SZENT ISTVÁN UNIVERSITY
BUDA CAMPUS
FACULTY OF FOOD SCIENCES
DEPARTMENT OF OENOLOGY

TECHNOLOGIES OF BLACK GRAPE PROCESSING IN PREMIERE RED WINE PRODUCTION

THESES OF DOCTORAL DISSERTATION

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The candidate has met all the requirements determined in the Doctoral Code Book of the Szent István University. He took the observations and suggestions arising during consultation into consideration when reworking this dissertation, thus the dissertation can be put to public debate.

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1. PRELIMINARY WORK

The competitiveness of a given red wine on the market can be greatly enhanced if it contains demonstrably more of the physiologically important components, being revealed in great numbers these days, as well as if it contains more such compounds that are favourable to the quality of the wine and to its sensory features. Besides the natural characteristics of the raw material, the grapes that is, all these factors are primarily subject to the technologies of Oenology.

In the increasingly fierce competition on the market, the following are now to be regarded as the minimum requirements in our country:

- to produce wines which have the composition demanded by the target consumer group, but at the same time such red and rosé wines should be produced that are unique and bear the distinct characteristics of the habitat.
- to find the most suitable processing and treatment technologies for local grape varieties in order to emphasise originality and habitat character.

Adapting the various technology research conducted worldwide is key to ensuring the competitiveness of our red wines on home market. Hungary, however, situated on the northern border of the wine-growing area, must not adapt in a slavish manner the experience accumulated in other wine-districts endowed with rather different climatic conditions, and this is especially so in the field of processing black grapes.

The Hungarian climatic circumstances, in weaker or even in average years, often cannot provide for sufficient accumulation of colouring compounds and tannin in the skin cells of the black grapes. The lack in quantity is often coupled with deficiencies in quality as well due to the fact that the low polymerisation state of the skin and seed phenols, which are unripe in terms of phenolic compounds, result in an unpleasant tannin taste in the final red wine.
In a situation like this, the appropriate selection of processing and maturing techniques can significantly outbalance the aforementioned negative characteristics. In my doctoral thesis I wish to contribute to this task of utmost importance by examining a few crucial factors influencing the quality of red wines.

2. OBJECTIVES

The Hungarian wine market is facing changes. In the near future, Hungary's EU joining is likely to bring drastic changes to the wine and grape sector already torn by many interests. The inland market will play an instrumental role in the future and the Hungarian consumers' willingness to buy Hungarian wines will be a key issue to those participating in the Hungarian wine and grape sector. For any wine producer or enterprise the only possible principle to rely on in terms of competitiveness can be no other but that of quality. In the field ranging from raw materials to the final product, there are numerous factors that can be clearly defined and that greatly affect quality, this study is seeking to find answers to the following of these:

- Does the type of fermenting vat chosen have any effect on the polyphenol composition of the final product? If so, in what ways? Can demonstrable difference be found in the wines produced in the fermenting vats recommended by manufacturers?
- Does the use of pressure impulse fermenters result in any remarkable gain in quality compared to the traditional red wine fermenters based on the principle of pumping over which are so widely-used in our country?
- To what extent do extended skin fermentation and soaking, most frequently used in premiere red wine production, alter the composition of red wine, especially as regards the polyphenol composition?
- Under Hungarian circumstances, in which stage of the extended skin fermentation and soaking are the elaborate anthocyanin-tannin compounds formed which then guarantee a solid colour for a long time?
- Could the so-called tannin-indices (HCl and gelatine index) so widely cited in international literature prove useful to Hungarian wine producers in predicting tannin-composition and sensory features?

3. SUBJECT AND METHOD

The experiments took place between 1997 and 2001 with completely different vintages. The grape varieties used in the experiment included all major black grape types. In processing them, I utilised methods of both micro-vinification and large scale production. As a scene of the experiments, I chose wine-growing regions with a typical 'Northern' character. All analytical tests were carried out at the Department of Oenology at the Szent István University.

3. 1. Production of red wines with different fermenters

Fermenting vats of different make and different operating principle have been compared in three vintages. The circumstances of processing (duration, temperature) were like in the usual practice of the given location.

3. 1. 1. Examination of fermenters based on the principle of pumping over

The grape varieties (Zweigelt and Merlot) vintaged in the same habitat were transferred to three fermenters set up in different wine-growing regions. All the fermenters were based on the principle of pumping over but they were of different make. The processing was industrial-sized. In both vintages examined, during the usual fermentation period of five to seven days, the changes were examined through daily samples fermented in micro-vinificaton. The primary aim throughout the analytical tests was to measure colour and polyphenol characteristics with spectrophotometric methods. In addition, as a special measurement, we also measured the sediment ratio in the daily samples.

3. 1. 2. Examination of fermenters based on pressure impulse

In 1999 there were two sites, while in 2001 there was one where the operation of Hungarian and Italian pressure impulse fermenters was studied. In such fermenters, the submerging of the cap is achieved through the pressure of the carbon-dioxide produced in the fermenting process, similarly to some old fermenters based on the automatic principle.

The extended skin fermentation of the Kékfrankos, Cabernet, Merlot and Kékoportó types lasted for the duration recommended by the fermenter manufacturers, that is six or seven days. The pressure values controlling the frequency of watering (usually as many as 4 to 10 during the main fermentation) were also set by the experts installing the fermenters.

Once the black grape raw materials had been transferred to location, they underwent a series of processing steps and auxiliary materials addition. After that, they went directly into the experimental fermenters and the conventional pumping over control fermenting vats. The samples taken daily and fermented in micro-vinification were examined to understand the polyphenol composition, the changes in the intensity and shade of colour and sediment ratios. The red wines were exposed to sensory evaluation in both years. We had the chance to measure the resveratrol contents of the 2001 vintage, thanks to the so-called direct injection method developed by the Oenology Department. The device used for the measurements was a HP- 1050 HPLC with the following ratios: bi-distilled water : acetonitril : ethanol, 90:5:5% From the tannin-indices, the HCl-index and gelatine-index were measured (see their

description at the relevant topic)

3. 2. Examination of extended fermentation and soaking

The first investigation related to extended fermentation technologies was carried out in Eger in 1997. In this series of different examinations Kékfrankos samples were produced in industrial quantities (400 hl). The fermentation and soaking period was 20 days, and we took samples 5 times during this period. Processing also took place on a micro-vinification level including Blauburger and Cabernet varieties, but in this case, the experiment took as many as 30 days with samples taken every 5 days.

In 1999 we had the opportunity to conduct similar research only at one site. The experiments were carried out in small-scaled wine-cellars with Kékfrankos (35-day cycle), Merlot (16-day) and Cabernet (28-day). All the types were produced through spontaneous fermentation with samples taken every 2 to 6 days, and gradually becoming less frequent with time.

The red wines of the two vintages mentioned above were tested for polyphenol composition and colour character using the common spectrophotometric measuring methods.

In the year 2000 vintage I completed another experiment in the Sopron wine-growing region. Of the same Kékfrankos raw materials another two red wines were made but this time with a processing duration of 6 and 15 days. In this case I examined only the final products and once the usual measurements detailed above were done, the wine was bottled. The samples were then 3 and 8 months later exposed to another series of analytical (intensity and shade of colour) and sensory evaluations to prove the favourable effects of extended fermentation and soaking.

3. 3. Measuring tannin-indices in red wines

The introduction of tannin-indices as a means of predicting the tannin quality of red wines was first proposed by French scientist Glories. The measuring principle of the HCl index is based on the fact that procyanidins become unstable in a highly acidic environment. The speed of condensation depends on the degree of polymerisation. Its value is usually between 5 and 40.

During the measurement we have to add 15 millilitres of 12N HCl and 5 millilitres of water to the 10 millilitres of wine to be measured. The solution is diluted to thirty times its original volume and it is measured immediately in a 1-centimetre cuvette at 280 nm (d_o). This

very same measurement is then repeated on a sample where the acidic solution was left standing for 7 hours before dilution and it was then spinned. (The data acquired in this way is marked by d_1) The HCl index can be worked out as follows:

$$\frac{(d_0 - d_1)}{d_1} \times 100$$

The gelatine-index of red wines refers to the reactivity of the tannins and it also indicates the harsh taste that can be expected on the tongue. Average gelatine-indices between 40 and 60 mean a limited reactivity of the tannins and such values are usually the characteristic of premiere and mellow red wines.

During the measurement 1 millilitre of 18 g/l gelatine solution is added to 50 millilitres of red wine. After leaving it standing for three days, it is spinned and after being diluted to fifty times its original volume, absorbency is measured with a spectrophotometer at 765 nm. The data acquired here is marked by c_1. The value of c_0 can be obtained by measuring the red wine without the gelatine treatment. The gelatine-index can be worked out using the formula below:

$$\frac{(c_0 - c_1)}{c_o} \times 100$$

These indices have not been used in Hungary so far.

In order to examine this problem, I set up an experiment focusing on the use of these indices in Hungarian red wines in 2001. The two commonly-used indices, namely the HCl and the gelatine indices, were tested on the wines of the State Wine Competition held in Budapest this year earlier.

One month after the competition, 53 wines of different varieties, regions and vintages were randomly selected from the total number of 200 different wines. The samples were then tested in the laboratories of the Oenology Department of the Szent István University. The samples included wines from all major wine-growing regions, all vintages of the past eight years, and all major Hungarian black grape varieties.

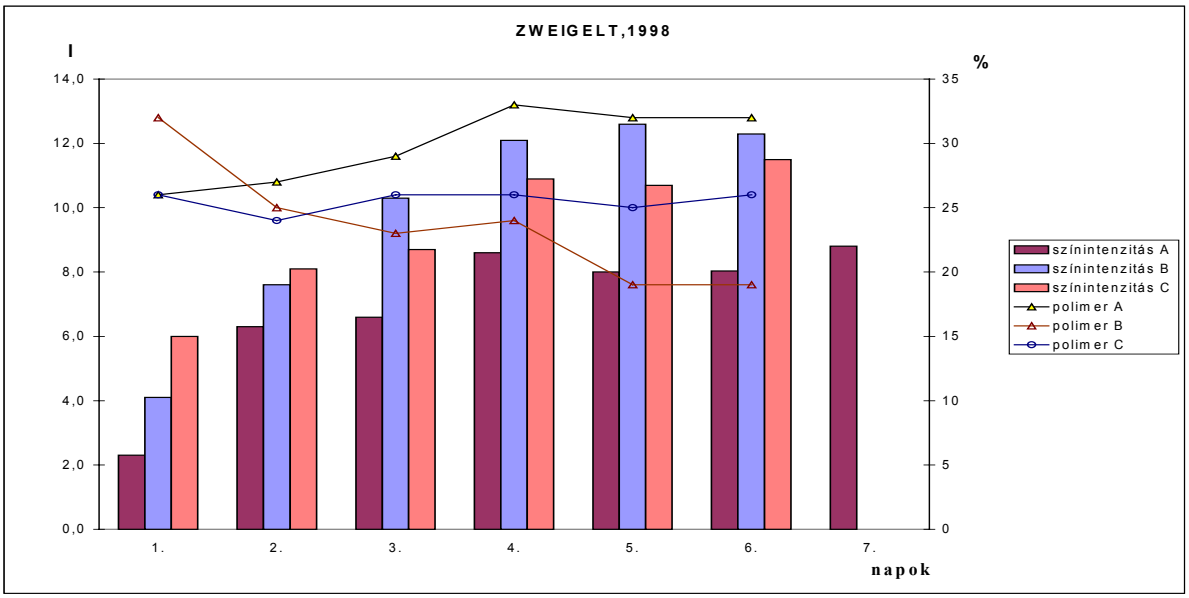
The index values measured could then be compared to the data cited in international literature and they also lay the basis for further analysis as regards prizes, habitat, vintage and so on.

4. FINDINGS

4. 1. Examination of different fermenting vats

Based on the research I conducted using different vintages and grapes of various variety and habitat, I came to the conclusion that there are no major differences in the quality of the fermenters available on the Hungarian market. In case of all the fermenters examined based on the conventional principle of pumping over, the extraction processes crucially influencing the colour character of the red wine were intensive enough. The anthocyanin values measured proved to be satisfactory (220-330 mg/l and 106-158 mg/l) and were determined only by the type of the grapes processed and the vintage.

The measurements I carried out seem to have proven that intensive extraction around the 4th and 5th days of main fermentation, as can be seen on the sediment level measurements, results in a too high amount of sediment which in return greatly affects colour intensity. (shown by value as much as 8.8 in vat 'A') The sediment that is formed has an adsorbing effect which leads to a colour loss of 30 per cent as shown on the figure below.



The 2-year-long series of experiments with fermenters utilising the movement of carbon-dioxide arising during fermentation (pressure impulse fermenters), has clearly demonstrated that these modern devices can in fact compete with fermenters based on the principle of pumping over in all respects. Extraction of polyphenols and colour materials is

efficient and the chief characteristics of the wines produced in this way are either as good as those of the wines produced using the method of pumping over or they even surpass those.

A too intensive movement of the cap is by no means found desirable in this case either. In case of a fully ripe berry having an enzymatic tissue structure (e.g. Cabernet sauvignon), sediment ratios higher than 10 per cent might result in a significant colour loss. This phenomenon is observable with pressure impulse fermenters mainly. In the early stages of fermentation the number of rinsing times, as many as 10 daily, must be decreased.

The red wines produced in pressure impulse fermenters are characterised by a 50 per cent higher concentration of resveratrol, which can be probably attributed to a reduced level of oxidation.

4. 2. Examination of the effects of extended skin fermentation

I completed experiments on four different grape varieties in three vintages to find out about the behaviour of a few typical polyphenol compounds when fermentation and soaking periods range between 16 and 35 days. I have determined the leeching-out characteristics of the total polyphenol content, the non-flavonoid phenols and tannin-flavonoid compounds in the wines I used throughout my experiments. I also found out about the periods of peak values and the behavioural characteristics of leucoanthocyanin and anthocyanin compounds. Some of the values have also been shown on diagrams.

After analysing the phenol compounds of red wines made of varieties which were different in their ripeness (and in their ripeness in terms of phenols), I concluded that the favourable effects that extended soaking has on colour stability and quality can only be taken full advantage of only in case of ripe enough raw materials. Unripe grapes do not contain the necessary tannin compounds which are washed out of the skin during soaking and which balance the losses coming from phenols binding with colloids. These tannin compounds can also form long-lasting compounds by binding with anthocyanin.

I have proven the positive effects of extended fermentation and soaking which can be observed in the colour intensity and shade values in the long-run. Eight months after production, my experimental wines showed better characteristics than their counterparts made with a 6-day-long fermentation process.
The ‘B’ column of the chart below shows the experimental samples.

SAMPLE	A	B	A	B	A	B
	October 9		January 29		April 24	
Total polyphenol content (mg/l)	1700	1861	1678	1849	1617	1784
Anthocyanin content (mg/l)	286	297	267	268	247	258
Leucoanthocyanin content (mg/l)	2456	3090	2290	2491	2135	2647
Colour intensity	8,92	10,58	6,85	6,75	4,64	5,51
Colour shade	0,48	0,47	0,49	0,52	0,72	0,64
Sulphurous acid content (mg/l) (free/total)	64/82	58/74	46/72	52/84	40/66	48/78

4. 3. Measuring tannin indices to predict quality

Having measured the HCl and gelatine indices of 53 different red wines that participated in the State Wine Competition, I compared the given wine's tannin indices with its result in the competition, as well as with the factors coming from the wine's origin and I have found the following:

- Only three of the first eight wines that were found to be the best in the competition had HCl indices within the 10 to 25 range which international literature considers to be the most favourable. Another two wines were near this value (27 and 28) but most of the wines had values well above 30.
- In terms of gelatine indices, however, most of the wines that were awarded a golden medal had values between 40 and 60 which is the desired value range. The rest of the gold-medal wines are also close to these values. At the same time, the average of the gelatine indices was closer to the lower limit of 40. This data reflects both our country's Northern position, which is less favourable for making red wine, and the influence of differing vintages.
- The wines that were awarded gold and silver medals had very similar gelatine indices. The average for wines with gold medal was 41.71, while this value was 41.60 with the ones awarded silver. Compared to this, the wines awarded the bronze medal had a much harsher tannin taste due to the average index value of 34.73. As for the gelatine indices, carrying out a single-factor variation analysis I found that the probability of significant differences between the groups is 98 per cent. However, this is not the case with the other index.

- In Hungary, vintage has a huge influence on the quality of the black grapes as raw materials, that is, on whether the grapes are ripe in terms of phenols or not. Half of the 17 different wines that had the ideal tannin indices given in international literature (mentioned above) were from the 1999 and year 2000 vintages.
- It can now be stated with confidence that although tannin indices can be a very efficient informative tool for predicting quality and their introduction could be definitely useful, in this country we cannot rely on them as the primary means of determining quality. Under Hungarian circumstances, I suggest fixing the acceptable values of tannin indices as 10 to 30 for the HCl index and 35 to 60 for the gelatine index.

5. NEW SCIENTIFIC ACHIEVEMENTS

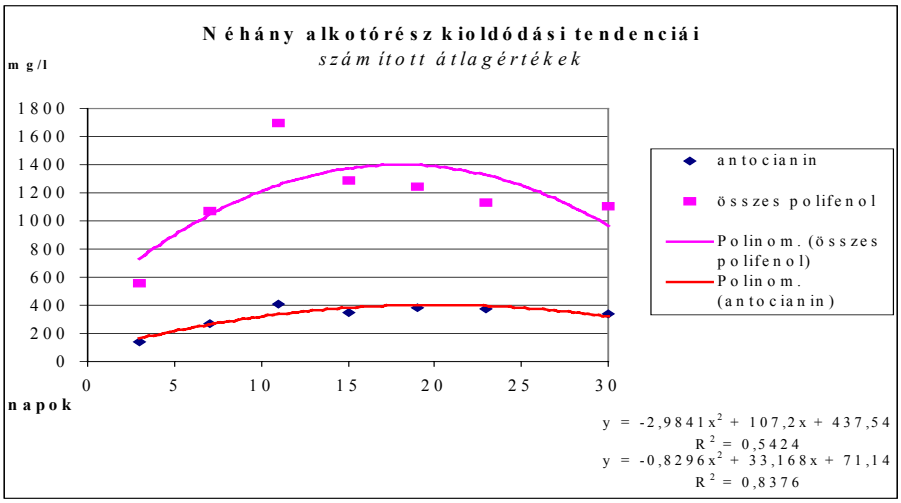
5. 1. Analysis of the examination of extended skin fermentation

The experiments have verified the hypothesis that, in premiere red wine production, extended skin fermentation is an efficient tool for creating stable and long-lasting colouring compounds and smooth tannins on the palate. In wines produced with the method described above, better values of colour intensity and shade can be observed just within seven or eight months after production.

5. 1. 1. Some general characteristics of the process

Through evaluating the results of several experiments, I described the kinetics of typical changes of a few polyphenols during extended maceration. I concluded the following:

- The change of polyphenol content is characterised by a sharply rising value which hits its peak around day 15 or 16 after filling the vat.
- On the contrary, colour intensity (and antocyanin content) values reaches their height only another 5 or 6 days later, around the 20^{th} or 23^{rd} day. These facts can be seen on the diagram below.



Leeching-out tendencies of a few substances

5. 1. 2. Conditions of the application of extended soaking

The aforementioned crucial reactions, in which anthocyanin molecules form long-lasting complexes with tannin compounds, can take place around the 5th and 6th day of the process only in case of such red wines that are made of raw materials well ripe in terms of phenols and contain seed and skin phenols which are polymerised to the desired extent.

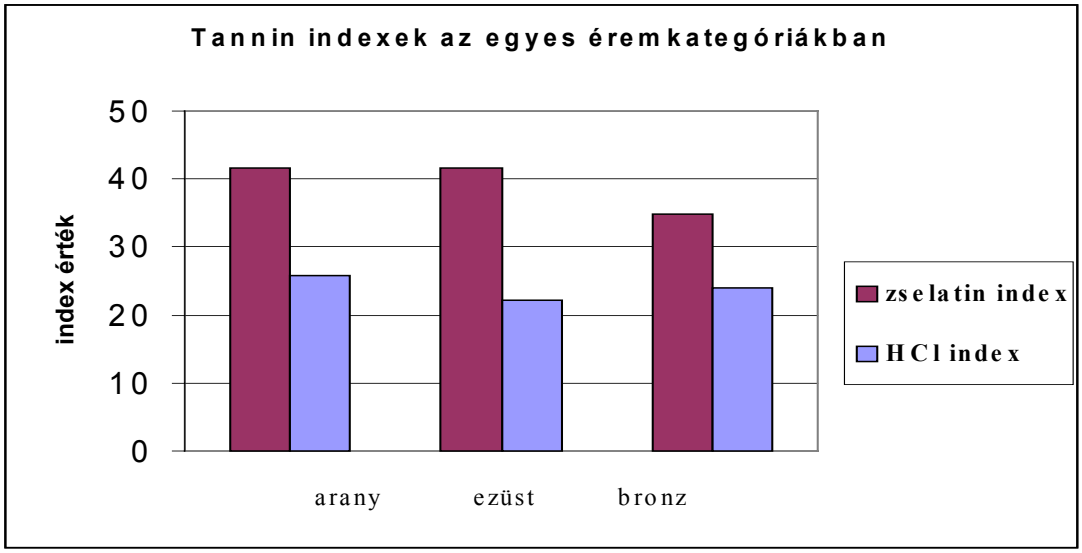
If the raw material lacks active polyphenols (catechines and tannins with low and medium molecule mass) during soaking, the abundance of leucoanthocyanin in the compounds added might give the wine a harsh, bitter taste. Due to the extremes in the effect that vintage has on the red wine in Hungary and to the tannin structure often incapable of reactions, the use of this technology should not be obligatory.

The length of the fermentation and soaking period to be chosen also badly depends on the raw materials. In vintages considered to be average in this country, the phenolic ripeness of most grape varieties requires only a shorter (15 to 22 days) fermentation and soaking period. To make full use of the positive effects of an extended skin fermentation longer than this (that is 20 to 30 days), outstanding raw materials (mostly Cabernet franc or sauvignon) and a vintage above the average are needed.

5. 2. Definition of tannin indices to indicate quality of red wines

Under Hungarian circumstances, the introduction of tannin indices, widely used in other countries, to predict the tannin character of the red wine and to prove its ideal sensory features, can only be recommended with certain restrictions.

- I suggest modifying the limit values cited in literature in a way that the accepted range should be wider. The desired value of the HCl index in Hungarian red wines is between 10 and 30, and the acceptable values of the gelatine index range between 35 and 60.
- These two indices can prove to be more than useful in predicting sensory features. The gelatine indices, which characterise the so much important tannin smoothness of red wines, were very similar in wines awarded the golden and the silver medal (average values of 41.71 and 41.6), but at the same time wines awarded the bronze medal seriously lag behind in this respect with an average value of 34.7. These facts clearly demonstrate that the quality differences that can be felt in a sensory way, can also be expressed by indices.



Tannin indices in different medal categories

6. CONCLUSIONS AND SUGGESTIONS

The effects of the constructional differences in the traditional fermenters based on the principle of pumping over, available to Hungarian wine-growers, are not significant in terms of the quality of the red wine produced. The only but important difference can be seen in the amount of sediment that is formed. The great amount of sediment, which can reach levels as high as 25 or 30 per cent, can be a source of major colour loss. Because of this, certain types can be regarded as weaker.

The pressure impulse red wine fermenters developed in Hungary can compete with their foreign counterparts in all respects. They showed excellent degrees of colour extraction, are easy to handle and are reliably constructed. Due to the method's great extraction efficiency and its ability to reduce oxidation, in a closed system filled with carbon dioxide,

resveratrol concentration in red wines produced in this way (in the case of acceptable raw material) was higher than in the other experimental wines (3.9 g/ml).
However, during the beginning phase of main fermentation, the intensity of mash movement significantly increases the quantity of sediment.
I suggest altering the operation program in a way that a part of the gas formed in the process should be let off on day 2 to 4 after filling the vat, and thus the frequency of watering the cap could be decreased. As a result, extraction could be milder.

I find tannin index measurement useful to be introduced in every day practice as an informative element. However, it cannot be the sole factor determining Hungarian red wine quality. Whether the desired gelatine and HCl indices can be achieved or not depends not only on the given vintage but on the habitat and the grape variety chosen as raw material as well. In this respect, it is recommended to launch a series of systematic measurements in each and every wine-growing region that deals with producing red wine to determine the tannin index values achievable locally. Based on my extensive investigation and taking the Hungarian characteristics into consideration, I suggest defining the acceptable HCl index values to be within the 10 to 30 range, and the gelatine index values to be within the 35 to 60 range in Hungarian red wines.

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