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RELATIONSHIP BETWEEN RICE TOCOPHEROLS CONTENT AND WATER ABSORPTION IN NEAR INFRARED REGION

T. M.P. Cattaneo[1,*], G. Cortellino[1], S. Barzaghi [2]

[1] Council for Agricultural Research and Economics, CREA-IAA, via Venezian, 26 - 20133 Milan, Italy
[2] Council for Agricultural Research and Economics, CREA-FLC, via A. Lombardo, 11 - 26900 Lodi, Italy

Corresponding author: tiziana.cattaneo@entecra.it

ABSTRACT

Italy accounts for 50% of the European production of rice with about 1,551,272 tons of paddy rice produced on a cultivated area of 235 052 ha. Italian rice, however, shows a shortage of assessments that enable its enhancement, both in terms of quality and content of health components. The purpose of this study was to evaluate the content of tocopherols, in different rice varieties currently grown and to monitor its content with rapid technique to support genetic improvement actions. The influence of tocopherols content on water absorption spectra was also investigated by Aquaphotomics approach to verify its suitability in highlighting water changes in the presence of micro-lipo compounds in biosystems. Spectra of about 60 ground flour samples were collected, in duplicate, in reflectance mode in the range of 4000-10000 cm^{-1} by a NIRFlex N500 spectrometer (Büchi Italia srl, Italy - 4 cm^{-1} resolution; 64 scans). The Total Tocopherols Content (TTC) was measured by HLPC. The calibration models were calculated with PLS regression using PLSToolbox (Eigenvector, WA, USA). The model performances (autoscaling; 4 LV) were: RMSEC=0.836, RMSECV=0.888 and RMSEP=0.699 and an RPD of 3.47. Pre-treated spectra (MSC + 2nd derivative) were grouped in 4 classes related to the TTC. The corresponding Aquagram showed a quite regular decreasing of water absorption bands in the NIR region from 1300 to 1550 nm in correspondence of TTC increasing. The explanation was found considering the different chemical nature of water and tocopherols and their low hydrophilicity.

KEYWORDS: NIR spectroscopy, tocopherols, rice, Aquaphotomics

INTRODUCTION

Over the last thirty years there has been a strong transformation of the concept of food nutrition; in fact, while in the past foods were considered almost exclusively as factors essential for the development and the body growth, it is today recognized them have a key role in determining the quality of life. The concept of functional foods went so developing to improve the health and well-being. Cereals, as basic components of the Mediterranean diet, may play an important role in modern society as raw materials for functional foods, as they contain some regulatory components of important vital functions, such as fiber, antioxidants, phytosterols, etc.. Tocols, commonly known as "Vitamin E", chemically constituted by two groups of compounds (tocotrienols and tocopherols) each of which comprises four homologous (α-, β-,γ-,δ-), are among the most important micronutrients with nutraceutical properties in rice. Italy accounts for 50% of the European production of rice with about 1,551,272 tons of paddy rice produced on a cultivated area of 235 052 ha as reported in the Italian Annual Report on rice production at www.enterisi.it. The domestic consumption of rice, which consumes about a third of the national production, is oriented towards historical rice varieties used for traditional "risotto" (such as Carnaroli, Arborio, Baldo and Roma). At the present, Italian rice varieties show a shortage of assessments that enable their enhancement. NIR spectroscopy applied for evaluating macro- and micro-component in food and biological systems can have a chance as fast and reliable technique for Italian rice characterization both in terms of quality and content of health components. In particular Aquaphotomics[1], a radically new scientific approach, can be useful for that goal. As a new "omics", Aquaphotomics can afford an opportunity to substitute highly expensive "Genomics", "Proteomics" and, especially, "Metabolomics" for better understanding of biological systems. Biotechnology and Food technology, disciplines that meet diverse processes where biological systems and living organisms are

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used, are the areas with major applicability of Aquaphotomics, including qualitative and quantitative analysis for diverse objectives, biomaterials production, and classification of individuals for breeding programs in agricultural sciences [2-4]. Diverse advantages of Aquaphotomics techniques such as speed, minimal sample preparation and its non-destructive character are enhanced when multivariate analysis is applied on the spectra [5-7]; thus, chemical components of complex samples as biological samples can be evaluated by diverse multivariate calibration methods and this is also one of the most important advantage of this technique in the future. In this contest, the aim of this study was firstly to evaluate the content of tocopherols in different Italian rice varieties and to determine their content with NIRS to support genetic improvement actions. The Aquaphotomics concept[1] was then applied to prove, trough the variations in water absorbance spectra, the suitability of this new approach, in characterizing Italian rice varieties on the basis of their tocopherols content.

MATERIALS AND METHODS

About 50 flour samples obtained by grinding were analyzed, in duplicate, in reflectance mode in the range of 4000-10000 cm^{-1} by a NIRFlex N500 spectrometer (Büchi Italia srl, Italy) with a resolution of 4 cm^{-1}, each spectrum was the result of 64 scans. The α-, γ- and δ-tocopherols content (Total Tocopherols Content=TTC) of the same samples was measured by HLPC [8]. The calibration models were calculated using TTC values, after converting the spectra in absorbance. Partial Least Squares (PLS) regression with venetian blind cross validation was applied, using PLSToolbox (Eigenvector, WA, USA). The raw spectra were also pre-treated applying MSC, and grouped in 4 classes related to the TTC (very low: < 0.5 ppm; low: >0.5 <4.0 ppm; high: >4.0 <6.0 ppm; very high: >6.0 <10 ppm: different colours were associated to TTC amount in Figure 2). The corresponding Aquagram [9] was then built.

RESULTS AND DISCUSSION

Table 1 reports the TTC content of the analyzed rice samples, expressed as ppm (mg/kg), obtained by HPLC[8].

Table 1. TTC content in brown and white rice samples.

		TTC (mg/kg)
Brown rice	average	5.047
	min	2.871
	max	6.862
	#	23
White rice	average	0.406
	min	0.112
	max	1.861
	#	27

The model performances for TTC content, obtained after the autoscaling of spectra and using 4 LV, were: RMSEC=0.836, RMSECV=0.888 and RMSEP=0.699. An RPD of 3.47 was found. The value of RPD index, defined as the ratio of the standard error in prediction and the standard deviation of the reference values, allowed the acceptability of TTC calibration for routine analyses[10].

The obtained results showed good prospects in the use of NIR technology in supporting the genetic improvement programs of Italian rice.

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Figure 1 shows the collected spectra in the whole NIR range after MSC pre-treatment and absorbance conversion.

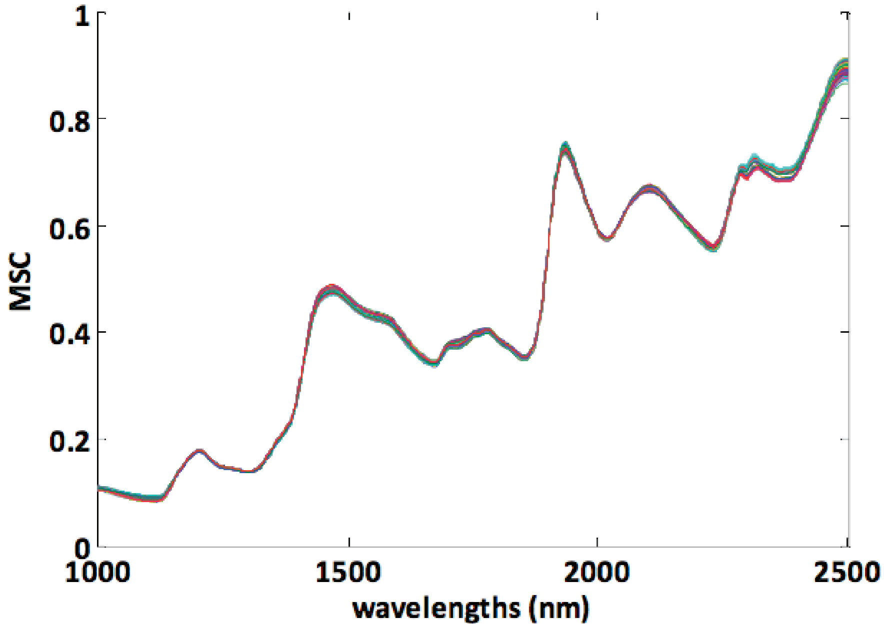

Figure 1. MSC pre-treated spectra of the whole set of Italian rice samples.

This NIR zone was used to study changes in water absorption between 1340 and 1520 nm, applying the Aquaphotomics theory[1]. Distribution of free and bonded water molecules can be highlighted, respectively on the right and left side of the diagram reported in Figure 2, named Aquagram[9].

The spectra of rice samples were divided in four groups on the basis of their TTC content, as reported in "Materials and Methods" section. The graphic representation showed a quite regular decreasing of water absorption bands in the NIR region from 1340 to 1520 nm in correspondence of an increasing in TTC. TTC concentration higher than 4.0 ppm didn't seem to have further significant influence on water NIR response.

Studying the presence of TTC in rice throughout water absorption changes, suggested the possibility to identify rice varieties with high TTC content, with high nutraceutical power for human consumption, in a fast and reliable way. These outcomes could be ascribable to the different chemical nature of water and tocopherols and their hydrophobicity: the higher the TTC content the lower the water absorbance at the same wavelengths

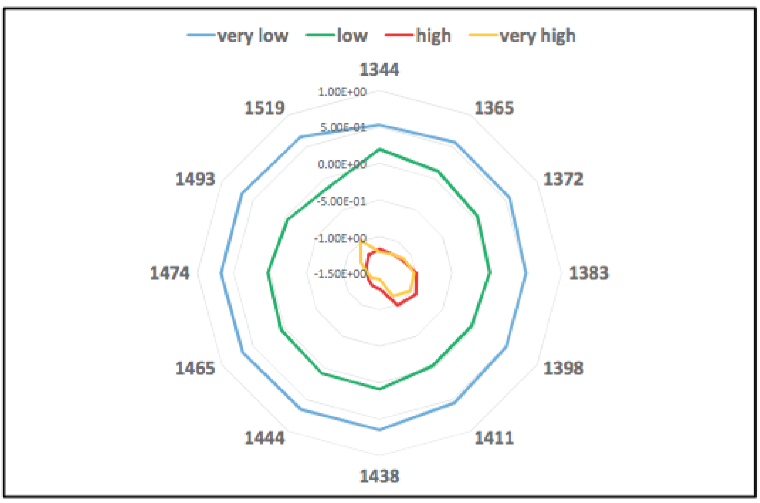

Figure 2. Aquagram showing the relationship between water absorption and TTC content.

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CONCLUSION

The obtained results allowed the improvement of information concerning the content of tocopherols in different rice varieties currently grown in Italy. Despite the low content of tocopherols in rice, NIR spectroscopy has proven suitable to monitor, for routine scope, TTC content so as to suggest its use in supporting actions of genetic improvement.

The Aquaphotomics approach was found to be highly informative when applied for evaluating the presence of nutraceutical micro-compounds, such as total tocopherols in rice flours. The information provided can support, also in this field of applications, the use of Aquaphotomics as suitable tool in explaining and monitoring the evolution of bio-systems through the study of water absorption pattern.

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