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THE COMPARISON OF PRESSED SEED OILS FEATURES

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The grape seed oils are characteristic by a very high content of substances. However, a lipid oxidation is the fundamental problem of the seed oils quality degradation. The important indicator for determining the specific type's purity, stability and level of oil degradation might be its colour parameter. The aim of this study was to identify the different varieties of oils, to evaluate its development during storage and to identify changes in different pressed seed oils. The CIELAB method and NIR spectroscopy were used during the research. Its main advantages include speed, accuracy and simplicity. The use of NIR seemed to be unsuitable as it could not reliably identify different kinds of grape seed oils. Only three kinds of grape seed oils out of six were identified. Contrary, the colour values obtained, using the CIELAB method, correlated significantly with the maturity of the individual varieties. This method can help to verify the authenticity of the oil. The CIELAB method also enabled colour changes in storage. The results show that after six months of storage, the oil got browner and the L^* value had decreased. After another 6 months, the shift in values was not so significant. Similarly, the values of other parameters had changed. Using the CIELAB method can be recommended for testing of larger sample sizes for future use in the evaluation of the authenticity and quality of seed oils. The CIELAB method will not replace the standard methods but it might be used for pre-selection of tested samples.

Keywords: CIELAB method, colour parameter, grape seed oils, NIR spectroscopy, oil degradation

INTRODUCTION

Oil from grape seeds is commercialized as a food as well as a substance for cosmetic and pharmaceutical applications (Fiori, 2007). Products of selected seed oils are an interesting raw material in the food industry for its dietary value (Nyam et al., 2009). It has a high content of essential fatty acids and tetraphenols (Anastasiadis et al., 2010). The production of these oils in Czech Republic and abroad as well has been growing significantly and it opens up new possibilities for vineyard and winery operations in the application of the residual primary products (Dědina et al., 2013).

Important to mention as well, is higher selling price compared with regular vegetable oils. For each product on the market there must be guarantee of the genuineness and typicality of it, watched by the quality control of foods (Giuffrida et al., 2011). These parameters can influence consumers in their purchase decisions (Ranalli et al., 2005; Aparicio and Aparicio-Ruíz, 2000). An important indicator for determining the variety's purity, stability and oil degradation due to storage is their colour intensity (Criado et al., 2008). Moyano et al. (2008) claim that the colour intensity of oils is among others related to the content of healthy substances, e.g. anthocyanins (Liang et al., 2011).

A variety of methods can be used for evaluation of colour intensity of oils. For example, Moyano et al. (2008) and Vik (2015) claim that the best method for the assessment of colour intensity of olive oil is the CIELAB method, which is fast, inexpensive, and objective. Nyam et al. (2009) had successfully used this method to compare selected seed oils. Moreover, Meléndez-Martínez et al. (2007) claim that this method is suitable for long-term examinations of a large number of analysed oil samples.

In recent years, it is possible to observe a rapid progress in the application of NIR spectroscopy – a method that enables to measure the quality of horticultural products without any destruction of fruit (Bobelyn et al., 2010). NIR spectroscopy is widely used as an alternative method to the so called wet chemistry. It is used for both quantitative and qualitative analyses (Burns and Ciurczak, 2008). Its main advantages are speed, accuracy and simplicity of individual estimations (Liu, 2011). However, when estimating content substances in individual samples, it is necessary to carry out an exact calibration of the NIR spectrometer on the base of a suitable set of calibration standards (matrices). The main disadvantages of this method are the dependence on reference methods and a weak sensitivity to minor components (Büning, 2003).

Both analysis can be selected and used in order to reach more comprehensive and precise results. For the target consumers, the colour intensity of oils is the only evaluable parameter that can be biased by partially subjective approach.

The aim of this paper is to verify the possibility of using colour system method (the CIELAB method) and NIR spectroscopy to identify difference in colour in grape seed oils and cheaper vegetable oils.

MATERIAL AND METHODS

Samples

For the purpose of this paper, six varieties of grape seeds were used. All of them were grown in Czech republic, wine region of Moravia, wine sub-region Velké Pavlovice, town Čejkovice, producer Víno Sýkora s.r.o.. The varieties included Dornfelder (DR), Blaufränkisch (BF), Pálava (PA), Riesling (RR), Pinot Gris (PG), and Zweigelt (ZW). The oil was pressed on the screw press UNO FM 3F by the Farmet Company, Czech Republic. This press model is designed for cold pressing of all oily seeds. The speed of the screw press was at 80 rpm (this speed is commonly used by the producers of oils) and the nozzle of average size 10 mm. From each variety of grapes, 3 oil samples were pressed out, each of them with 1-hour delay. After pressing, the oils were settled by gravity, then filtered and poured into glass jars (volume 500 ml). Oils were not technologically treated or stabilized in any way. The samples were then evaluated using the NIR spectroscopy and CIELAB method. Another evaluation was carried out after six and twelve months of storage in conditions of absence of light at 12 °C.

The NIR measurements

NIR spectra were measured by the instrument Antaris II, using the OMNIC software. This program enables not only to setup suitable parameters of the spectrometer and to control the course of the measuring but also to adjust and analyse measured spectra. Each sample was measured twice, in two batches and the resulting spectra were pooled to obtain an average spectrum. The NIR spectra were measured as an attenuation of light after passing through the sample (transmission measuring) placed in a quartz cell Suprasil, Type 110-QS. The measurements were performed under the following conditions: no. of scans 50, resolution 16 cm^{-1}, spectral range 4 000–10 000 cm^{-1}, gain 1x, InGaAs detector, CaF_2 beamsplitter.

The analysis of measured spectra was performed using the chemometric package TQ Analyst and algorithm Discriminant Analysis. This spectral technique enables to determine the classes that are the most similar to the unknown material. There are several classes in the calibration model and each of them is described by means of a deliberate number of standards (at least two) (Downey, 1996).

CIELAB measurements

Colour changes in the oils were monitored by determining transmittance on the Lovibond RT850i (X-rite Incorporated, USA), in 3 repeated measurements for each variety. The resulting colour was defined as a colour space L^* a^* b^*. Oil samples were measured in plastic cuvettes with 10-mm optical path length. The evaluation was carried out by OnColor™ Premium software application by Lovibond. The differences between the colour changes of the individual samples were expressed through the colour difference ΔE^*ab in colour space L^* a^* b^*, which indicates the size of the difference but not its direction. It is defined by the following equation:

$$\Delta E^*ab = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}, \quad (1)$$

where: ΔL^*, Δa^*, and Δb^* are the differences of these values between the samples just after pressing and after six (twelve) months of storage.

Statistics

A statistical analysis was carried out using the software package 'Statistica 12.0' (StatSoft Inc., USA). Moreover, the standard deviation and Spearman's correlation analysis was used. For all statistical tests, a 95% confidence level was used.

RESULTS AND DISCUSSION

The NIR spectroscopy

Ferrer-Gallego et al. (2010) explored the possibilities of distinguishing different grape varieties from different regions by comparing the flavanols contents of samples, by using the NIR spectroscopy. The results indicated the use in order to distinguish between possible vineyards of origin. Techniques based on spectral data have been applied to determine composition, characterization and detection of adulterations of oil in work of authors Rohman and Man, (2011), Rodríguez-Pulido et al. (2013), Luna et al. (2013), Pizarro et al. (2013). The partial results by using the NIR spectroscopy achieved Yang et al. (2005) as well.

According to Szłyk et al. (2005), the NIR spectroscopy can be applied in quality control of edible oils and fats to monitor their oxidative stability in routine analyses.

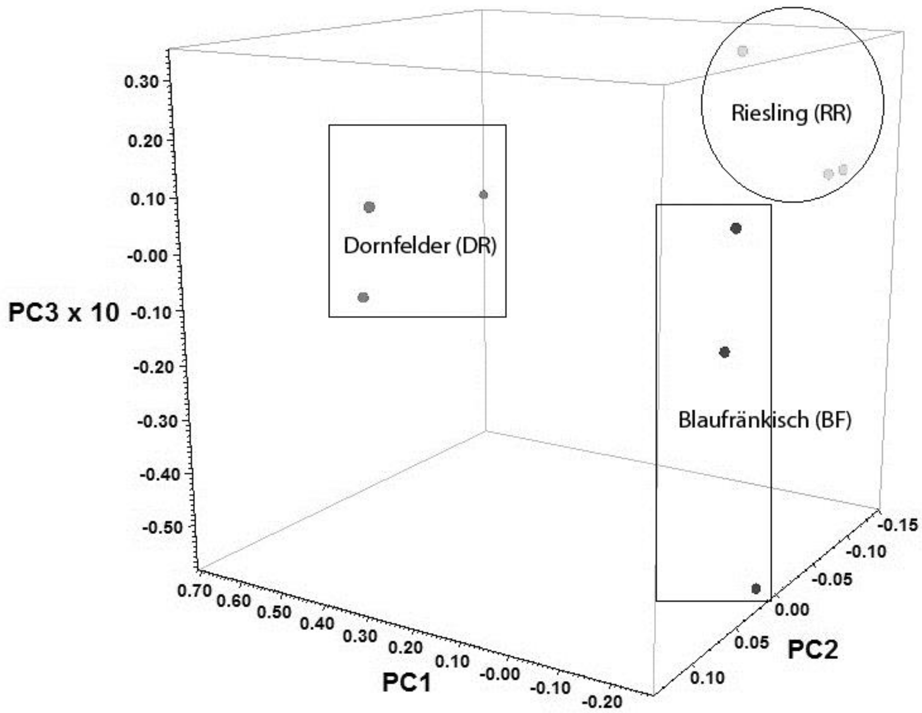

Figure 1. Distribution of Oil Classes measured using Principal component score 3D display using the TQ Analyst software.

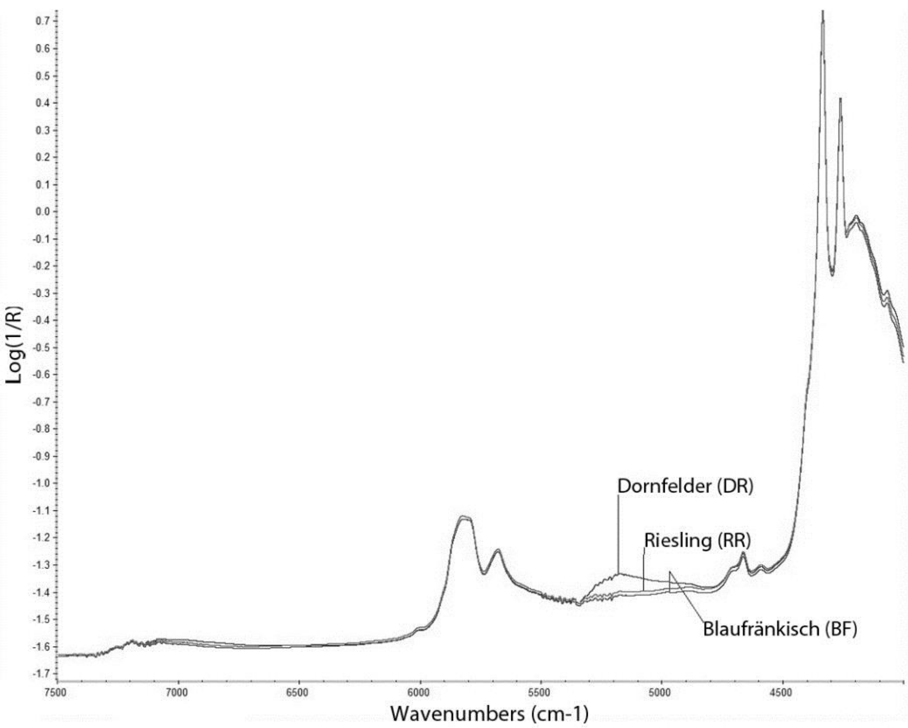

Figure 2. Spectrums Grape Seed Oils measured using the OMNIC software

The spectrums of selected oils were divided into individual clusters by the discriminatory analysis. The differences can be found between them, as it can be seen from Figures 1 and 2, on which the differences between spectra are clearly distinct.

Other varieties could not be identified by the above-mentioned methods due to the minimal spectrum differences between varieties. For this reason, NIR spectroscopy cannot be recommended for use of the purpose of identifying the varietal purity of grape seed oils.

The CIELAB method - Colour assessment

Table 1 shows the average measured values of the six monitored varieties. The measurements did not show significant differences between white and red groups of varieties. However, the obtained results confirm a relatively wide range of hue values (*hab*) and chroma (*C*ab*), which is typical for these oils. The grape seed oils show greater shade balancewhen compared with the results by Moyano et al. (2008) and their virgin olive oil samples in parameters hue (*hab*) and chroma (*C*ab*). In parameter lightness (*L**) reported authors similar results.

The factors hue (*hab*) and chroma (*C*ab*) of the DR and RR varieties were both at the ends of the spectrum. In the lightness factor (*L**) it was again the DR and ZW varieties.

Table 1 Average values of measurements of grape seed oils using the CIELAB method (n = 3).

The order of maturation	Var.	*L**	*L** STD	*a**	*a** STD	*b**	*b** STD	*C**	*C** STD	*h°*	*h°* STD	*ΔE*ab*
First measurement												
1	DR	77.65	0.06	5.55	0.02	111.67	0.00	111.81	0.00	87.15	0.02	–
2	PG	86.87	0.01	-2.75	0.00	79.36	0.00	79.40	0.00	91.99	0.02	–
3	ZW	90.53	0.02	-1.83	0.00	75.81	0.00	75.83	0.00	91.39	0.01	–
4	PA	89.87	0.02	-2.34	0.03	81.96	0.00	82.00	0.00	91.64	0.02	–
5	BF	86.52	0.02	-3.09	0.01	71.56	0.00	71.63	0.00	92.47	0.01	–
6	RR	89.77	0.01	-4.75	0.02	63.52	0.00	63.69	0.00	94.26	0.01	–
Measured after 6 months												
1	DR	44.40	0.01	13.02	0.01	75.60	0.17	76.71	0.17	80.23	0.03	49.61
2	PG	65.89	0.05	10.42	0.02	108.63	0.11	109.13	0.11	84.52	0.01	38.36
3	ZW	77.29	0.02	10.94	0.02	124.86	0.22	125.34	0.22	84.99	0.02	52.39
4	PA	73.15	0.02	10.71	0.01	119.46	0.14	119.94	0.14	84.88	0.01	43.09
5	BF	63.62	0.02	10.36	0.01	104.62	0.18	105.13	0.17	84.35	0.02	42.41
6	RR	71.13	0.00	8.11	0.02	113.15	0.02	113.44	0.02	85.90	0.01	54.55
Measured after 12 months												
1	DR	43.68	0.01	12.82	0.03	74.40	0.06	75.49	0.06	80.22	0.02	50.95
2	PG	64.05	0.02	9.81	0.02	105.50	0.12	105.95	0.12	84.69	0.01	36.90
3	ZW	74.25	0.00	10.63	0.01	120.40	0.10	120.87	0.10	84.96	0.01	49.08
4	PA	72.70	0.01	10.59	0.02	118.75	0.09	119.22	0.09	84.90	0.01	42.61
5	BF	63.91	0.01	10.03	0.00	105.09	0.15	105.57	0.14	84.55	0.01	42.52
6	RR	68.44	0.00	7.67	0.02	108.73	0.20	109.00	0.20	85.97	0.02	51.51

Ripening stage

Table 1 shows the average values of the first measurement after pressing as well as the second and third measurement after six and then twelve months of storage. When comparing the values of the two measurements for each variety (after 6 months and 12 months), the overall darkening of oils and the lower *L** values become obvious.

Moyano et al. (2008) and Criado et al. (2007) presented similar results. Significant changes of value were recorded in the factor *b**, which represents intensifying of yellow colour. This change corresponds with a decrease in lightness (*L**). The DR variety was the only one, where there was a drop in the *b** value from the original 111.67 to 75.60. In combination with the most significant decrease of lightness (*L**), after six months of storage, this variety was the darkest. The measure of colour difference, defined as deviation delta E (*ΔE*) for each oil stored for six months reached relatively high levels. Vik (1995) reported that values greater than three units express colour difference that can be perceived visually by the human eye. The results in Table 1 show that the smallest influence of the storage on the colour was found in the oil from the seeds of PG variety, while the largest changes were observed in the RR variety. The change in colour after another 6 months was not that significant anymore, on the other hand, it was more stable.

Comparison with the results by Moyano et al. (2008) and Criado et al. (2007 and 2008), it is proved that the change in the colour of grape seed oils is more pronounced than in virgin olive oils. The claim of Dufossé et al. (2005), that the change of colour depends on the length of storage, were confirmed.

The maturing of varieties

Table 2. The correlation between the order of maturation lenght and each parameter of CIELAB method (n = 3).

Correlation	Spearman R	t(N-2)
Nr vs. *L**	0.35	1.48
Nr vs. *a**	-0.83*	-5.97*
Nr vs. *b**	-0.82*	-5.69*
Nr vs. *C**	-0.82*	-5.69*
Nr vs. *h°*	0.79*	5.10*

*correlation is significant at the 0.05 level

Another parameter examined was the influence of the maturation on the colour characteristics of the oil. According to our previous research (Mašán, 2017), the greatest influence on the characteristics of oil has the variety of seeds and the date of harvesting. The same conclusion was reached by Ohnishi et al. (1990) and George and Cenkowski (2007).

The results have shown the significant dependence on the variety maturation length and parameters *a**, *b**, *C** a *h*°. The dependence of parameter *L** was low.

CONCLUSION

The obtained results from evaluation of six varieties of grape seed oils confirm a relatively wide range of hue values (*hab*) from 87.15 to 94.26 and chroma (*C*ab*) from 111.81 to 63.69, that is typical for these oils. Measurements did not show significant differences between oils from seeds of white and red groups of varieties. The CIELAB method system gave also good results for differentiation of colour varieties of grape seed oils in dependence on the maturation. The results had shown significant dependence on the level of R = 0,82. When comparing the values of the two measurements for each variety (one after 6 months of storage and one after 12 months of storage), the overall darkening of oils and lowering *L** values become obvious. The measure of colour difference, defined as deviation delta E (ΔE) for each oil stored for six months, reached relatively high levels (numbers between 38.36–54.55). The total darkening of oil after 6 months was in between 14.6% until 42.8% and after 12 months it became from 18.0% until 43.7%.

By using the NIR spectroscopy, only three varieties of grape seed oils had been identified, specifically Dornfelder, Blaufränkisch and Riesling. Therefore, the use of NIR spectroscopy method had proven to be unsuitable as it could not reliably identify various kinds of grape seed oils.

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