INTEREST IN THE VISNIR SPECTROSCOPY FOR GLOBAL CHARACTERISATION OF THE RIPENING OF CABERNET FRANC

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ABSTRACT
In the wine sector, it is allowed that the quality of the wine bases widely on the quality of the grape at the time of the grape harvests. Today, the only evaluation of the technological parameters of classic maturation (sugars and acidity) is not sufficient. The research for new indicators of maturity and new fast and not destructive measures are stakes waited by the professionals. The spectroscopic methods can be an effective alternative in the traditional analyses. In this context, the works led by the laboratory GRAPPE is to approach the maturity of the grape through an approach multicriteria basing on the reproduction of the methods of measure. We suggest presenting in this work, the results obtained to characterize the global quality of the grapes of Cabernet franc by means of the visible/ near infrared method.

INTRODUCTION

Nowadays, grape tasting [1, 2] is more and more used by wine professionals directly at the vineyard and seems to be a good decision tool for harvesting date. Tasting, unlike traditional chemical analyses, allows to evaluate phenolic, aromatic and technologic grape maturity. However, grape tasting is mostly based on personal experience and little work has been carried out to validate this method. Besides, rheological characterisation of grapes seems relevant to follow berry softening during ripening[3]. The modifications of cell wall structure involve changes in mechanical properties. The knowledge of texture indices may thus give some new information to define technological maturity and optimise phenolic extraction. On other fruits such as apples or tomatoes, texture is the main characteristic for determining fruit maturity [4-7]. In addition, spectroscopy in the visible and infrared regions[8] is becoming an attractive analytical technique for measuring quality parameters of food, such as texture. NIR provides in a few seconds a spectra that may be used as a fingerprint thanks to chemometrics tools. The first aim of this study was to evaluate the ability of sensory profiles and compression measurements to follow grape maturity for two vintages. In a second step, regression models (PLSR) were established to attempt prediction of rheological parameters from VisNIR spectra.

MATERIALS AND METHODS

The sample collection was composed of Cabernet Franc grapes collected weekly during September 2005 and 2006 (vintages coded A and B, respectively), and belonging to three parcels in the Loire Valley: Chinon, Bourgueil and Saint-Nicolas de Bourgueil (coded P1, P2, P3, respectively). The reference point of the two vintages is the end of veraison (t3= 3 weeks after veraison end).
Sensory profile: a descriptive sensory analysis of grapes was assessed by 12 and 16 trained subjects (vintage 2005 and 2006, respectively). Descriptive quantitative analyses during grape maturation (4 ripening stages for each vintage) were based on 30 descriptors [9, 10], leading to a complete characterisation of berry, skin and seeds. The judges (or panelists) evaluated the intensity perceived for each descriptor on an unstructured scale anchored with the terms "very weak" and "very intense". All products were systematically duplicated within a session.
Compression of the berries, in equatorial position, was performed with a universal testing machine by using a two-parallel plate. Berries were compressed twice with a 20 % deformation of their height

at 50 mm.min^{-1}. Pressure versus percentage of deformation curves were analysed and eight parameters were studied. Expression of results in pressure made it possible to work independently from fruit diameter.

VisNIR spectra (400 to 2500 nm) were acquired directly on two opposite faces of an intact berry using a Visible-NIR spectrometer. The obtained reflectance spectra, formed by 1050 individual log 1/R values, were corrected using the standard normal variate correction [11].

RESULTS AND DISCUSSION

Evolution of grapes during maturation using sensory analysis and compression

Analyses of variance were assessed for the 30 descriptors studied. Twenty-five descriptors were significant at 5% level according to the vintage, 24 descriptors according to the ripening stages and 13 descriptors according to the parcel type. A principal component analysis (PCA) was performed on the sensory data (Figure 1), which were normalised by vintage to study the relative position of each grape within a vintage. The first axis of the PCA showed that *facility to detach the pedicel, sweetness, jam notes, roasted aroma* and *seed cracking* increased from the stage t3 until the stage t6. On the contrary *touch resistance, elasticity, firmness perception, vegetal notes, sourness* and *astringency of skin* and *seed* decreased during ripening. Hence, grapes evolved regularly between the 4 stages. The second axis of the PCA enabled grapes to be distinguished according to the parcel type. Grapes of parcel 1 were more *resistant*, less *difficult to dilacerate skin*, less *astringent* in the skin and in the seeds than the grapes of the two other parcels.

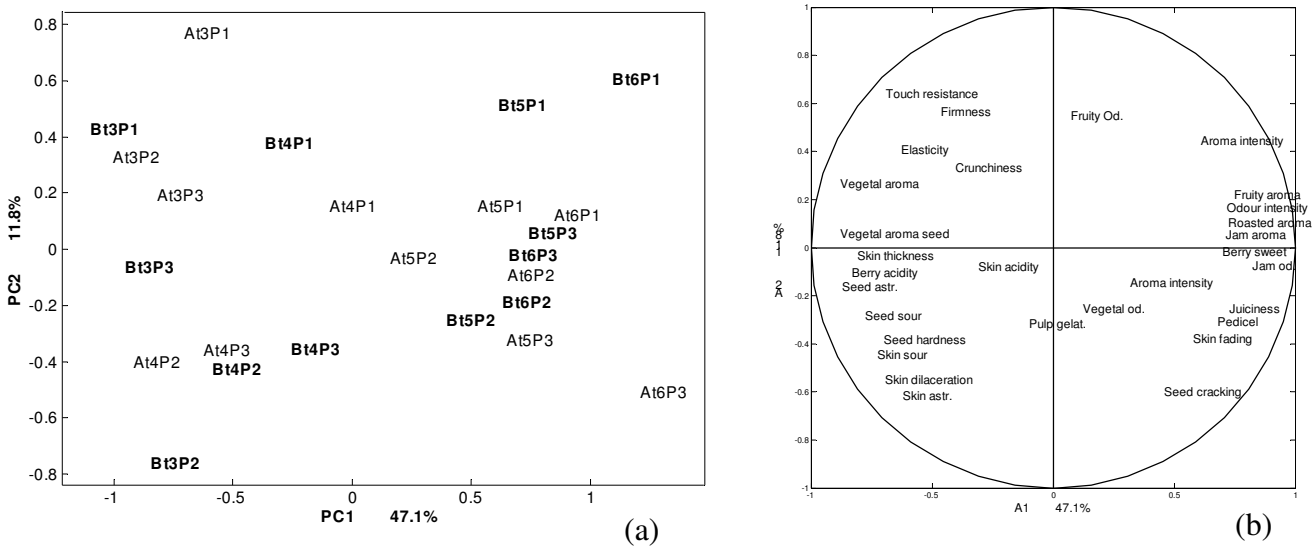

Figure 1: *(a) PCA map on sensory data in the plane defined by principal components 1 and 2; (b) PCA correlation plot of the significant descriptors in the plane defined by principal components 1 and 2*

The ability of compression parameters to differentiate maturity stages and parcel type was investigated by applying FDA with cross validation. If 2 barycentric ellipses of FDA map corresponding to two ripening stages do not overlap, then both stages are different and can be predicted. Figure 2 shows the factorial map obtained by FDA to predict the ripening stages of the two vintages. For each vintage, the five last stages were represented. For vintage 2005, grapes were logically classified according to the first discriminant score contrary to vintage 2006. These results can be connected with the rainfalls. Vintage 2005 were very dry and grapes became softer and softer during ripening contrary to vintage 2006, which were very rainy. The second discriminant score underlined the difference between the parcels. Grapes of parcel 1 were harder than those of the other parcels, as demonstrated in sensory analyses. Rheological properties of grapes at harvest could present some fundamental qualitative information for phenolic extraction.

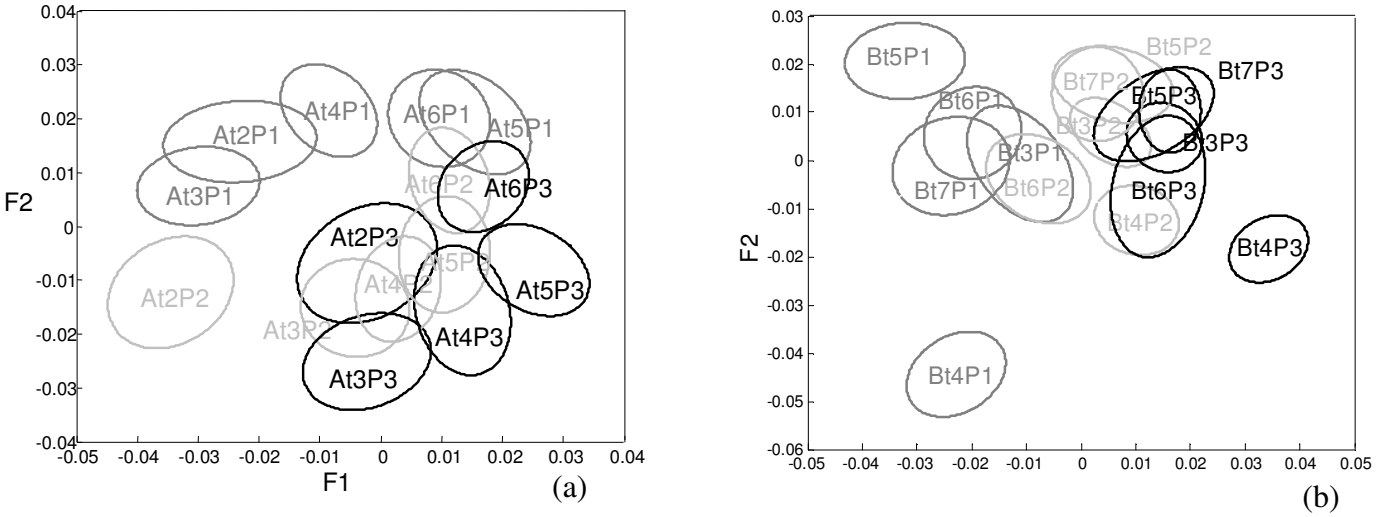

Figure 2: *FDA map on compression data in the plane defined by principal components 1 and 2: (a) 2005 vintage and (b) 2006 vintage. The ellipses present the confidence intervals of the barycenter at a probability threshold of 0.05 for one ripening stage.*

Prediction of compression parameters from VisNIR spectra

In order to evaluate VisNIR spectroscopy as a tool to predict the rheology parameters, PLS regressions with cross validation were performed (Table 1).The prediction models were significant in regression terms for all parameters, except for "Gumminess'". The best parameter, which gave high correlation coefficients and low root mean square errors, is Grad2.

Predicted parameters	LV	R^2_c	R^2_{cv}	RMSEC	RMSECV	Range
Pressure1 (kPa)	7	0.68	0.71	2.68	4.28	62-84
Pressure2 (kPa)	6	0.70	0.89	2.38	3.69	58-77
Grad1	8	0.87	0.87	0.50	0.76	9-15
Grad2	**6**	**0.92**	**0.93**	**1.04**	**1.37**	**17-32**
Wp1 ($kJ.m^{-2}$)	6	0.77	0.95	0.98	0.99	8-15
Wp2 ($kJ.m^{-2}$)	6	0.82	0.82	218	274	2100-3600
Cohesiveness '	6	0.80	0.93	0.0061	0.0077	0.215 -0.275
Gumminess '	7	0.57	0.75	632	1059	15000-21000

LV: number of latent variables introduced in the PLS models
R^2_c: determination coefficient of calibration model
R^2_{cv}: determination coefficient of cross-validation model
RMSEC: Root mean square error of calibration
RMSECV: Root mean square error of cross validation

Table 1: *PLS values of compression parameters prediction.*

CONCLUSION

Sensory profiles provided a consistent description of grape ripening. From one date to another, maturity advance was evaluated at the aromatic, textural, phenolic and technological levels. This method will soon be transferred to the professionals for direct field application. Compression results illustrated berry softening during vintage 2005. Finally, using PLS regression, very good correlations were obtained for prediction of rheology parameters by VisNIR spectra. The near infrared spectroscopy allowed satisfactory estimations of the technological indicators (sugars and acids) for 2005 and 2006. The phenolic indicators were indeed esteemed for the year 2006. Visible/near

infrared spectra allowed to estimate in a very satisfactory way 12 sensory descriptors, representing the technological, phenolic, aromatic and textural maturities.
The visible/near infrared spectroscopy thus allows in a reliable way, a good estimation of the technological indicators, phenolic indicators, and sensory descriptors. This technique turns out very promising for the wine sector.

RESUME

La qualité des fruits est une notion complexe qui revêt plusieurs dimensions. Dans la filière vitivinicole, il est admis que la qualité du vin repose largement sur la qualité du raisin au moment des vendanges. Aujourd'hui, l'évaluation seule des paramètres technologiques de maturation classiques (sucres et acidité) ne sont plus suffisants pour prédire de façon complète et objective, le potentiel œnologique des raisins. La recherche de nouveaux indicateurs de maturité accompagnée si possible de nouvelles mesures rapides et non destructives sont des enjeux attendus par les professionnels de la filière, permettant de lever des verrous technologiques que sont la définition de la maturité optimale du raisin en lien avec l'itinéraire de vinification et le type de vin souhaité. Les méthodes spectroscopiques peuvent être une alternative efficace aux analyses biochimiques traditionnelles. Leur rapidité est un atout important, et peuvent de plus s'appliquer de façon non destructive sur les échantillons.

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