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Study on the interaction between gliadins and a coumarin as molecular model system of the gliadins–anthocyanidins complexes

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ABSTRACT

To clarify the conformational changes of gliadins (**Glia**) upon complexation with anthocyanidins (in particular cyanidin, **Cya**), the interaction of **Glia** with a coumarin derivative (3-ethoxycarbonylcoumarin, **3-EcC**), having a benzocondensed structure similar to that of **Cya**, has been investigated by NMR, IR, and Raman spectroscopy under acidic and neutral conditions. Raman spectra showed that both molecules produce a similar effect on the **Glia** structure, i.e. an increase in the α-helix conformation and a decrease in β-sheet and β-turns content. In the presence of both molecules, this effect is more marked; the spectroscopic results showed that both **Cya** and **3-EcC** interact with **Glia** and **3-EcC** favors the complex formation with **Glia**. The results obtained in this study provide new insights into anthocyanidins–**Glia** interactions and may have relevance to human health, in the field of the attempts to modify gluten proteins to decrease allergen immunoreactivity.

1. Introduction

Gliadins (**Glia**) represent the alcohol soluble fraction of gluten, the wheat storage protein. They are a family of prolamines, heterogeneous polypeptides of molecular weight ranging from 30 to 55 kDa. **Glia** are monomeric and disulphide-bonded proteins formed by a non-repetitive domain rich in α-helix structures and heterogeneous repetitive domains rich in β-reverse turns (Tatham & Shewry, 1995). The repetitive domains consist of short repeated sequences, with high content of proline and glutamine. They are classified according to their structure into α-, β-, γ-, and ω-type (Weiser, 2007).

Unfortunately, **Glia** may be strong food allergens. They cause IgE-mediated allergies, such as asthma, atopic dermatitis, urticaria, angioedema, food allergy and anaphylaxis (Bürk, Melms, Schulz, & Dichgans, 2001; Varjonen, Vainio, & Kalimo, 2000), or may aggravate coeliac disease, a genetically-determined gluten-dependent disease (Weiser, 1996). Because gluten plays a significant role in the human diet, many research efforts have been aimed at exploring the mechanisms of its allergenicity. Attempts to modify gluten proteins have appeared useful since they may considerably decrease allergen immunoreactivity.

In a previous study it has been reported that several anthocyanins and anthocyanidins interact with **Glia** in conditions similar to those of the stomach (Mazzaracchio et al., 2011). Anthocyanidins are flavylium salts, the pigments of the vascular plants. They are present in vegetables and flowers and give them brilliant red to violet colours. Anthocyanidins are powerful antioxidant molecules, with noteworthy biological activity, even if they do not have a long-lasting stability in solution (Antal, Garban, & Garban, 2003).

The complexes formed between anthocyanidins and **Glia** appeared quite "stronger" than those between anthocyanins and **Glia** (Mazzaracchio et al., 2011). Among all the tested molecules, cyanidin (**Cya**, see Fig. 2) was found to show the highest affinity for **Glia**. The previous studies on the interaction between anthocyanidins and **Glia** were carried out by using several spectroscopic techniques, such as nuclear magnetic resonance spectroscopy (NMR), UV–visible spectroscopy and infrared spectroscopy. At pH 2.5, anthocyanidins are present mainly in the flavylium form, but a little amount of pseudo-base could be present and this feature complicates the analysis of the interactions with **Glia**. To simplify the study, we have chosen a coumarin derivative, i.e. 3-ethoxycarbonylcoumarin (**3-EcC**, see Fig. 1), as a model since it is present in a sole form and its structure is similar to that of **Cya**. Moreover, **3-EcC** can be easily synthesized. **3-EcC** and **Cya** have a similar benzocondensed structure, although **Cya** is a cationic species,

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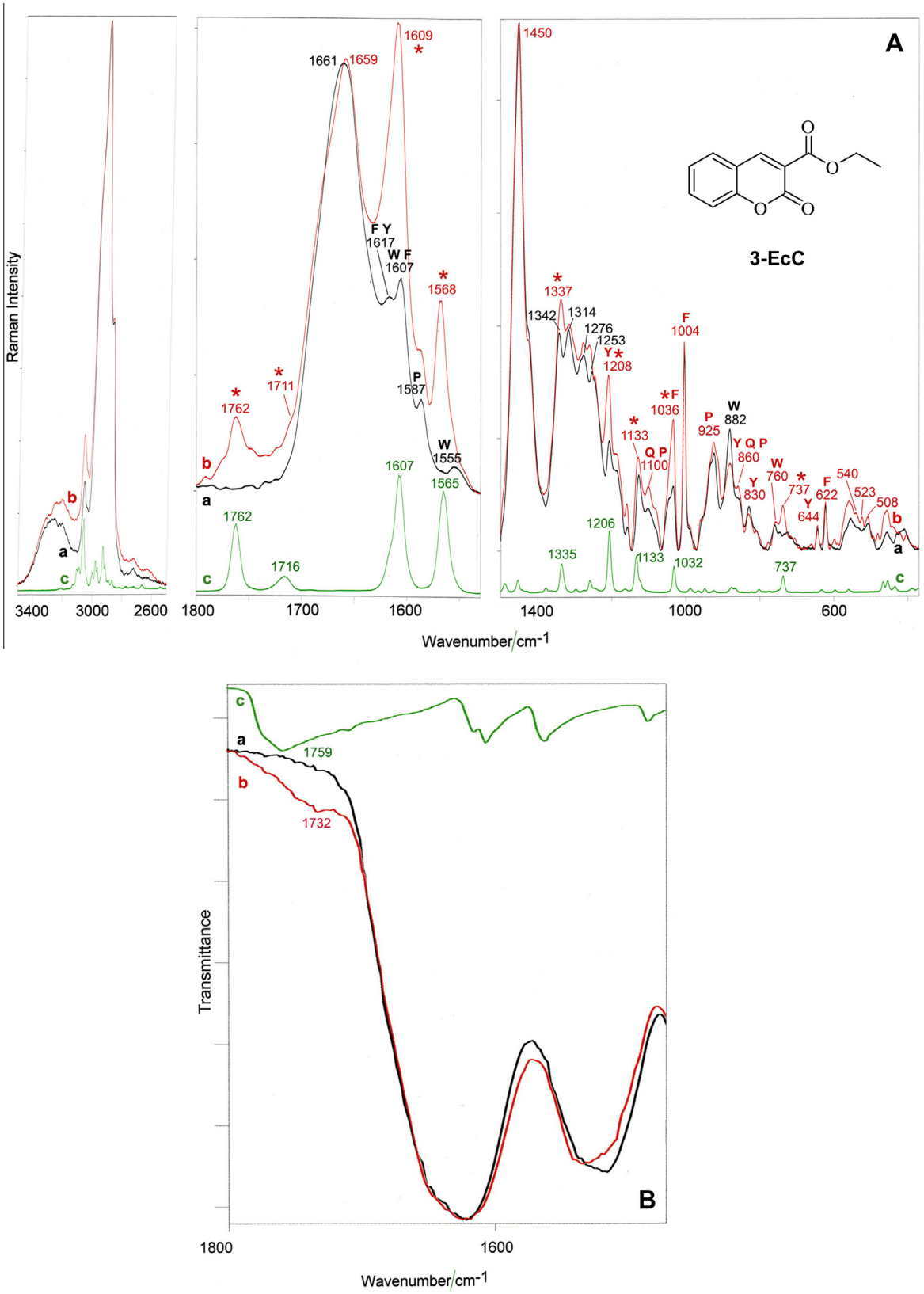

Fig. 1. Raman (A) and IR (B) spectra of lyophilized **Glia** (a) in the presence of **3-EcC** (b) at neutral pH; the spectra of **3-EcC** (c) are reported for comparison. The bands prevalently due to phenylalanine (F), tyrosine (Y), tryptophan (W), glutamine (Q) and proline (P) are indicated. The bands due to the bonded **3-EcC** are marked with an asterisk.