Chapter Eleven

ASTRINGENCY AND POLYPHENOL PROTEIN INTERACTIONS

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INTRODUCTION

The earliest of Man’s uses of plant materials rich in polyphenolic metabolites was in the conversion of animal hides to leather, and archaeological records relate to this operation in Mediterranean regions around 1500 BC. Whilst a complete scientific understanding of the traditional tanner’s art remains, at best, incomplete,1 different light has been thrown on facets of this question from other sources. Thus, polyphenol interactions with proteins (and other biological molecules and macromolecules) underlie a wide range of other apparently unrelated properties of plant materials. These include: astringency; ecology and chemical

defense in plants; foodstuffs, nutrition and beverages; fruit and floral pigmentation; natural glues, varnishes, and exoskeletons; and the influence of diet and the application of herbal medicines in the treatment of certain pathological conditions.²

PROTEIN: POLYPHENOL COMPLEXATION

The interaction between polyphenols and other molecules may be either reversible or irreversible (Fig. 1). Irreversible complexation, which frequently takes place autocatalytically under the agency of oxygen or in the presence of enzymes (polyphenoloxidases), creates new covalent bonds between the polyphenol and the other substrate(s) and may lead to the formation of clearly defined new products (e.g. as in the manufacture of black tea). Conversely, reversible complexation (Fig. 1) is mediated by the gamut of non-covalent forces (hydrophobic effects, hydrogen bonding, solvation, desolvation) which fall under the umbrella description of molecular recognition. Reversible polyphenol: protein interactions, which are believed to underlie the property of astringency, may be studied in solution or by an investigation of the precipitation processes which ultimately ensue following extensive complexation. It has been generally assumed, although rarely proven, that there is a straightforward relationship between the results from these two types of study.

Scientific studies of the reversible association of polyphenols with proteins have a history going back almost 200 years to Sir Humphry Davy³ in 1803. However, until such time as structurally defined plant polyphenols became available, they were poorly understood. Various quantitative investigations, completed over the past 25 years, have given considerable insights into the area; “structure—activity” relationships have been delineated and mechanisms proposed. Although

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Protein (H₂O)ₐ + Polyphenol (H₂O)ₖ

[ Protein (H₂O)ₖ : Polyphenol (H₂O)ₖ ]
[ soluble complexes ]

New Products

[ Protein : Polyphenol ] (H₂O)ₘ
[ insoluble complexes ]
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Figure 1. Reversible and irreversible protein: polyphenol complexation.