# ORANGE WINES: TANNIN EXTRACTION KINETICS DURING MACERATION OF WHITE GRAPES

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## Introduction

Orange wines are obtained from white grapes fermented on their skins. They are the oldest type of white wine and date back to a time when the pressing of grapes was not usual or not possible. This tradition has been preserved to this day, especially in Georgia and adjacent areas of the South Caucasus, where a small proportion of the production is still made using this method. Since the turn of the millennium, it has also attracted increasing interest in the western world. In part, this was the anti-enological response to an increasingly scientific and technical approach to winemaking, which is thus countered by an artisanal and deliberately antiquated way of working that is frequently guided by emotions and considered more natural. In some cases, orange wines are also produced without microbial defects but with remarkable enological perfection. Thus, a wide spectrum of different types of orange wine has emerged.

All orange wines share an amber appearance and pronounced tannins, ferment on the skins after or without destemming and, after the end of primary fermentation, usually undergo a phase of post-maceration for several weeks or months. Subsequently they are separated from the must solids by simple draining off or, in modern form, also by pressing. The enhanced tannin levels resulting from the prolonged skin contact period differentiates them from contemporary standard white wines. However, this is where similarities between orange wines ends. In principle, their production is not linked to a particular type of fermentation and storage containers or the presence or absence of enological interventions.

The overlapping of different production methods has unfortunately led to a lack of conceptual clarity. Orange wine can be fermented and aged in clay amphorae. It is only in this case that it is an amphora wine. Furthermore, it can be left to its own destiny without any enological interventions such as $SO_2$ additions and filtration in order to be marketed as what is called a natural wine. However, such a definition is debatable because wine does not come into being by itself, but is always the result of human intervention such as the timing of harvest, pressing and bottling. Furthermore, orange wine can also be aged in wooden barrels, concrete egg-shaped vessels, or even stainless steel tanks after pressing. When aging is performed in a controlled manner regardless of the vessel used for that purpose, the microbial disorders frequently observed in orange wines can be avoided.

The long skin contact period of white grapes used for the production of orange wines aims at extracting, to a greater or lesser extent, the tannin present in the skins, seeds, and possibly stems. This is done analogously to red winemaking by maceration. The extraction of grape-derived aromas plays a subordinate role in this context, as it is usually completed after a few days of skin contact. The decisive factor is that, due to the lack of red-blue anthocyanins in white grapes, the extraction is exclusively of tannins. These are responsible for the mouthfeel and the amber appearance of such wines. Among the various in-mouth sensations associated with tannin, astringency is particularly noteworthy. It is its primary sensory expression.

In contrast to red winemaking, there is little knowledge and experience in orange winemaking regarding the amounts of tannin extracted, the technical parameters ruling its extraction, and the mouthfeel attributes resulting therefrom. In practice, the time point of solid-liquid separation (pressing) is often chosen arbitrarily, so that the sensory outcome is the result of chance. Therefore, simple measurement methods would be useful to assess the tannin concentration during maceration before pressing too early or too late, and thus to adapt the wine style to the

desired purpose and market segment. Such measurements should in particular be suitable for use under commercial winery conditions. This study was performed under the said conditions and presents the first results on the time course of tannin extraction of orange wines during maceration.

## Differentiation of orange wines by different total phenols and tannin contents

It is well known from red winemaking that the extraction of tannins during the skin contact period depends on its duration, its technical implementation with particular regard to temperature and the frequency of cap management techniques such as pumping over or punching down, and grape variety. This results in highly variable tannin contents, which make the most important contribution to the differentiation of red wine styles. In contrast, there are only a few reports on the concentration of tannin in commercial orange wines. In these studies, tannin was measured as total phenols. Thus, total phenol levels of 200 to 1,700 mg/L (as gallic acid equivalents, GAE) were measured in 20 orange wines of different European and Georgian origin and aged in amphorae (Diaz et al. 2013). For six other such wines of the Malvasia variety grown in Croatia, total phenol concentrations of 476 to 800 mg/L and of total flavonoid phenols of 296 to 585 mg/L GAE were determined (Lukić et al. 2015). In comparison, total phenols of red wines range from 2,000 to 4,500 mg/L GAE.

Using different white varieties in South Africa, a maceration period of only 10 days resulted in total phenol contents of 279 to 484 mg/L GAE (Singleton et al. 1975). In the Veneto area of Northern Italy, a prolonged maceration period of the Bianchetta Trevigiana cultivar resulted in total phenol levels that in some cases exceeded those of red wine (Lomolino et al. 2010). Reductive storage of the must under air exclusion during primary fermentation and post-fermentation maceration contributes to its accumulation and preservation (di Lecce et al. 2013). Thus, it is well established that maceration length and grape variety strongly affect the final tannin concentration, expressed as total phenols.

## Interpretation of total phenol data

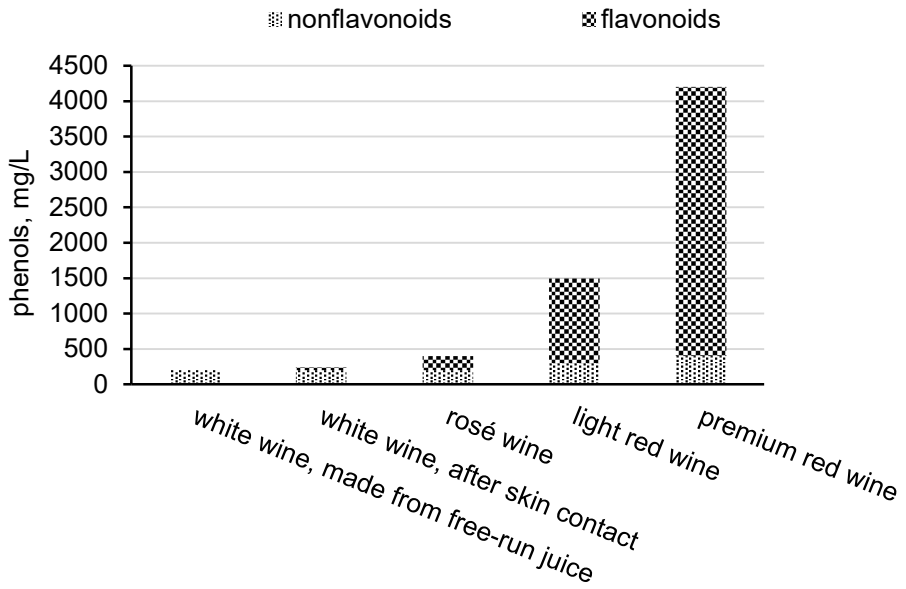
Tannins are composed of a vast number of different phenols undergoing compositional changes during aging. Their individual determination is impossible and would in any case complicate the interpretation so that real-time decisions during the winemaking process become impossible. Therefore, their amount is frequently assayed by measuring the total phenol content and expressed as a reference phenol, mostly gallic acid or catechin. This approach is similar to the determination of total acidity, which includes the various individual acids in a sum parameter and expresses them as tartaric or sulfuric acid.

Total phenols of grapes are composed of two main fractions:

- Nonflavonoid phenols consisting of phenolic acids, which are dissolved in the berry juice at relatively constant concentrations across all kinds of wine. At these concentrations they do not significantly contribute to mouthfeel sensations.
- Flavonoid phenols, which are mainly released from the solid parts of the grape as a function of maceration length and conditions, and which constitute the actual tannin.

Simplified, it can be stated that the total phenol content increases as the tannin content increases. Conventional white wines contain about 200 mg/L total phenols. They comprise only small amounts of flavonoid phenols, which cannot be quantified by measuring total phenols. In contrast, total phenols of red and similar wines are essentially made up by flavonoids acting as tannins, compared with which the nonflavonoid fraction has little quantitative importance and can be neglected. These proportions are schematically shown in figure 1. As a result, total phenols are a useful parameter for roughly assessing tannin content and style of red wines and of wines with similar tannin levels.

*Figure 1: Total phenol levels in white, rosé, and red wines and their composition of nonflavonoid and flavonoid phenols.*




Tannins are the key driver of astringency, related in-mouth sensations, and color. Hence, correlations can be expected between total phenols and astringency. For red wines, such correlations ($r^2$) have been found in various studies. These include:

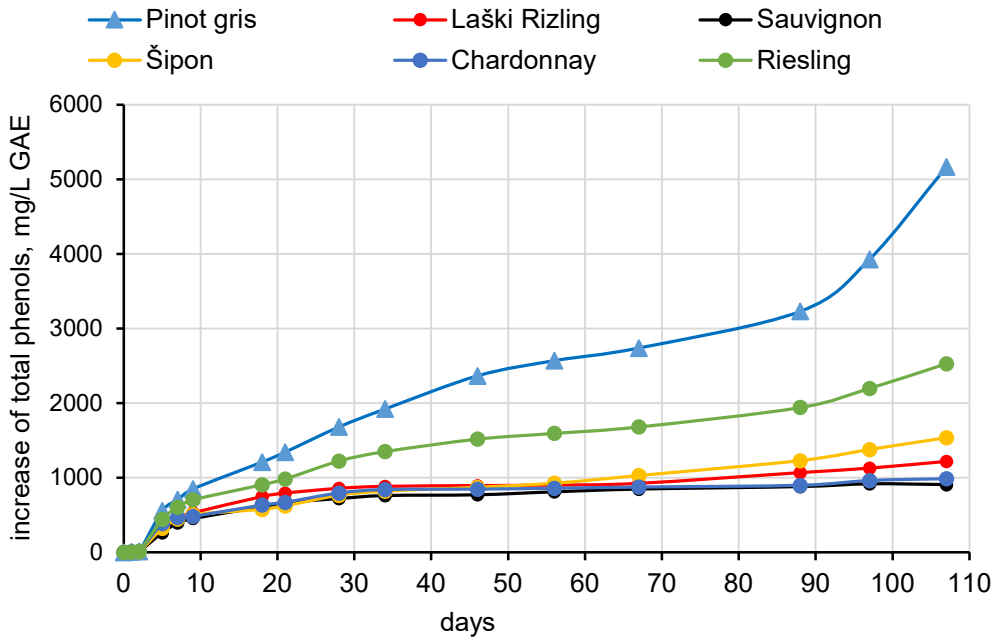
- $r^2$ = 0.40 in a set of 40 red wines from Washington State when total phenols were measured as the UV total phenol index at 280 nm (Kennedy et al. 2006),
- $r^2$ = 0.59 in European wines when total phenols were measured with the Folin-Ciocalteu reagent (Schneider 1998a),
- $r^2$ = 0.74 in 35 wines from British Columbia when total phenols were measured with the Folin-Ciocalteu reagent. However, a predictive one-way model based on this correlation yielded only $r^2$ = 0.42 in another set of red wines (Cliff et al. 2002).

Summarizing, total phenol measurements in red and similar wines give useful information about the tannin content and the astringency to be expected therefrom. Hence, these measurements are widely used in the wine industry. For that purpose, simple measurement of the UV index at 280 nm or the colorimetric Folin-Ciocalteu method are the most applied approach. The latter has been extensively investigated (Singleton and Rossi 1965). It reports results as gallic acid (GAE) equivalents. An extension of this method using a previous fractionation step also allows breaking down total phenols in their flavonoid and nonflavonoid fraction (Kramling and Singleton 1969). All three kinds of measurements have been used in this study.

## Extraction kinetics of total phenols during maceration

Figure 2 shows the time course of tannin extraction, measured as the increase of total phenols, during the maceration of six white Vitis vinifera varieties. After crushing/destemming without $SO_2$ addition and inoculation (20 g/hl) with active dry yeast, primary fermentation conducted at a constant temperature of 25° C and three punch-downs per day was finished after approximately 10 days. Subsequent storage of the must for post-fermentation maceration was performed during 3.5 months at pilot scale and 15 ± 5° C under exclusion of air. The following features can be observed:

*Figure 2: Extraction of total phenols during maceration of white grapes of different V. vinifera varieties (Slovenia, 2017). Must homogeneization by punching down three times per day during active fermentation.*




- The amount of extractable tannin and its extraction rate are highly variable.
- During the first two days of maceration and before the onset of fermentation, no phenol accumulation was observed. This effect corresponds to that of must oxidation due to the presence of dissolved oxygen in the must devoid of $SO_2$. The associated precipitation of phenols can be prevented by a pre-fermentation $SO_2$ addition (Schneider 1998b). In the absence of $SO_2$, the solubility of tannic phenols only improves considerably in the alcoholic environment.
- By the end of primary fermentation, relatively little tannin had been extracted. The time course of its extraction is not related to the fermentations rate.
- In three of the six lots, tannin extraction was largely completed after one month, after which the extraction curves flattened permanently.
- In the remaining three lots, extraction kinetics accelerated again after three months of maceration. This phenomenon resulted in extremely high tannin levels accompanied by accordingly high astringency ratings. Apparently, additional tannin was mobilized and made accessible to extraction without any mechanical intervention on the must. The cause of this behavior might be improved extractability of seed tannins after complete hydrolysis of the lipid layer around the seeds.
- As a general trend, exhaustive tannin extraction in orange winemaking requires more time than in red winemaking. This can be partially explained by the lack of anthocyanins able to complex tannins and to better retain them in solution (Singleton and Trousdale 1992).
- After only one week of maceration, tannins measured as total phenols differed between lots by a factor of 1.8, after 4 weeks by a factor of 2.3, after 8 weeks by a factor of 3.2, and after 15 weeks by a factor of 5.7.

## Highly variable tannin contents in young orange wines

At the end of the 107-day maceration period, the musts were pressed under standardized conditions at 1.0 bar using a research scale water bag press, and the phenolic composition of the young wines and their press yields were determined. Results are shown in Table 1.

*Table 1: Phenolic composition and press yield of orange wines after 107 days of maceration.*

| | total phenols, mg/L GAE | nonflavonoid phenols, mg/L GAE | flavonoid phenols, mg/L GAE | press yield, % v/v |
|---|---|---|---|---|
| Pinot gris | 5051 | 124 | 4927 | 78,6 |
| Laški Rizling | 1218 | 148 | 1070 | 80,4 |
| Sauvignon | 883 | 103 | 780 | 78,2 |
| Šipon | 1696 | 198 | 1498 | 83,5 |
| Chardonnay | 1098 | 131 | 967 | 83,3 |
| Riesling | 2319 | 128 | 2191 | 68,9 |

The data given in table 1 can be summarized, including the practical consequences, as follows:

- The total phenol levels closely correlate with those of flavonoid phenols ($r^2 = 0.99$), similarly to red wines. Their measurement can therefore replace the more elaborate determination of flavonoid phenols in orange wines.
- The contents of total phenols varied by a factor of 5.7, and those of flavonoid phenols by a factor of 6.3. These variations are exclusively due to the variable "fruit".
- Gentle pressing did not significantly change the tannin contents measured as total phenols compared to those measured directly before pressing (Figure 2). It can be concluded from this that gentle pressing can replace simple draining off the wine, which is frequently practiced for orange wines.
- The press yield is an index for the original solid-to-juice ratio of the berries. The higher the press yield, the lower the solid content and the less tannin would be expected to be extracted from the solids, i.e. skins and seeds. However, the total phenol content showed no significant correlation $r^2 = 0.05$) with the press yield. Furthermore, there was no correlation with the original Brix readings. Rather, grape variety and phenolic ripeness appear to be the key factors affecting tannin concentration.
- The range of variation in total phenols indicates that for the targeted production of orange wines, the parameters of the maceration period (duration, temperature, frequency of punch-downs or pump-overs) must be adjusted to the fruit and the desired wine style in the same way as for red wines.
- Even under comparable maceration conditions, it is not possible to predict how much tannin will be extracted in a given time period. Frequently practiced maceration periods of 6-9 months can lead to over-extraction in individual cases, while early pressing immediately after fermentation will not yield a typical orange wine.
- Therefore, by analogy with red winemaking, some form of measurement of the tannin content achieved is extremely useful for optimizing the timing of pressing or drawing off. Monitoring total phenols using the Folin-Ciocalteu assay or, alternatively, UV absorption at 280 nm are useful approaches for that purpose.
- Must before pressing is not as homogeneous as a liquid. Hence, careful must homogenization is required immediately before sampling to obtain representative samples yielding reliable phenol measurement results.

**Seed and skin tannins, and the effect of seed removal**

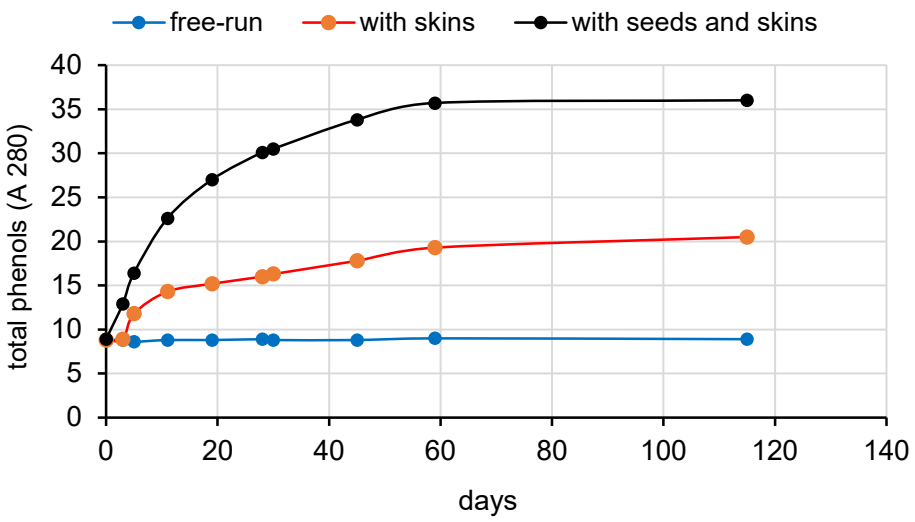
Seed tannins endure a bad reputation with winemakers. At a comparable concentration, skin tannins display a limited astringency and provide a perception of mellowness and fullness on the palate, whilst seed tannins cause a sharp increase of astringency (Canals et al. 2008). Since both seed and skin tannins are commercially available with an acceptable degree of purity, it is easy to understand the sensory difference between them by tasting a white wine or model solution after a 200 mg/L-addition of one or the other. Therefore, some winemakers strive to perform partial seed removal within their technical capabilities as a contribution to differentiating their orange wine styles and to obtain softer tannins. This also means that they dispense with a part of the tannin that the fruit provides.

The contribution of seed tannin to total tannins is highly variable. In general, the concentration of seed tannins decreases during grape ripening, while skin tannin concentration increases. Under conditions of orange winemaking, preliminary results showed that skin tannin accounted for 30-60% of total tannins. Sometimes, but not regularly, a stronger extraction of skin tannin than of seed tannin can be observed at the beginning of maceration, in analogy to what is known from red winemaking. This delay of seed tannin extraction can be explained by the prior requirement for hydrolysis of the lipid layer around the seeds as well as hydration of the seed tissue itself.

Figure 3 shows the effect of total seed removal before the start of maceration by the example of a Chardonnay. Total seed removal was achieved by driving the crushed grapes across a sieve by means of a blade such that the seeds and juice pass through apertures of the sieve while retaining the skins. Subsequently the juice was separated from the seeds and recombined with the skins and pulp for maceration. Thus three fractions were obtained: free-run juice, free-run juice with skins in the ratio of the free-run juice, and the original must with skins and seeds. The time course of total phenols measured as A 280 nm was monitored for each of these fractions.

Total phenols in the free-run fraction showed no significant changes over time, because they essentially represent the nonflavonoid phenols predetermined by the pulp juice and dissolved in it. It is a base value that must be subtracted because any increase in a sample reflects the extraction of tannin. Under these conditions, skin tannin comprised 38 ±3 % of total tannins after the fifth day of maceration and 42.8 % after 107 days of maceration, with the remainder predominantly corresponding to seed tannin.

*Figure 3: Extraction of total phenols (A 280) as affected by total seed removal during fermentative and extended maceration of a Chardonnay (Slovenia 2020).*



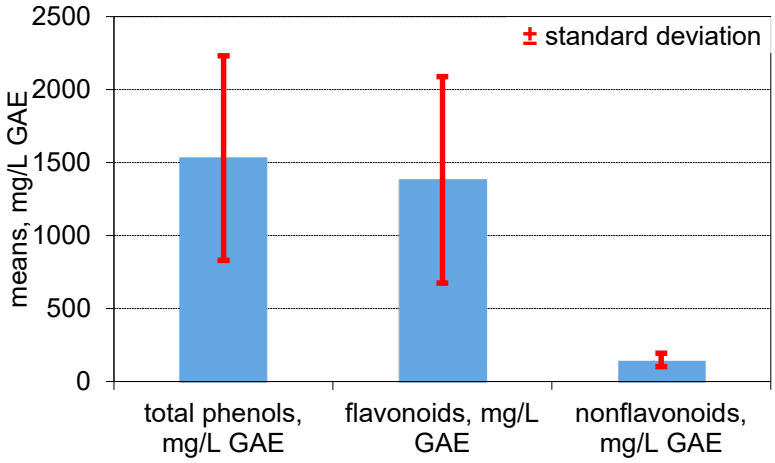
There are no technical means of complete seed removal in commercial winery settings, but partial seed removal may be a valuable technical instrument to diversify orange wine styles, comparable to what is sometimes done in red winemaking. However, regardless of the concentration of total phenol and tannin, there is a significant sensory difference between red and orange wines: When white grapes are fermented in the presence of seeds and skins like a typical red wine, the resulting wines tend to be lower in viscosity and astringency as a result of lower phenol extraction and the absence of anthocyanins. This suggests that even with comparable tannin content, orange wines cannot be directly compared to red wines because anthocyanins – absent in orange wines and present in red wines - play an additional role in mouthfeel properties (Singleton and Trousdale 1992, Oberholster et al. 2009).

## Range and mean values of the tannin content of commercial orange wines

The data shown in table 1 illustrate that the tannin contents of orange wines can vary widely, depending on fruit and maceration length. As a logical consequence, considerable variations in the mouthfeel of such wines are also to be expected, in particular in texture sensations such as astringency and body.

Due to the limited number of samples, the phenol data given for the varieties used in this study do not allow extrapolation from them to all orange wines obtained from these varieties. On the other hand, there is an urgent need for a database to better classify the tannin contents of future orange wines. Figure 4 shows preliminary data for mean values and standard deviations of the contents of total, flavonoid, and nonflavonoid phenols of 19 commercial orange wines sampled in 2018. The means of total and flavonoid phenol concentrations indicate that the tannin contents of orange wines can easily reach those of light red wines. However, the considerable standard deviations reflect the wide range of their actual tannin levels.

*Figure 4: Concentrations of total, flavonoid, and nonflavonoid phenols in 19 orange wines from Europe and Georgia.*




## Outlook: Aroma and aging.

When oxygen uptake occurs, flavonoid phenols in white wine exert a catalytic effect with respect to the formation of compounds responsible for the aroma of aged white wines, which are primarily higher aldehydes and sotolone (Pons et al. 2015, Schneider 2018). This reaction is accompanied by a gradual loss of fruity varietal aroma.

As early as during the maceration period as well as during subsequent storage, most orange wines pick up considerable amounts of oxygen, be it in wooden barrels or in amphorae. In conjunction with their high levels of flavonoid phenols, it is therefore understandable that their

aroma is not a fresh-fruity one, but rather is reminiscent of aged white wines. Its sensory features depend on the precursors of higher aldehydes available in the wine, and thus ultimately also on grape maturity. Ripe fruit can be sensorially clearly distinguished from unripe fruit. Typical aroma attributes of orange wines that are not affected by microbial disorders are figs, dry quinces, toasted almonds, tobacco, nuts, honey, coffee, mocha, hay, curry, and black tea. Often the grape variety is difficult to identify by smell, although there are varietal differences.

On the palate, these wines experience aging similar to that of red wines. It is not yet clear whether this maturation towards softer tannins is due more to reactions of polymerization and depolymerization the tannins are subject to, or more to their association with mannoproteins such as those released from yeasts. Depending on this, the usefulness of enological tools such as working with post-fermentative yeast lees or oxygenation will arise. Corresponding results will be reported in due course.

## Summary

Color, astringency and related in-mouth sensations of orange wines, also known as amber wines, are mainly attributable to their tannin. It is extracted in considerable but highly variable amounts and qualities during the long maceration period of such whites. This study focusses upon the assessment of tannin extraction using simple total phenol measurements accessible to commercial winery settings. They show that comparable to red winemaking, fruit characteristics (cultivar, ripeness) as well as the duration and technical framework conditions of the maceration period determine the content of extracted tannins. However, a longer maceration time is required for its exhaustive extraction than for red wine. Depending on the fruit, it can last from one to well over three months. The tannin levels obtained in this process approach those of light red wines and require appropriate measures for maturation during aging. For this reason, orange wines cannot be compared with either standard white wines or with red wines.

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