a neutral white wine. Group sensory thresholds were found to be the same in both matrices, 2 $\mu$g/L, indicating little masking of TDN due to the odorants in the neutral white. The TDN sensory threshold was a factor of 10 below the previously reported odor threshold. On the basis of this revised threshold, 27 of 28 Riesling wines had suprathreshold TDN, whereas only 7 of 69 non-Riesling wines had suprathreshold TDN. The monoterpenes linalool and geraniol were also measured in the Riesling wines, and odor activity values (OAVs) were calculated for the monoterpenes and TDN. The OAV for TDN was higher than for the monoterpenes in 25 of 28 Riesling wines.

**KEYWORDS:** *TDN, 1,1,6-trimethyl-1,2-dihydronaphthalene, odor threshold, varietal aroma, Riesling*

## INTRODUCTION

Riesling (*Vitis vinifera* cv. 'Riesling') is the second most widely planted aromatic white wine grape, covering ca. 120 000 acres worldwide as of 2004.[1] Along with Muscat and Gewürztraminer, Riesling produces one of the most readily identifiable varietal wines,[2] with aroma attributes that can include stonefruit, flowers, and wet stones.[3] The monoterpenes geraniol and linalool are reported to be largely responsible for the distinct aroma of Muscat.[4] Similarly, *cis*-rose oxide is reported to be responsible for the unique character of Gewurztraminer aroma.[5] However, the odorants responsible for the distinctiveness of Riesling aroma are more poorly defined. Several papers in the literature have stated that the desirable aroma of Riesling can be ascribed to monoterpenes,[6−8] generally in reference to earlier work by Rapp showing that the gas chromatography−mass spectrometry (GC-MS) monoterpene profile can be used to distinguish Riesling from other white cultivars.[9] Several other grape-derived odorants are also reportedly at or around threshold in Riesling, including 3-mercaptohexanol (3-MH, "citrus"), a thiol derived from S-conjugate precursors. 3-MH is reported to range from 400 to 1000 ng/L in Alsatian Riesling.[10] Whereas this range is in excess of its sensory threshold, 60 ng/L, it is well below concentrations reported in Sauvignon blanc wines, a varietal in which thiols appear to be critical for recognition.[10] Analysis of odor active compounds in Riesling by gas chromatography−olfactometry−mass spectrometry[8,11] identified several odorants commonly found in wines, including esters, fusel alcohols, and $\beta$-damascenone, but their contribution to the distinctiveness of Riesling aroma was not established.

1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN), a grape-derived $C_{13}$ norisoprenoid, is reported to contribute to the typical "kerosene" or "petrol" aroma of aged Riesling.[12,13] Like many other $C_{13}$ norisoprenoids, TDN is largely absent from grape berries and juice, but it can be formed by hydrolysis of glycosylated precursors and subsequent rearrangements during fermentation and/or storage.[14−16] TDN formation during fermentation varies with yeast strain, and higher concentrations of TDN precursors in wine grapes have been correlated with warmer growing regions and with greater cluster light exposure, particularly prior to veraison.[17] Conversion of precursors can continue during bottle storage, and the resulting TDN appears to be highly stable.[16] TDN concentrations up to 42 $\mu$g/L in 10-year-old Riesling wines[18] and ca. 200 $\mu$g/L in Riesling wines subjected to accelerated aging[14] have been reported, well in excess of the previously reported TDN sensory threshold, 20 $\mu$g/L.[13]

Discussions of the contribution of TDN to Riesling aroma in textbooks are largely limited to bottle aged wines,[19,20] likely because TDN concentrations in excess of the 20 $\mu$g/L sensory threshold are reported only in >5-year-old Riesling or young Riesling wines that had been stored at 50 °C.[12,13,18] One- and two-year-old Riesling wines produced from a research vineyard generally had TDN concentrations around 1−2 $\mu$g/L,[21] although some variability was found among clones. Higher concentrations of TDN, 7−20 $\mu$g/L, were reported in 1-year-old Finger Lakes Riesling,[17] although these concentrations are still not in excess of the 20 $\mu$g/L threshold. The presence of noticeable petrol aromas in young Riesling wines is reported in some warmer regions, where it may be considered a sensory defect,[1] but quantitative data to explain this observation are not available, and quantitative measurements of TDN in wines other than Riesling are nearly absent from the literature. Studies

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that have detected TDN in non-Riesling wines, for example, in Cabernet Sauvignon[22−24] and Shiraz,[25] have reported TDN relative to an internal standard, presumably due to the lack of an authentic standard. A study that profiled volatiles from wines stored at different temperatures reported that higher TDN concentrations were present in a young Riesling wine than in other international varietals,[26] and TDN precursors are reportedly at lower concentrations in most non-Riesling grapes,[12] but no survey of typical TDN concentrations in non-Riesling wines exists.

We report results from a survey of TDN concentrations in Riesling and non-Riesling commercial wines from New York state. We also have redetermined the odor detection threshold of TDN in a hydroalcoholic solution and in a neutral white wine. Finally, we compare odor activity values for TDN and monoterpenes in young Riesling wines. We demonstrate that TDN routinely exceeds its sensory threshold in young Riesling wines and only rarely exceeds its threshold in non-Riesling wines. Thus, the contribution of TDN to the varietal character of young Riesling wines may have been previously underappreciated.

## ■ MATERIALS AND METHODS

**Chemicals.** Linalool, geraniol, and 2-octanol were obtained from Sigma-Aldrich (St. Louis, MO) at the highest commercial purity (>97%). Tartaric acid was certified ACS granular (Fisher Scientific, Waltham, MA). Methanol, ethanol, and dichloromethane were of HPLC grade (Fisher-Scientific), except for threshold determinations for which 95% food grade ethanol was used (Pharmco Products, Brookfield, CT). TDN was synthesized from $\alpha$-ionone (Sigma-Aldrich, 99%) via ionene using the protocol of Miginiac.[27] The chemical purity of the TDN standard was estimated to be >99% by NMR, and the odor purity of the TDN standard was confirmed by GC−olfactometry.

**Wines.** Commercial varietal wines ($n$ = 97) produced from *V. vinifera* cultivars were sourced from New York state in late 2007. The wines were from the 2004 ($n$ = 13), 2005 ($n$ = 35), and 2006 ($n$ = 49) vintages. Wines from the 2007 vintage were not included, because they were not commercially available at the time of the survey. The majority of wines were donated directly by wineries, with a few wines purchased from local wine stores. Samples were stored on their sides at 15 °C prior to analysis. The chemical composition of wines was determined in February 2008. For threshold determinations of TDN in neutral wine, a commercial stainless steel 2009 Finger Lakes Chardonnay produced without oak contact was purchased in 2010. The neutral wine contained 12% alcohol by volume, according to the producer's label, and the TDN concentration of the wine was measured as 0.5 $\mu$g/L.

**Quantification of TDN and Monoterpenes.** TDN, linalool, and geraniol were isolated from wine using a solid-phase extraction (SPE) protocol adopted from conditions used in previous studies.[17,28] Twenty-five microliters of the internal standard (2-octanol, 0.5 g/L in acetonitrile) was added to 50 mL of sample. Samples were loaded onto SPE cartridges (Merck, Darmstadt, Germany) containing 200 mg of LiChrolut EN sorbent preconditioned with 4 mL of dichloromethane, 4 mL of methanol, and 4 mL of model wine. The model wine samples were prepared with 12% (v/v) ethanol and 5 g/L tartaric acid and pH adjusted to 3.5 using NaOH. Elution was facilitated by use of a Varian (Walnut Creek, CA) Cerex SPE processor and $N_2$ head pressure (1.7 bar, 2 mL/min). The cartridge was allowed to dry under $N_2$ for 20 min, and the analytes were eluted with 1.3 mL of dichloromethane. GC-MS analyses were conducted on a Varian CP-3800 gas chromatograph with a 1079 split−splitless injector coupled to a Varian Saturn 2000 Ion Trap-MS (Walnut Creek, CA). Separation was performed using a Varian CP-WAX 58 column (25 m × 0.25 mm i.d. × 0.2 $\mu$m). The initial oven temperature was 40 °C and held for 6 min, then ramped to 140 °C at 10 °C/min, then to 170 °C at 5 °C/min, then to 250 ° 10 °C/min,and held at 250 °C for 20 min. The GC was operated at a constant flow rate of 1 mL/min. One microliter of extract was injected splitless. The injector temperature was 250 °C, and the purge time was 0.75 min. The temperatures of the transfer line, manifold, and ion trap were 250, 50, and 170 °C, respectively. Data processing and quantification were performed using the native Varian Saturn GC-MS software (version 5.52). Peak identifications for linalool, geraniol, and TDN were confirmed by comparison of retention times and mass spectra to the authentic standards. The following ions were selected for quantification, as they yielded the best signal-to-noise ratio during standard addition experiments: TDN (quantifying ion $m/z$ 157, qualifying ions $m/z$ 142 and 172), geraniol (selected ion scan mode (SIS), $m/z$ 139), and linalool (MS/MS of $m/z$ 136, $m/z$ 91 + 105 + 119 + 79 product ions). The ratio of the analyte peak area to the 2-octanol standard ($m/z$ 43) peak area was calculated and converted to a concentration via calibration curves. Calibration standards ($n$ = 5) were prepared in duplicate in model wine over the following concentrations: TDN (1−300 $\mu$g/L), linalool (8−290 $\mu$g/L), and geraniol (8−290 $\mu$g/L). Calibration curves had $r^2 > 0.99$, with all calibration points within 30% of the value predicted by the best fit line. Detection thresholds, defined as the concentration that yielded a peak area 3-fold greater than the noise, were estimated from the lowest concentration standard and blank samples to be 0.2 $\mu$g/L for TDN, 3 $\mu$g/L for geraniol, and 3 $\mu$g/L for linalool. All wine samples were prepared and run in analytical duplicate, and the mean %RSD for replicate wine samples was <15%.

**Determination of TDN Sensory Threshold.** Ten paid participants, five males and five females, 25−50 years old, participated in the study. All were nonsmoking, healthy members of the Cornell Food Science community who had some experience with sensory evaluation of food odorants, including those found in wine. However, most of these panelists had limited previous experience with sensory panels and did not have prior experience with evaluating TDN in wines. Testing was performed in a well-lit, odor-free room routinely used for sensory testing. The experimental procedure was reviewed and approved by the Cornell University Institutional Review Board. All participants provided written consent and were compensated for their participation. Subjects were tested on their ability to perceive TDN in one of two matrices: a model wine (10% w/w EtOH and 1% w/w tartaric acid) and a commercial, 1-year-old stainless steel Chardonnay (Finger Lakes, NY), selected due its neutral character and low TDN concentration (<detection limit). Stock solutions of TDN were prepared at 593 mg/L in 95% ethanol. Testing standards were prepared by spiking stock solutions (30 mL) into appropriate matrices immediately prior to a testing session in 250 mL Teflon squeeze bottles (VWR model 16651-824, Radnor, PA), briefly stirred, and given 5 min to equilibrate before testing began. Standard solutions were replaced monthly, and working standards were prepared weekly. All stock solutions were stored in brown glass containers and refrigerated when not in use to prevent degradation. Sensory thresholds were determined by using a modified three-alternative forced-choice (3-AFC) method in which each trial consisted of three 250 mL Teflon bottles, one a "target" containing 30 mL of a TDN dilution step and the other two "blanks" containing 30 mL of the matrix and no TDN. Trials were performed with TDN dilutions at the following concentrations: 0, 1, 3, 30, and 100 $\mu$g/L, a range chosen to mimic typical concentrations found in Riesling wines. Participants were also provided with two bottles having contents that were were identified to serve as anchors, one a blank containing only the matrix and the other containing 100 $\mu$g/L TDN. During each trial, participants were asked to sniff each of the three test bottles and indicate which bottle contained the target odorant. After making a selection, participants were instructed to rate the intensity of the odor of the selected bottle on a scale of 1−9 with anchors provided for 1 ("no odor", blank matrix) and 9 ("very strong odor", 100 $\mu$g/L standard). Subjects sampled freely from the bottles within any given trial but were told to wait 1 min between trials to limit the effects of adaptation and fatigue. All testing bottles were labeled with a random three-digit number and otherwise appeared identical.

Two evaluation sessions were performed, with a session consisting of three trials. Each trial consisted of five concentration steps. Trials were performed in ascending order of concentration to reduce the amount of adaptation and fatigue over the course of the experiment. The position of the "target" bottle relative to the two "blanks" was randomized. Subjects were not informed of the order of trial concentrations, and an additional experiment in which every bottle was a "blank" was performed midway through testing to confirm that subjects were not automatically assigning higher scores as they progressed through the experiment. In addition to choosing the "target" bottle and assigning it an intensity score, subjects were asked to generate a descriptor for the "target" odor, if possible.

**Statistical Analysis.** Statistical analyses on wine volatile concentrations were performed using JMP version 8 (SAS Institute, Cary, NC). Statistical analysis of sensory data was performed on Mathematica version 8 (Wolfram Research, Champaign, IL).

## ■ RESULTS AND DISCUSSION

**TDN Concentration in Varietal Wines.** TDN concentrations in 97 New York state wines are depicted in Figure 1 as a box-and-whiskers plot. The varietal wines under study included Cabernet franc (14 wines), Chardonnay (17), Cabernet Sauvignon (4), Gewurztraminer (4), Merlot (9), Pinot gris (6), Pinot noir (9), Riesling (28), and Sauvignon blanc (6). On the basis of a Tukey test, TDN was at significantly higher concentrations in Riesling wines than in all other varietal wines, whereas there were no significant differences in TDN concentrations among the other varietals ($p > 0.05$). The mean TDN concentration in Riesling was 6.4 $\mu$g/L (SD =3.8), or 5-fold higher than the mean concentration of 1.3 $\mu$g/L (SD = 0.8) for non-Riesling wines. The highest TDN concentration was observed in a 2005 Riesling, with 17.1 $\mu$g/L TDN. Of the 18 wines that had TDN > 4 $\mu$g/L, only one was a non-Riesling wine (a 2005 Cabernet franc), with 6.4 $\mu$g/L TDN.

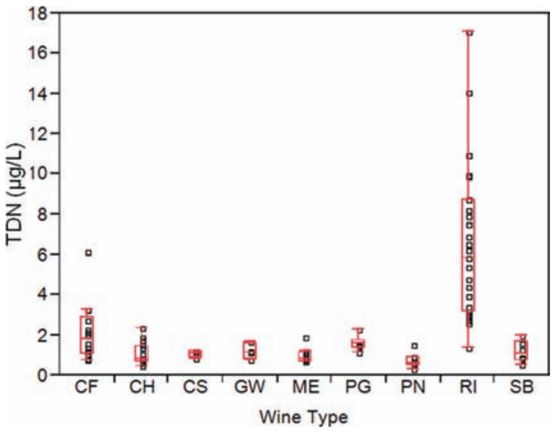

**Figure 1.** TDN concentrations in varietal wines from New York state. Abbreviations: CF (Cabernet franc, 14 wines); CH (Chardonnay, 17 wines); CS (Cabernet Sauvignon, 4 wines); GW (Gewurztraminer, 4 wines); ME (Merlot, 9 wines); PG (Pinot gris, 6 wines); PN (Pinot noir, 9 wines); RI (Riesling, 28 wines); SB (Sauvignon blanc, 6 wines). The bottom and top of the box represent the 25th and 75th percentile, respectively. The whiskers represent either 1.5× the interquartile range or the extrema, whichever is closer to the mean.

Although TDN is well accepted to be at higher concentrations in aged Riesling wines, in which it may contribute to "petrol" character,[19] to our knowledge this is the first demonstration that TDN is uniquely high in young Riesling wines as compared to non-Riesling wines. Additionally, this is the first study to provide quantitative measurements of TDN in a range of varietal wines other than Riesling, as opposed to the semiquantitative data reported elsewhere. Our observations support a previous study that detected higher concentrations of TDN precursors in Riesling juice (28 to 65 $\mu$g/L, depending on hydrolysis conditions) than in other cultivars, including Semillon, Chenin blanc, Sylvaner, Traminer, Muscat Gordo, and Palomino, in which <8 $\mu$g/L of TDN precursors was detected.[12] This previous paper also detected modest concentrations of TDN precursors, 13−30 $\mu$g/L, in Emerald Riesling and Sultana grape juices, although these varietal wines were not available in our current study for comparison.

Our results also parallel those from a study on vitispirane, a $C_{13}$ norisoprenoid with a camphoraceous aroma. Vitispirane was at significantly higher concentrations in young Riesling wines than in non-Riesling wines in this previous work,[29] albeit at concentrations, 0.5−80 $\mu$g/L, well below the vitispirane sensory threshold of 800 $\mu$g/L . Precursors of $C_{13}$ norisoprenoids, including vitispirane and TDN, are believed to be formed by either enzymatic or nonenzymatic degradation of carotenoids,[30] and at least one glycosylated precursor of TDN can be partially reduced by yeast during fermentation to yield a glycosylated precursor of vitispirane.[31] Thus, environmental or biological factors that increase TDN in wines are also expected to increase vitispirane in wines. Whereas differences in precursor concentration could potentially arise from either differences in carotenoid substrate concentration or differences in enzymatic activity, a biochemical explanation for why Riesling may have higher concentrations of certain $C_{13}$ norisoprenoids is not clear at this time.

We observed an order of magnitude range for TDN concentrations among our Riesling wines (1.3−17.1 $\mu$g/L). This is comparable to TDN concentrations in 1−2-year-old Riesling wines from Germany (1−2 $\mu$g/L),[21] 1-year-old Riesling from New York state (7−20 $\mu$g/L),[17] and 1−2-year-old Riesling from Australia (1−10 $\mu$g/L),[18] although all of these previous studies considered a limited number of wines. The maximum TDN concentration observed in our study is well below the TDN concentrations reported in aged Riesling wines from Australia (up to 54 $\mu$g/L),[12] potentially a function of the younger wines evaluated in this study. There are several potential explanations for the wide range of TDN observed in Riesling wines in our study. TDN precursors will hydrolyze and/or rearrange during storage, resulting in increasing wine TDN, but no significant effect of vintage year was observed on TDN concentration either in Riesling alone (one-way ANOVA, data not shown) or among all varietal wines (two-way ANOVA, data not shown), indicating that wine age alone cannot explain the observed differences in TDN concentrations. Riesling clone[21] and viticultural factors such as cluster light exposure[17,32] can reportedly increase the formation of glycosylated TDN precursors in grapes, and elevated wine storage temperature should increase the rate of formation during storage.[33] However, information on production practices and storage conditions prior to our acquiring the wines was not available to us.

**Group Sensory Thresholds for TDN.** Because TDN concentrations observed in young commercial Riesling wines in this study were less than the previously reported aroma threshold of 20 $\mu$g/L,[13] we did not expect TDN to contribute to the aroma of any of these wines. TDN is hydrophobic, with an estimated log *P* of 4.92 (ACD Laboratories), and is readily scalped by synthetic closures.[34] On the basis of preliminary experiments in our laboratory, TDN is also readily scalped by polyethylene bottles. The previous literature report on TDN thresholds provided minimal experimental details[13] and thus may have encountered TDN losses during experimentation. To avoid problems with flavor scalping of hydrophobic odorants, metal-lined sample bags (Tedlar) can be used to present odorants.[35] For convenience, we chose to use fluorocarbon (Teflon) squeeze bottles, which showed very little scalping of the TDN and could be easily cleaned for reuse.

The group sensory threshold of TDN was estimated by using two approaches in two different matrices: a model wine consisting of 10% ethanol in water and a neutral Chardonnay with low TDN concentration, below detection threshold. In the first approach, data on the ability of panelists to correctly identify a "target" bottle spiked with TDN concentrations are plotted in Figure 2. Using the ASTM definition of the detection threshold (http://www.astm.org/Standards/E1432.htm), the threshold value is defined as the concentration at which panelists can detect TDN 50% more than the amount expected by chance. Because the expected response by chance for a 3-AFC is 33%, the sensory threshold is the point at which 50% of trials are correct. The "50% correct" response rate is achieved for all concentrations ≥3 μg/L in both the model wine and Chardonnay, indicating that the group sensory threshold is between 1 and 3 μg/L. In agreement with this conclusion, the first point at which the correct response rate is significantly different from that predicted by chance is 3 μg/L (Figure 2). Taking the geometric mean, we arrive at a threshold of approximately 2 μg/L for both model wine and Chardonnay.

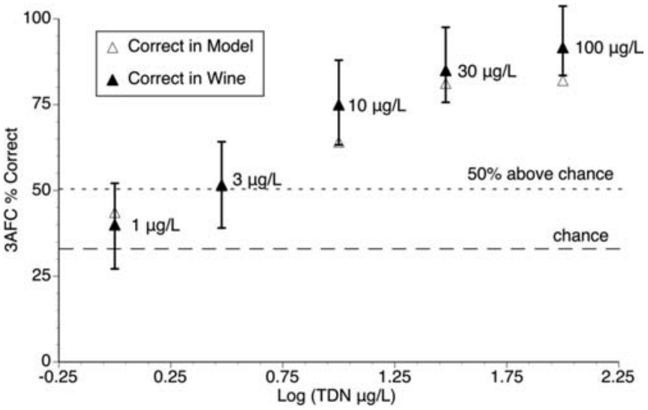

**Figure 2.** Results from the 3-AFC sensory tests depicting percent correct response across all panelists versus TDN concentration in either 10% hydroalcoholic solution (model wine) or a neutral white wine. Error bars represent the 95% confidence interval. The lower dotted line shows the value expected by chance, 33% correct. The upper dotted line shows the detection threshold or the value necessary to achieve 50% above chance.

As an alternative means to estimate threshold, we considered the dose−response curves obtained by plotting the mean perceived intensity reported for the correctly identified trials averaged over the replicates and subjects (Figure 3). For TDN in the neutral stainless steel Chardonnay matrix, significant differences in perceived TDN intensity are observed among all concentrations from 1 to 100 μg/L, indicating that the concentrations used are within the dynamic range for TDN sensory response. These data suggest that the TDN sensory threshold is between 1 and 3 μg/L in the neutral Chardonnay wine, in agreement with the results from Figure 2. Interestingly, there was no significant difference in the TDN intensity of the 1 and 3 μg/L spikes in model wine, indicating that the TDN threshold in model is slightly higher in model wine on the basis of this sensory test.

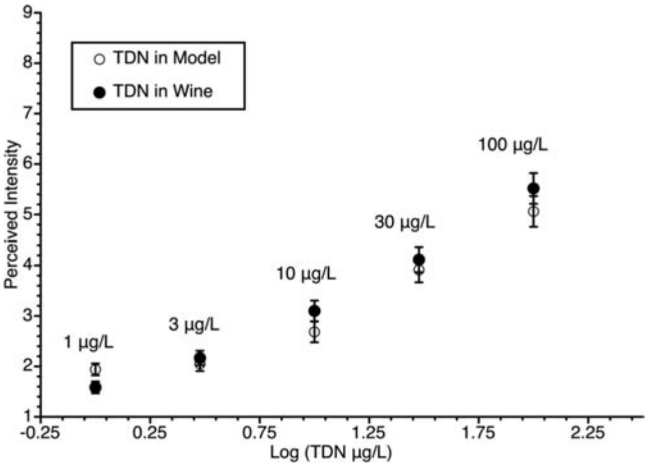

**Figure 3.** Dose−response curves depicting intensity of TDN versus TDN concentration in either hydroalcoholic solution or a neutral white wine. Error bars represent the 95% confidence interval. Only those trials in which the correct sample was identified in the 3-AFC were included in this analysis.

The correct response rates for detection of TDN in model wine and the neutral Chardonnay wine were not significantly different at any concentrations (Figure 2), indicating that masking or reduced volatility due to matrix interactions does not occur. Similarly, no significant differences were observed between model and real wines for TDN concentrations ranging from 3 to 100 μg/L (Figure 3), again suggesting that the wine volatiles do not significantly mask TDN. No significant difference was observed in thresholds between the two testing sessions (data not shown), indicating that any learning effect was minimal. These results are surprising, because the perceived intensity of odorants in mixtures is generally lower, and the detection threshold generally higher, than for the odorants in isolation.[36,37] As a striking example in wine, the sensory threshold of β-damascenone is reportedly 100-fold higher in red wine than in a hydroalcoholic solution.[38] One exception to this general rule is (*E*)-1-(2,3,6-trimethylphenyl)-buta-1,3-diene (TPB), which reportedly has an odor threshold 10-fold higher in 10% ethanol than in wine.[39] The reason for the absence of a "normal" masking effect with TDN and TPB unclear, although it is interesting that both TDN and TPB are nonoxygenated hydrocarbons. The authors of the previous TPB study speculate that the presence of other odorants may reduce the masking effect of ethanol.[39]

The wine matrix is also reported to enhance the volatility of some odorants,[40] although this effect was more pronounced for more polar odorants, and the effects on $C_{13}$ norisoprenoids were not significant. We did observe that 1 μg/L TDN was perceived as less intense in real wine as compared to model wine, potentially indicating that masking of TDN can occur at low concentrations in real matrices.

Our determined threshold for TDN in wine, 2 μg/L, is 10-fold lower than the previously reported threshold for TDN.[13] As seen in Figure 1, 27 of 28 Riesling wines had a TDN concentration in excess of this 2 μg/L sensory threshold, but only 7 of 69 non-Riesling wines had a TDN concentration >2 μg/L. In other words, TDN should be detectable by 50% of the population in almost all Riesling wines and seldom detectable in wines from other cultivars. Furthermore, our current study determined the "detection threshold" and not the "recognition threshold", so it should not be assumed that most young Rieslings have a noticeable petrol aroma. However, these results suggest that TDN likely contributes to the aroma of young Riesling wine and that this contribution is less likely to occur in non-Riesling varietal wines.

The reasons for the discrepancy between our measured threshold for TDN in wine, 2 $\mu$g/L, and threshold previously reported by Simpson, 20 $\mu$g/L,[13] are unclear. Very few details are provided in the earlier paper regarding how sensory evaluation was performed, including information on panel size or composition, so it is possible that the observed differences reflect biological differences among the panelists. Also, the wine selected by Simpson for determining TDN thresholds is not identified. This wine may have had a greater masking effect or higher native TDN than the neutral Chardonnay wine selected for our study. Finally, as mentioned earlier in this section, TDN is very hydrophobic and can be readily scalped by some plastics. Although we were careful to avoid this scalping in our own trials, it is not clear if similar precautions were taken in the previous study.

**Odor Activity of TDN and Monoterpenes in Young Riesling Wines.** Riesling reportedly produces one of the most readily identifiable varietal wines,[2] and several authors have stated that the aroma of Riesling is largely due to monoterpenes,[6−8] particularly linalool and geraniol These papers refer to earlier work by Rapp, summarized in ref 9, which demonstrated that Riesling could be distinguished by GC-MS from other white cultivars on the basis of its monoterpene profile. However, these earlier studies primarily considered grapes, not wine. Furthermore, no sensory analyses were performed, and the analytical data were semiquantitative rather than quantitative, so comparing concentrations to thresholds is not possible, either. Although the concentrations of linalool and geraniol, the two most odor active monoterpenes in young Riesling, are similar to their respective reported sensory thresholds in wine,[41] there are 10-fold higher concentrations of monoterpenes in Muscat type wines,[42] and to our knowledge it is not possible to simulate Riesling aroma by diluting a Muscat wine with a neutral wine. Thus, it seems plausible that other compounds in addition to monoterpenes, such as TDN, may contribute to the varietal character of young Riesling.

To roughly evaluate the relative importance of TDN and monoterpenes, the odor activity values (OAV) of TDN in the Riesling wines in our study were compared to the OAVs of linalool and geraniol. The concentrations of linalool, measured by GC-MS, ranged from undetectable to 230 $\mu$g/L, with a mean concentration of 48 $\mu$g/L, and concentrations of geraniol ranged from undetectable to 109 $\mu$g/L, with a mean concentration of 23 $\mu$g/L (data not shown). The observed concentrations for linalool and geraniol are slightly higher than the concentration range observed in young Washington state Rieslings, 14−27 and 6−14 $\mu$g/L, respectively,[6] although the Washington study considered only a single site with different nitrogen fertilization treatments. Our concentrations are comparable to the cumulative concentration of linalool, geraniol, and nerol in 20 Australian Rieslings, most of which were 1−2 years old at the time of study.[43] In the Australian study, total monoterpene alcohol concentrations ranged from 0.01 to 243 $\mu$g/L with a mean total monoterpene concentration of 61 $\mu$g/L.

OAVs for TDN were calculated using the 2 $\mu$g/L detection threshold determined in our sensory study, and OAVs for linalool and geraniol were based on thresholds of 50 and 130 $\mu$g/L, respectively.[41] The OAV for TDN and the cumulative OAV for monoterpenes in each Riesling wine are shown in Figure 4. Wines are ranked in order of increasing monoterpenes. The OAVs for TDN ranged from <1 to 8.5 (median = 3.0), and the OAVs for the monoterpenes ranged from <1 to 4.9 (median = 0.9). Most Riesling wines, 25 of 28, had a greater OAV for TDN than monoterpenes. As a caveat, the odor detection thresholds for the monoterpenes were drawn from a separate study using different panelists, a different methodology, and a different wine matrix. Determining odor thresholds on our panel would, presumably, have yielded different apparent OAVs.

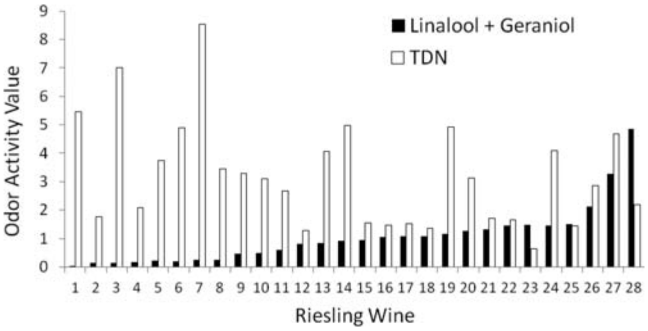

**Figure 4.** Odor activity values for TDN and monoterpenes (linalool and geraniol) in 28 Riesling wines from New York state.

Considering that TDN is uniquely high in Riesling as compared to other varietal wines, and because TDN is present at peri- or suprathreshold concentrations in all Rieslings under study, it seems plausible that the varietal character of young Rieslings may derive at least in part from TDN. However, this statement is made with the caveat that OAVs are well-known to be imperfect in predicting the effects of individual odorants on wine aroma, and addition studies coupled to descriptive analysis would be a more accurate means to assess the relative effects of the odorants.[44] Additionally, beyond monoterpenes and TDN, several other volatiles are expected to contribute to Riesling aroma. The first published GC-O-MS analysis of New York Riesling wine reported that the most potent odorant in both polar and nonpolar extracts was another $C_{13}$ norisoprenoid, $\beta$-damascenone, having a "cooked apple" aroma.[11] However, this compound is nearly ubiquitous in wines, and its impact in the presence of other odorants is greatly diminished.[45] Other odorants identified in this earlier GC-O study[11] and a more recent study of Riesling wine[8] include linalool as well as several fermentation-derived odorants, such as ethyl 2-methylbutanoate, ethyl hexanoate, 2-phenylethanol, and isoamyl acetate, that are commonly observed in GC-O analyses of wines.[44] Interestingly, neither of these previous studies identified TDN by GC-O, although the compound has been detected by GC-O in artificially aged Portuguese white wines.[46] 2-Vinyl-2-methyltetrahydrofuran-5-one is reported to be uniquely high in Riesling and Muscat,[47] but the sensory impact of this compound has not been demonstrated.

In summary, we have observed that TDN is on average 5-fold higher in young Riesling wines than in other varietal wines from

New York state. The group odor detection threshold was determined to be approximately 2 μg/L, or 10 times lower than a report from decades ago. Of the Riesling wines included in the study, 27 of 28 had TDN in excess of this 2 μg/L threshold. The OAV of TDN in Riesling was greater than the combined OAV of two monoterpenes, linalool and geraniol, in nearly all Riesling wines analyzed. Whereas this suggests that TDN may be as important, if not more important, to the varietal character of young Riesling wines than monoterpenes, confirmation of this possibility will require more thorough sensory analysis. This current work has determined the TDN detection threshold, but it has not characterized the odor quality of TDN at various concentrations in real wines. To our knowledge, there are no reported attempts to recreate the varietal character of Riesling wine through reconstitution studies, as has been demonstrated for *cis*-rose oxide in Gewurztraminer and 4-methyl-4-mercaptopentanone in Scheurebe wines.[48] A chemical explanation for flavor characteristics assigned to some Rieslings, for example, “the taste of water running over stones in a mountain stream”[3] is not available, and it would be of interest to see if these perceptions are due to perithreshold concentrations of TDN in combination with other tastants or odorants.

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