## *Reactions of Plant Proteins with Oxidation Products of Polyphenols*

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Plants contain *o*-diphenols, liable to enzymic or spontaneous oxidation to *o*-quinones or semiquinone-radicals. Besides undergoing oxidative polymerization, these may react with thiol, amino, thio-ether, indole and perhaps other functional groups of proteins. Since nutritionally important cyst(e)ine, lysine, methionine and tryptophan residues carry such groups, damage to nutritive quality seems likely, a possibility so far largely neglected by nutritionists. In protein-rich supplements to basal cereal diets for pigs and poultry, lysine is critical; quinone reactions can damage it in leaf-protein concentrates and oilseeds. My colleague R. Davies is studying reactions of *o*-quinones with aliphatic amines; R. Davies, W. M. Laird and I are hydrogenating model compounds and proteins over rhodium in 70% (*v*/*v*) aqueous acetic acid, for stabilizing lysine-quinone adducts as cyclohexane derivatives.

Oxidative polymerization of quinones seems important in the formation of soil organic matter; simultaneous coupling to proteins provides a "bank" of slowly mineralizing N and S. $^{14}C$-Dating shows the protein moiety to be degraded faster than the aromatic "core"; lysine residues are important for attaching "protein" to "core". Such reactions may begin in senescent subaerial parts of plants before they enter the soil. A major evolutionary determinant of massive polyphenol accumulation by plants could be the *post mortem* establishment of a humus favourable for growth of later generations.

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## *The Metabolism of N-containing Fungicides in Plants*

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Foreign compounds in plants are metabolized by a variety of processes including oxidation, hydrolysis, dealkylation and conjugation with sugars, amino acids and other plant constituents. Each of these processes is illustrated by reference to the pattern of metabolism of fungicides. Dimethyldithiocarbamate salts are metabolized in plants to three fungicidally active compounds, namely a glucoside, an L-alanine conjugate and an unidentified material. An inactive compound thiozolidine-2-thion-4-carboxylic acid is also formed but by a non-biological process. The related ethylene *bis*-dithiocarbamates give rise to ethylenethiourea which because of its toxicity has given rise to some concern.

The metabolism of the systemic pyrimidine fungicides, ethirimol and dimethirimol has been studied in detail. Dealkylation, conjugation, hydroxylation and ring cleavage are all important in producing a wide range of metabolites and degradation products. The conversion of a range of broad spectrum fungicides such as benomyl and thiophanate-methyl to a common fungicidally active metabolite, methyl benzimidazole carbamate is discussed. This metabolite is also further metabolized.

The anilide fungicides, carboxin and 2,3-dimethyl-3-furancarboxylic acid anilide are metabolized by oxidation, the former to a sulphoxide and sulphone and the latter to hydroxymethyl derivatives. There is no evidence for hydrolysis of the amide linkage in these compounds. The metabolism of dodecylguanidine, triforine and other newer fungicides is mentioned briefly.

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# SHORT PAPERS

## *The Occurrence of* D-*alanyl*-D-*alanine in* Phalaris tuberosa—(*Gramineae*)

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D-Alanine is one of the few D-isomers of protein amino acids known to be present in plant tissues. It probably occurs in the free state in corn roots [1] and it has been isolated in conjugated form as *N*-malonyl-D-alanine and as γ-L-glutamyl-D-alanine [3] from pea seedlings.

We have now found that the dipeptide, D-alanyl-D-alanine, occurs consistently in the pasture grass *Phalaris tuberosa* L, growing in South Australia, its content being *ca* 0·02% of the dry wt of the grass. The dipeptide has a characteristic electrophoretic mobility on paper impregnated with borate buffer (pH 9·2) on which it separates cleanly from all common amino acids present in the extracts. Its preparative isolation was achieved by electrophoresis on cellulose thin layers using dilute acetic acid as the electrolyte. The sample was hydrolyzed and yielded α-alanine as the only detectable amino acid, and this was shown to be of D-configuration by enzymic assay.

D-Alanyl-D-alanine is known to be the terminal dipeptide in the peptide-glycan precursor of bacterial cell-wall material [4] and it has been isolated as a freely-occurring dipeptide in *Streptococcus faecalis* [5]; but as far as we know, its occurrence in plant material has not been reported previously.

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## *Experiments with Stereospecifically-labelled Amino Acids: Convenient Synthesis of* (2SR, 3SR)-[3-$^2H_1$]*Phenylalanine*

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Amino acids, stereospecifically-labelled at the β-centre, have been used to provide valuable information on the stereochemistry and mechanism of action of enzymes (e.g. phenylalanine