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APPENDIX

Allelopathy.

The term allelopathy was introduced by the Austrian botanist Hans Molisch (1937) to cover biochemical interactions, both deleterious and advantageous, between all types of plant and interactions involving microorganisms. Now the term is usually limitted to detrimental effects that one species of higher plant, the donor, has on another, the recipient, especially those involving gross reduction in the germination efficiency, growth, and development of the latter (Rivora, 1969; Tukey, 1969) and this restriction is kept here. In all cases studied, allelopathic effects have been shown to be due to the release from the donor of phytotoxic secondary metabolites (allelochemicals) that have an adverse effect on any recipient species growing in the vicinity (Tukey, 1969). Allelopathy is thus separated from competition which involves the removal or reduction of some factor from the environment that is required by some other plant sharing the habitat. Factors that may be reduced include water, food, minerals, and light. Thus, allelopathic interactions are only one aspect of interference between plants and the struggle for moisture, light or nutrients are of equal importance (Muller & Chou, 1972).

Biosynthesis of Phenolic Acids.

Shikimic acid, a name derived from shikimi-no-ki which is the Japanese name for the *Illicium religiosum* plant (Herbert, 1981), is a key intermediate in the biosynthesis of the amino acids;

L-phenylalanine, L-tyrosine and L-tryptophan, in plants and microorganisms (animals cannot carry out de novo synthesis using this pathway). These three aromatic amino acids are individually important precursors for numerous metabolites, including phenolic acids.

Phenolic acids and their derivatives may be classified according to their chemical structure into cinnamic and benzoic acid derivatives.

1. Biosynthesis of Cinnamic Acid and Its Derivatives in Higher Plants.

An important reaction in formation of cinnamic acid and Their derivatives is the formation of trans-cinnamic acid. The enzyme L-phenylalanine lyase catalyzes the deamination of phenylalanine, to give trans-cinnamate, an important precursor of the remaining hydroxycinnamic acids. Four hydroxycinnamic acids are common, in fact almost ubiquitous, in plant; p-coumaric, caffeic. ferulic and sinapic acids. p-Coumarate is formed readily in a wide variety of species by addition of one oxygen atom from molecular oxygen gas and an hydrogen atom from NADPH to the para position of cinnamic acid. Subsequent addition of another hydroxyl group adjacent to the hydroxyl group of p-coumarate by a similar reaction forms caffeic acid. Addition of a methyl group from S-adenosyl methionine to an hydroxyl group of caffeic acid results in ferulic acid. Sinapic acids usually occur in plant cells in combine forms as esters (at -COOH) or glycosides (at phenolic - OH).

Caffeic acid which is one of the most widespread of all plant phenolic compounds frequently occurs regularly as chlorogenic acid in which the alcohol portion is supplied by quinic acid (Robinson, 1963).

2. Biosynthesis of Benzoic Acid and Its Derivatives in Higher Plants.

From the cinnamic acid and its derivatives as mentioned above, β-oxidation and truncation of the side-chains yields a series of benzoic acids. Among these are the acids benzoic, salicylic, p-hydroxybenzoic, protocatechuic, vanillic, and syringic acids. Like cinnamic acid and its derivatives, benzoic acid and hydroxylated benzoic acids usually occur as esters or glycosides (Geissman & Crout, 1969). Biosynthesis of cinnamic, hydroxycinnamic, benzoic and hydroxybenzoic acids is shown in Figure 2. Biosynthesis of gallic acid, another hydroxybenzoic acid, remains something of an enigma (Haslam, 1979).

Biosynthesis of Monoterpenes.

Monoterpenes are made up essentially of dimers of isoprene unit :

$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH = CH_2$$

However, isoprene itself is not the in vivo precursor. Instead, the basic building block actually involved is isopentenyl pyrophosphate (C_5) formed from three molecules of acetyl-CoA via mevalonic acid. By means of an isomerase, isopentenyl pyrophosphate exists in living cells in equilibrium with the isomeric dimethylallyl

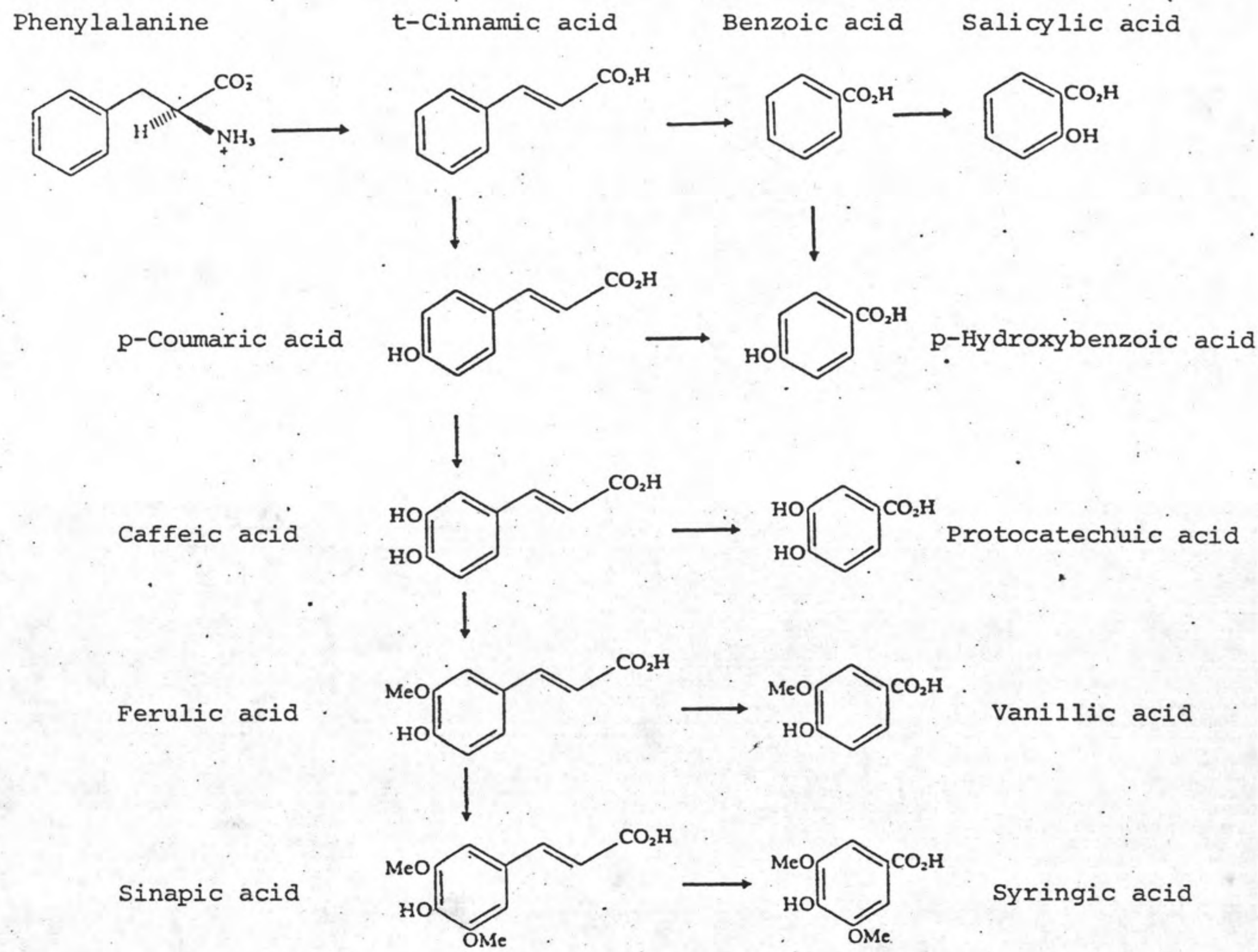

Figure 2 Biosynthesis of cinnamic, hydroxycinnamic, benzoic, and hydroxybenzoic acids (adapted from Haslam, 1979).

pyrophosphate. In biosynthesis, these two compounds are linked together to give geranyl pyrophosphate (C_{10}), the key intermediate in monoterpene formation. Fig. 3 shows the synthesis of terpene precursors isopentenyl pyrophosphate and dimethylallyl pyrophosphate.

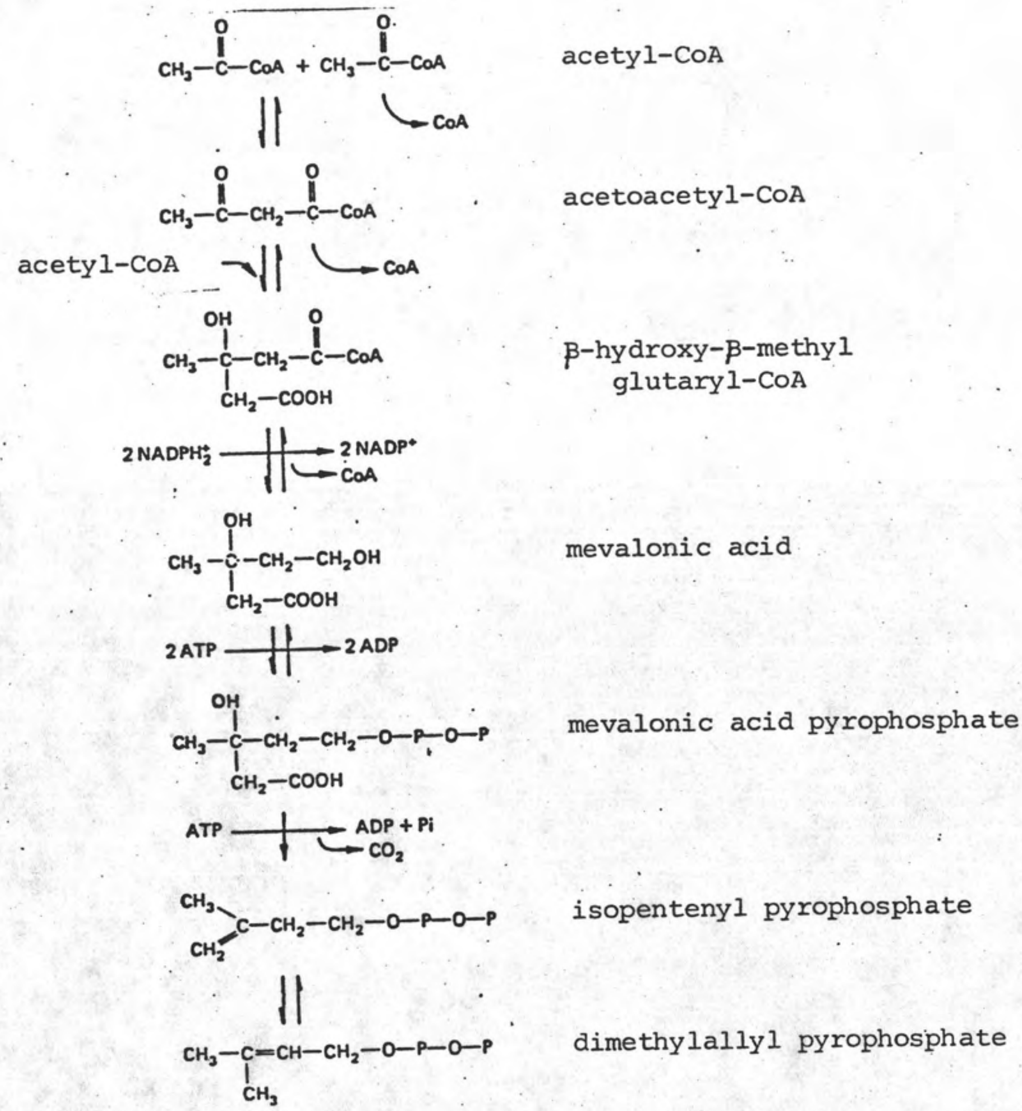

Figure 3 Synthesis of terpene precursors isopentenyl pyrophosphate and dimethylallyl pyrophosphate (from Bidwell, 1979).

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