Captivating Coconut or Pesky Prune?
Quantification of γ-Nonalactone in Botrytised and Non-Botrytised New Zealand Wines

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γ-Nonalactone: An Overlooked Aroma Compound?

- The volatile compound γ-nonalactone is associated with coconut and stone fruit descriptors, as well as undesirable prune aroma in prematurely aged red wines (Figure 1).[1] A range of linear aliphatic lactones are found in wine, but γ-nonalactone may be one of the most significant for wine aroma, due to its low odour detection threshold in wine (30 μg/L),[2] and relatively high concentrations in some wines (for example 133 μg/L in Pinot noir).[3]
- Several studies have been conducted looking at concentrations of linear aliphatic lactones in wines and their associated aroma descriptors. However, it is not clear where these lactones come from (Figure 2).
- The New Zealand (NZ) wine industry is world-renowned for producing exceptional Sauvignon blanc and Pinot Noir wines.[4] NZ also produces high quality noble rot wines (made from grapes infected with *Botrytis cinerea* fungus, which has been linked to increased levels of γ-nonalactone – Figure 1).[5,6] Little research has investigated γ-nonalactone in NZ wines.
- Can better understanding of the importance of this aroma compound enable NZ winemakers to produce better wines?

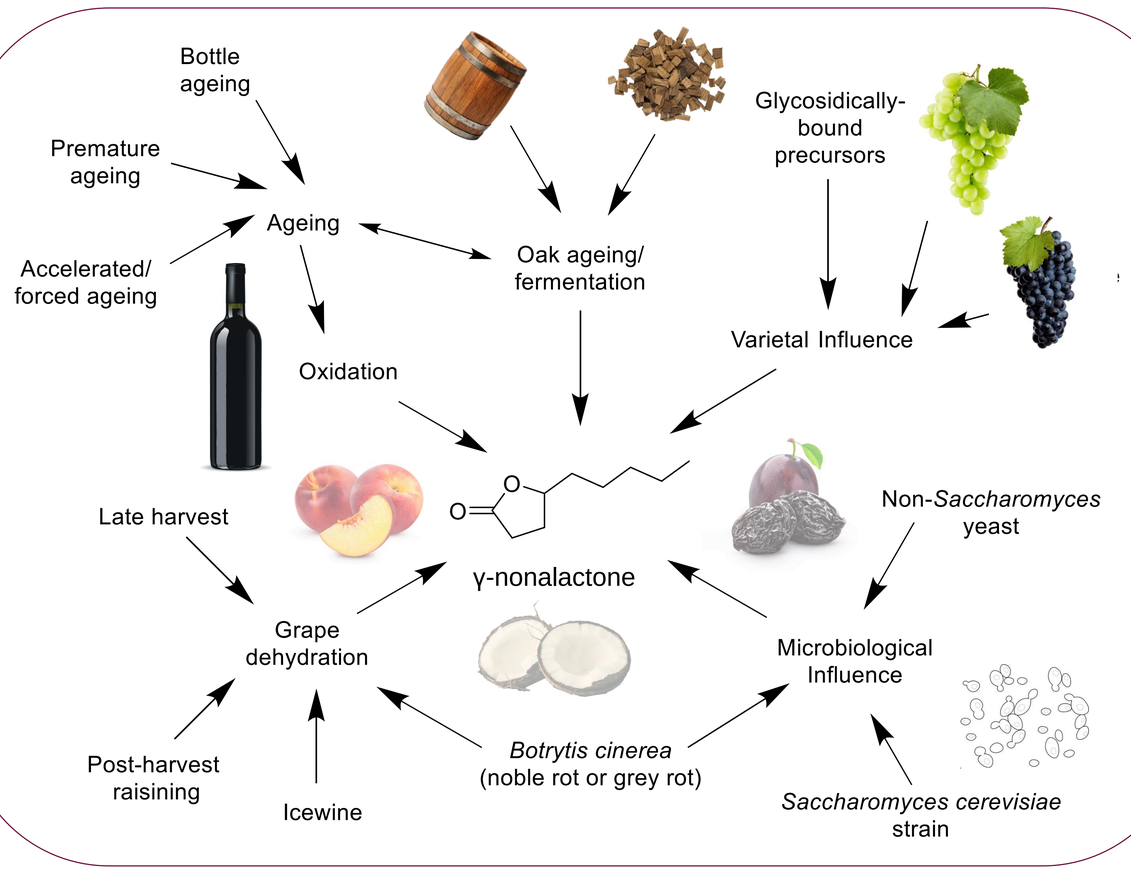


Figure 1: Summary of possible sources of γ-nonalactone in wine, and associated aroma descriptors.

Synthesis of $^{13}C^{2}H$-Labelled Internal Standard

- ^{13}C atoms will be introduced in a Wittig olefination step, using Wittig reagent synthesised from commercial $^{13}C_2$-bromoacetic acid (Figure 2).
- ^{2}H atoms will be introduced *via* deuterogenation (hydrogenation using deuterium gas).
- Will synthesise $^{13}C_2$-$^{2}H_2$-γ-nonalactone for use as a novel isotopically labelled internal standard (Figure 4).

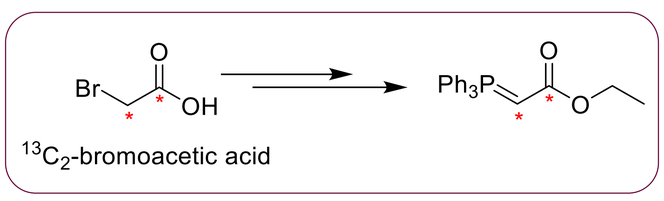


Figure 2: Synthesis of $^{13}C_2$-labelled Wittig reagent.[7] Red asterisks show ^{13}C atoms

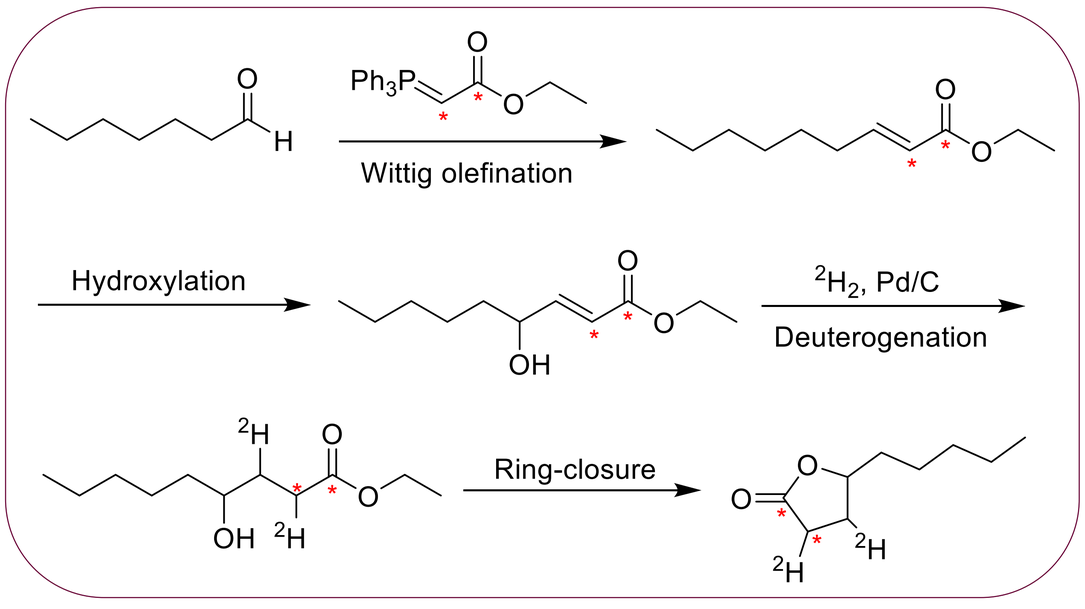
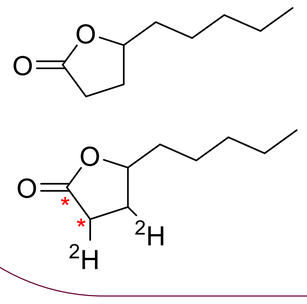


Figure 3: Synthesis of novel $^{13}C_2$ -$^{2}H_2$-γ-nonalactone *via* two Wittig olefination steps. Based on synthesis by Sadhukhan *et al.*[8] Red asterisks show ^{13}C atoms.



Unlabelled γ-nonalactone (Natural)
Molecular weight = ***156.23*** *g/mol*
$C_9H_{16}O_2$

$^{13}C_2$ -$^{2}H_2$-γ-nonalactone (Synthetic)
Molecular weight = ***160.13*** *g/mol*
$C_5{}^{13}C_4{}^{2}H_2H_{14}O_2$

Thus these compounds are distinguishable by mass spectrometry!

Aims

- To carry out a comprehensive survey of NZ wines to quantify γ-nonalactone.
- To identify trends in concentrations associated with different grape varieties, and noble rot infection of grapes.
- To use these results to inform future mechanistic studies of the biogenesis of this important aroma compound.

Analytical Method

- A solid phase extraction (**SPE**) method by Ferreira *et al.*, optimised for the extraction of linear aliphatic lactones in wines will be used.[9]
- Wines will spiked with $^{13}C_4$-γ-nonalactone internal standard, extracted, and analysed by gas chromatography-mass spectrometry (**GC-MS**) (Figure 4).
- Calibration curves with known standards will be constructed for three different matrices (dry white wine, dry red wine, sweet wine).
- Stable isotope dilution analysis (**SIDA**) will be used for quantification of γ-nonalactone naturally present in NZ wines. SIDA is the "gold standard" for quantification of compounds using mass spectrometry.[5]
- It is expected that γ-nonalactone and its isotopically labelled analogue (known concentration) will act essentially the same during extraction and analysis, so their mass spectrometry signals can be directly compared for quantification.

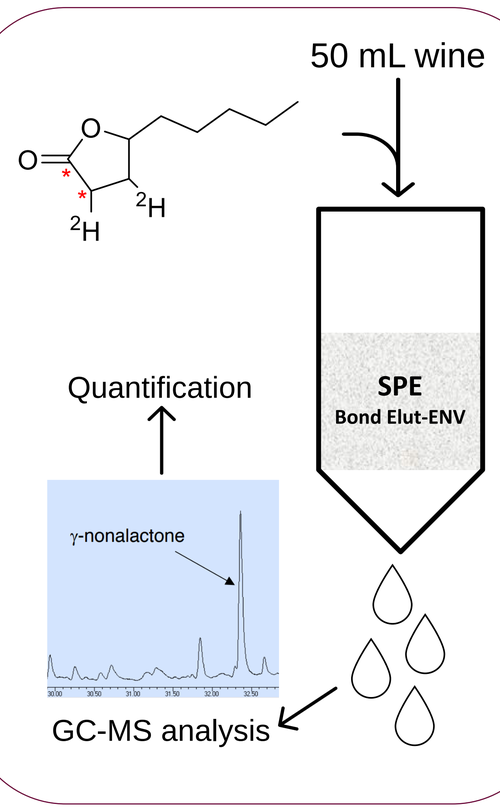
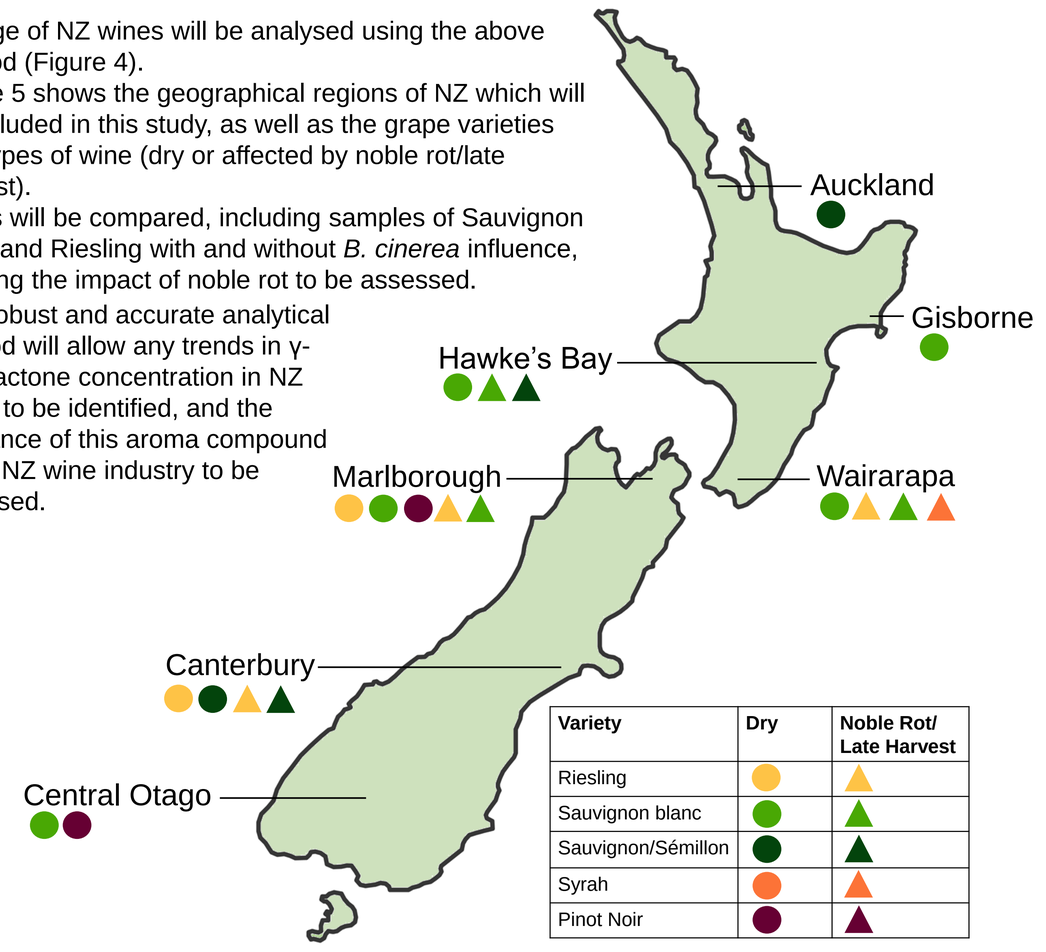


Figure 4: Summary of method to be used for analysis of NZ wines.

Future Work: γ-Nonalactone in New Zealand Wines

- A range of NZ wines will be analysed using the above method (Figure 4).
- Figure 5 shows the geographical regions of NZ which will be included in this study, as well as the grape varieties and types of wine (dry or affected by noble rot/late harvest).
- Wines will be compared, including samples of Sauvignon blanc and Riesling with and without *B. cinerea* influence, allowing the impact of noble rot to be assessed.
- This robust and accurate analytical method will allow any trends in γ-nonalactone concentration in NZ wines to be identified, and the relevance of this aroma compound to the NZ wine industry to be assessed.



Variety	Dry	Noble Rot/ Late Harvest
Riesling	●	▲
Sauvignon blanc	●	▲
Sauvignon/Sémillon	●	▲
Syrah	●	▲
Pinot Noir	●	▲

- Biogenesis studies will be carried out to investigate possible sources of γ-nonalactone in wine.
- This will include fermentation with and without putative precursors and oak chips.
- A selection of different fermentative yeast species and stains will also be investigated to assess their impact on γ-nonalactone concentration in wine.
- Better understanding of wine aroma will enable NZ winemakers to better control winemaking processes and produce more desirable wines – benefiting the consumer and the NZ wine industry as a whole!

Figure 5: Geographical distribution of NZ wines to be analysed, with associated grape varieties and types to be investigated.

References

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