

Spectroscopy and Chemometric Analysis of Brazilian Cabernet Sauvignon Wines

R. P. Maraschin, M. Maraschin*, C. Ianssen

Laboratório de Morfogênese e Bioquímica Vegetal, Departamento de Fitotecnia, Universidade Federal de Santa Catarina. Caixa Postal 476, 88049-900, Florianópolis, SC, Brazil
m2@cca.ufsc.br

M. S. B. Caro

Central de Análises, Departamento de Química, Universidade Federal de Santa Catarina. Florianópolis, SC, Brazil

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Abstract: This study investigated the use of liquid chromatography (LC), ^1H NMR spectroscopy and multivariate analysis as a means to gain more insights as to changes in the qualitative chemical composition of Cabernet Sauvignon (CS) wines originated from Serra Gaúcha, a traditional wine production region in South Brazil. For that, CS wine samples (300 mL - vintages 1985, 1988, and 1990) were collected and liquid chromatographed, and the ethyl acetate fraction was analyzed by nuclear magnetic resonance (^1H NMR - 200 MHz, Bruker AC 200, chemical shifts relative to acetone- d_6 - 2.20 ppm). The chemical shifts data were further statistically analyzed (cluster analysis), using the vintage 1991 as control due to its higher organoleptic properties. The chemometric analysis of ^1H NMR spectra chemical shifts revealed similarity index relative to the control of ca. 24.2%, 55.2%, and 67.7% for the vintages 1985, 1988, and 1990, respectively. Interestingly, the data indicated that the older the vintage, the lower the similarity index found relative. These findings might be explained considering that the wine's chemical composition is expected to change over time so that longer storage periods should lead to more pronounced modifications in the chemical constituents profile of the CS wine samples relative to the control. LC- ^1H NMR off line and multivariate analysis seem to be a suitable methodological approach to evaluate the qualitative changes in the chemical composition of CS red wines over vintages, as well as the effect of the storage period of that beverage.

Over the past 10-15 years meaningful progress have been noticed in nuclear magnetic resonance (NMR), which continues apace. Also, NMR has markedly increased its range of applications in chemical and biological investigations.¹ Modern NMR techniques provide an enormously powerful set of tools to study the chemical composition of complex matrices such as red wines. Additionally, chemometric analysis of ^1H NMR spectral profiles has allowed the identification of beer origin² and make it possible to determine the chemical composition of red wines from the vintages under study.³ These findings led us to investigate the use of liquid chromatography (LC), ^1H NMR spectroscopy and multivariate analysis as a means to gain more insights as to changes of qualitative chemical composition for Cabernet

Sauvignon (CS) wines from the vintages 1985, 1988, and 1990 produced in south Brazil. For that, samples (300mL) were investigated by LC and ^1H NMR – (200 MHz, Bruker AC 200, chemical shifts relative to acetone- d_6 - 2.20 ppm), as previously described.⁴ The chemical shifts data ($\delta = 0.00$ to 8.00 ppm) were statistically analyzed (*cluster analysis*) through NTSys v. 2.0 statistical package, using the vintage 1991 as control for its higher organoleptic properties.⁵ Qualitative differences in terms of chemical composition were found for the Cabernet Sauvignon wines under study, as shown in Table 1. The cluster analysis of ^1H NMR spectra chemical shifts revealed similarity index relative to the control (vintage 1991) of ca. 24.2%, 55.2%, and 67.7% for the vintages 1985, 1988, and 1990, respectively. Interestingly, the data

revealed that the older the vintage, the lower the chemical similarity index found. These findings might be explained considering that the chemical composition of CS wine samples is expected to change over time. Thus, longer storage periods should lead to more pronounced modifications in the chemical constituents profile of CS wines, as herein shown. Besides, since the vintage 1991 is qualitatively superior (internationally awarded) to the other vintages under study, the results agree

with the popular saying “*the older the wine, the better it is*”. In fact, that assumption does not currently have scientific basis. However, multivariate analysis of experimental data obtained through LC-¹H NMR *off line* seems to provide that basis. We have suggested a suitable methodological approach to evaluate the changes in the chemical composition and quality of CS red wines from the vintages under study.

Table 1. Chemical similarity index (%) of Brazilian Cabernet Sauvignon wines, vintages 1985, 1988, and 1990 determined by LC-¹H NMR *off line* and multivariate analysis. For comparative analysis of the chemical shifts ($\delta = 0.00$ to 8.00 ppm) data set of all wine samples, the CS wine vintage 1991 was used as control.

Cabernet Sauvignon vintages	Chemical similarity index (%)
1985	24.2
1988	55.2
1990	67.7

According to our results, our experimental approach seems to be appropriate for quality studies of wine, sensorial analysis, as well as to differentiate wines according to the year of production. Also, the practical possibility of obtaining the rapid characterization of wine chemical composition points to the likely application of LC-¹H NMR *off line* as the method of choice in quality control processes for production of higher quality wines.

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