IVES Technical Reviews
vine & wine

https://doi.org/10.20870/IVES-TR.2025.9480

The role of skin-contact time and heads fraction on Pisco terpene content

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Pisco is a traditional Peruvian spirit, and Muscat of Alexandria ("Italia") is amongst the main grape varieties used to produce it. Pisco production is mainly artisanal and varies widely across regions and producers; more information is needed on the impact of different operations on its composition. This study demonstrated the effect of changes in skin-contact duration and the amount of "head fraction" discarded on terpene content to guide producers during Pisco manufacturing.

Italia piscos

Italia piscos are characterised by floral and fruity aromas which are mainly due to their high terpene concentrations. The main terpenes present are linalool, geraniol and nerol[1] which can be found in both the skin and pulp of muscat berries. At harvest 4.6 and 31 % of free and glycosidically bound terpenes can be found in the skin of muscat grapes, respectively. Variations exist: geraniol and nerol are located mainly in the skins while linalool is evenly distributed between the skin and pulp[2]. Skin-contact has been recognised as an effective technique to increase the intensity of varietal aromas in wines and spirits thanks to increased extraction of free and bound terpenes found in the skins[3 4].

Other operations such as fermentation and distillation also impact final Pisco terpene concentration. Peruvian piscos are produced through discontinuous distillation in a copper Charentais-style alembic (INDECOPI, 2006) where distillation conditions affect the release of glycosidically-bound terpenes and their volatilisation[5]. Traditionally, only the middle-run fraction of the distillate (heart) is retained, and the fore-run (head) and after-run (tails) are discarded. How different compounds behave during distillation depends on their boiling points and solubility in water and ethanol in the liquid and vapour phase. Information on which fractions contain the most terpenes are contrasting. According to Migone-Repetto (1986)[6] and Versini *et al.* (1993)[7] they distil preferably in the first fractions of the distillate. However, Lukić *et al.* (2011)[8] reported that most terpenes increase in concentration towards the end of distillation and non-polar hydrocarbons (β-myrcene and α-terpinolene) increase during the first half of the distillation. Linalool, which has a relatively lower boiling point and higher sensitivity to acid hydrolysis than other terpenes, decreased in concentration in the later fractions[8].

Skin-contact

Pisco production varies widely across producers and regions, with the use of skin-contact ranging from a complete fermentation with marc to no skin-contact at all (INDECOPI, 2006). Three maceration times (0, 18 and 36 h at room temperature) were trialed (Table 1) to determine their effect on free terpene concentration[9]. Linalool was the most abundant terpene, with concentrations ranging from 11900 - 21243 µg/L, followed by geraniol and finally nerol. Significant differences were observed between all treatments for all three compounds, with longer maceration times resulting in higher terpene extraction. Samples macerated during 36 h had approximately twice the content of total terpenes than samples without maceration (0 h). The largest increment was observed for nerol (269 %) and the least for linalool (179 %).

Polynomial curves were also fitted to assess the relationship between maceration time and the rate of extraction (ΔConcentration/ΔTime) of each terpene evaluated (Figure 1). Evaluation of the slopes and the fitted models showed that terpene transfer rate was higher during the first 18 h of maceration than during the last 18. Maximum extraction rates of linalool, geraniol and nerol occurred at 18.96, 21.1 and 20.6 h respectively. At 36 h, extraction rates had slowed considerably, from 435 to 84 µg linalool/L.h (-80 %), from 109 to 56 µg nerol/L.h (-49 %) and 44 to 19.5 µg geraniol/L.h (-56 %) indicating decreasing extraction efficiencies over time. According to the models, extraction rates would plateau at around 40 – 42 h for all compounds. This is favorable from a technological point of view; since no sulfur dioxide (INDECOPI, 2006) or any other conserving agent can be used in Pisco production the duration of any pre-fermentation operations needs to be limited. Prolonged skin-contact not only favors

TABLE 1. Effect of skin-contact duration (h) on terpene concentration (values are means (n = 3); within a row, values followed by different letters between are significantly different according to Fisher's LSD test at P < 0.05)).

	Concentration (µg/L)			P-value
	0 h	18 h	36 h	
Linalool	11900 ± 589 a	19736 ± 1448 b	21243 ± 1368 c	< 0.001
Geraniol	2020 ± 247 a	3973 ± 237 b	4976 ± 355 c	< 0.001
Nerol	678 ± 36 a	1470 ± 113 b	1821 ± 112 c	< 0.001

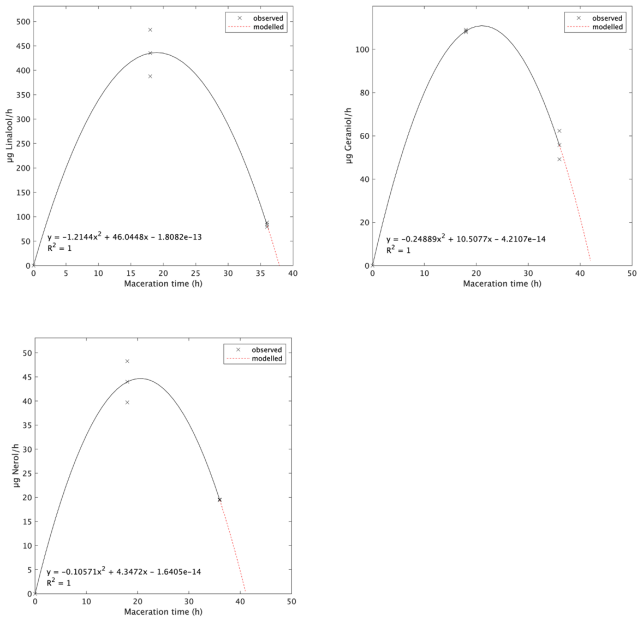


FIGURE 1. Polynomial fit of terpene extraction rate.

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the increase of positive aromas (e.g., terpenes), but that of undesired aroma compounds (e.g., C_6 alcohols) and polyphenols[6]. It also causes other reactions that could be negative to the quality of the base wine such as polyphenol oxidation and, in the absence of SO_2, can lead to microbial spoilage. Increased browning was observed in the longer treatments when compared to the controls.

Amount of head fraction discarded

Removal of different head proportions (0, 1 and 2 %, with respect to the base wine volume) was evaluated in combination with different maceration times (Figure 2). No significant differences were found for any of the three compounds or for the interaction skin contact time*proportion of head[9]. Contrary to Versini *et al.* (1993)[7], who observed that linalool, hotrienol and α-terpineol distill preferably in the head fraction during grappa production; and Migone-Repetto (1986)[6] who reported that nerol and linalool concentrations were 2 and 3 times (respectively) higher in the head of Chilean piscos than in the heart, this was not the case in Peruvian Italia pisco. Several factors can be responsible for these differences such as the type of stills used. Peruvian piscos are produced through single distillation in a Charentais-style copper alembic heated with an open flame and without rectification (INDECOPI, 2006) while Chilean pisco and grappa production often include rectification, heating is usually done by jackets or gas heaters, and the shape of the stills vary widely[10]. The different distillation cut criteria used to produce these spirits would also add to these differences. As indicated by Piggot (2003)[11], the amount of heads removed in batch distillations will mainly affect compounds with low boiling points such as acetone (56 °C) and methanol (65 °C) rather than compounds with higher boiling points like linalool, geraniol and nerol (>198 °C). This has been confirmed by Lukić *et al.* (2011)[8], Awad *et al.* (2017)[12] and Peña y Lillo *et al.* (2005)[5], who observed that when base wines are batch distilled in Charentais-style alembics, terpene concentration actually increases towards the later fractions of the distillate and higher levels of monoterpene alcohols occur in the low-alcohol tails than in the heads. Other factors contributing to this behaviour include their high polarity and hydrophilicity[8]. Thus, inclusion of larger proportions of heads in the distillate would not increase the amount of linalool, geraniol and nerol in the final spirits as observed in this study.

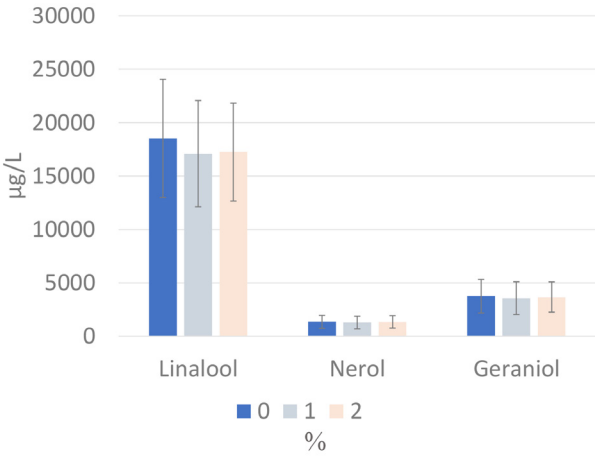


FIGURE 2. Effect of discarded %head fraction on terpene concentration.

Error bars represent standard deviations (SD) of three replicate. Where present, letters denote significant differences (ANOVA; P<0.05) between treatments for each terpene analysed.

From these results, it can be concluded that skin-contact is an effective technique to increase the amount of terpenes present in pisco Italia, and thereby its varietal character and aroma. However, inclusion of higher proportions of head fraction had no significant effect on the final concentrations of linalool, geraniol and nerol. Skin-contact duration should be optimized with regards to grape maturity level, variety, and technological capability. ■

Acknowledgments : *We thank Luis Cisneros and Romina Pedeschi of Texas A&M University for supplying all chemical standards. Special thanks to Andrea Belancic, Eduardo Agosin and Lenka Torres from the Centro de Aromas y Sabores, Pontificia Univesidad Católica de Chile, for their technical support on terpene analysis. The authors would also like to acknowledge Peter Watkins, who helped with the statistical analysis of the data.*

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