Chemical studies on plant polyphenols and black tea pigments

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Plant polyphenols are bioactive secondary metabolites widely distributed in plant kingdom. Recent biological studies proved that the polyphenols in foods and medicinal plants have many health benefits. The polyphenols are also interesting research targets in the research fields of chemical ecology and plant physiology. Previously we revealed the chemical mechanisms of insolubilization of persimmon tannins in the fruits, and the dramatic change of tannin metabolism at the border of heartwood and sapwood in Chestnut tree are also demonstrated. The results indicated that the tannin metabolism is dynamically changed at some plant growing stages. In addition, enzymatic oxidation of polyphenols is observed in many plants, especially when the plants were mechanically damaged. Black tea polyphenols are produced by enzymatic oxidation of tea catechins during the mechanical crushing and subsequent fermentation process in black tea production. Despite its importance as food constituents, the chemistry of the polyphenols remained ambiguous. Our *in vitro* fermentation studies using purified catechins as substrates revealed some characteristic chemical mechanisms. The reaction was initiated by formation of *ortho*-quinones of the tea catechins followed by quinone-phenol coupling reactions. The cascade type reactions, including decarboxylation, redox dismutation, intramolecular ether formation, and further coupling with another quinone, generated a complex mixture of oxidation products. The reactions are affected by the structures of the catechin B-rings, concentration ratio of pyrogallol- and catechol-type catechins, configuration at the C-ring, and presence of galloyl groups at C-ring. Our study revealed initial stage of catechin oxidation during black tea production; however, the thearubigins, uncharacterized oxidation products first designated in 1950's, still remained to be clarified.