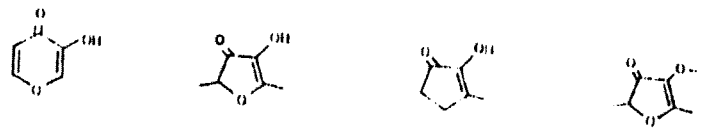
XVII. XVIII. XIX. XX.

Reaction schemes have been presented for the formation of these heterocyclics (Tressl *et al.* 1985a). As is shown in Figure 3.6A, pyruvaldehyde and L-proline form an iminium carboxylate intermediate which is transformed by decarboxylation to a reactive ylide or iminium ion. These two intermediates then may undergo hydration to yield 1-pyrroline and acetol or pyrrolidine and pyruvaldehyde. Reduction would yield 1-acetonyl pyrrolidine.

The pyrrolizines may arise from proline/dicarbonyl reactions as shown in Fig. 3.6B. This involves aldol type reactions via the iminium ion intermediate. Further reaction by Michael addition or aldol condensation and dehydration would yield the pyrrolizines.

f. Furanones and Pyranones

The furanones and pyranones are oxygen containing heterocyclic compounds associated with both caramelized and NEB flavors. The odor characters most common to this group of compounds would be caramellike, sweet, fruity, butterscotch, nutty or burnt. They predominate both in proportion and absolute amount in condensates of carbohydrates that are subjected to browning reactions (Ohloff and Flament 1979). It is of interest that about 70 furan derivatives have been identified in coffee aroma, 25 in the volatiles of bread and 37 in caramel (Ohloff and Flament 1979).



XXI. XXII. XXIII. XXIV.

The caramel character is associated with a planar, contiguous C alkyl enol carbonyl group (alkyl C C(OH) C:O) in the molecule (Pittet *et al.* 1970). Maltol (XXI) was one of the first compounds in this class to be identified in foods. Ethyl maltol (2 ethyl 3 hydroxy 4(*1H*) pyranone) also has a caramel odor but is approximately four to six times stronger in flavor strength than maltol. Furaneol (4-hydroxy 2,5 dimethyl

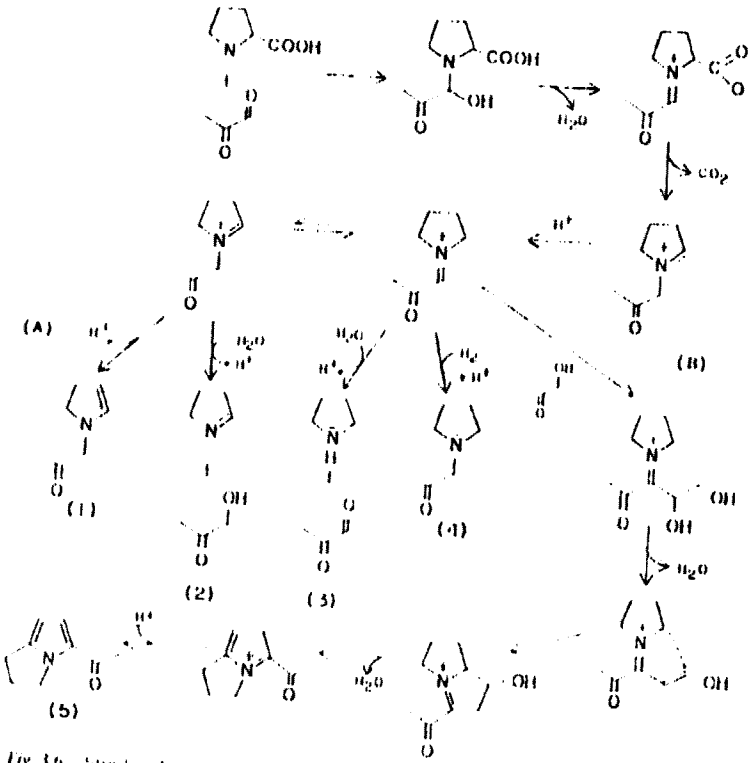


Fig. 3.6. Strecker degradation of proline to yield (1) 1-acetonyl-2-pyrroline; (2) 1-pyrroline, (3) pyrrolidine, (4) 1-acetonyl pyrrolidine; (5) 5-acetyl-2,3-dihydro-1*H*-pyrrolizine (Tressl *et al.* 1985a)

3(2*H*)furanone, XXII) is the tradename of a compound used extensively in the flavor industry and, like maltol and ethyl maltol, is a flavor enhancer for sweet products. Furaneol itself has a "burnt pineapple" odor.

The five carbon analogs of maltol (XXIII) and furaneol possess odor properties similar to their oxygen containing counterparts. Cyclotene (tradename for compound XXIII) has a very characteristic sweet maple character. The related compound, 3-ethyl-2-hydroxy-2-cyclopenten-1-one, also finds extensive use in the flavor industry for similar applications (caramel, nut, maple and butterscotch flavorings).

Compounds of this class that do not meet the structural requirements for being caramel in character may have quite different sensory prop

erties. For example, 4 methoxy 2,5 dimethyl 3(2*H*) furanone (XXIV) has an odor similar to sherry. The *n*-butyl ether version of this furanone has a jasminelike odor.

This group of compounds does not contain nitrogen. Therefore, the mechanism of formation generally involves the cyclization of nonnitrogen containing browning intermediates (Fig. 3.7). These intermediates may be products of major browning pathways involving sugar dehydration or the Strecker degradation (Reynolds 1970, Hodge *et al.* 1972).

g. Sulfur Heterocyclics

Several different types of heterocyclic compounds containing sulfur are produced via NEB. These include thiophenes, dithioles, dithianes, dithiins, trithiolanes, trithianes, tetrathianes, thiazoles, thiazolines and

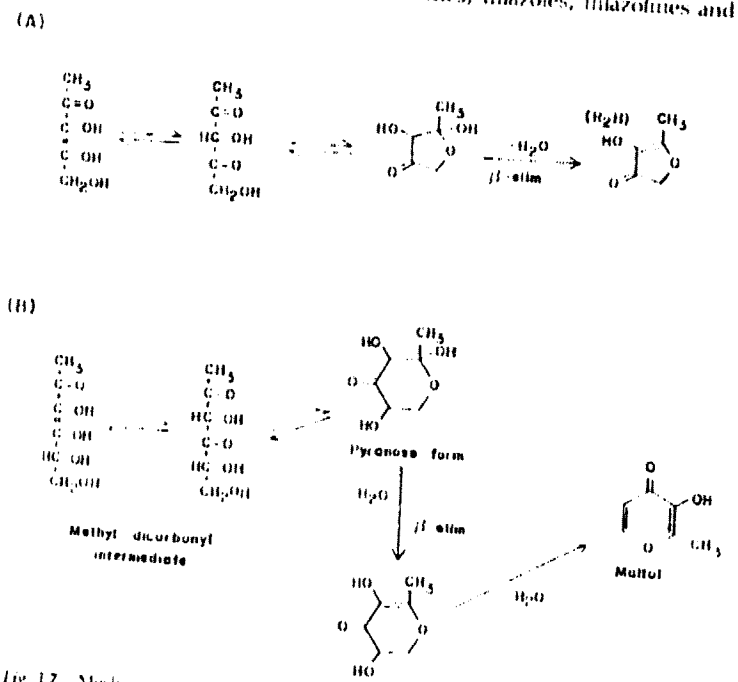
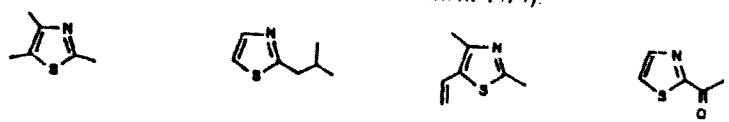


Fig. 3.7. Mechanisms proposed for the formation of furans and furanones. (A) Formation of a dihydrofuranone. (B) Formation of maltol. *Hodge et al. 1972*

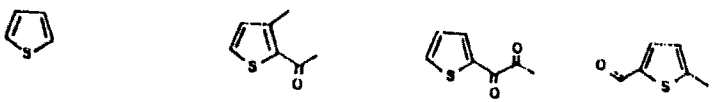
thiazolidines. The major heterocyclic sulfur compounds produced via NEB are thiazoles and thiophenes.

Thiazoles and pyrazines have somewhat similar sensory properties. Pittet and Hruza (1974) and Ho and Jim (1985) have reported that the alkylthiazoles give green, nutty, roasted, vegetable or meaty notes. Trimethyl thiazole (XXV) is reported to have a cocoa, nutty character. The 2-isobutyl thiazole (XXVI) is one of the best known as having the strong green odor of tomato leaf. This compound is considered to be important to tomato flavor. The 2,4 dimethyl 5 vinyl thiazole (XXVII) has a nutlike odor. The 2 acetyl thiazole (XXVIII) is characterized as having a nutty, cereal and popcorn flavor (Ohloff and Flament 1979).



XXV. XXVI. XXVII. XXVIII.

Thiophenes have only recently been identified as food flavors. With the exception of cranberries, thiophenes have only been found in cooked or roasted food products (Ohloff and Flament 1979). The sensory properties of many of the thiophenes have been summarized by Ohloff and Flament (1979). Thiophene (XXIX) has a pungent character while 2,4 dimethyl thiophene is well known for its importance to the flavor of fried onions. The 2 acetyl 3-methyl thiophene (XXX) has a honeylike sensory quality at 0.25 g/100 L concentration but is nutty and starchy at 0.11 g/100 L concentration. Praline and woody notes are characteristic of compound XXXI. The 5 methyl thiophene-2 carboxaldehyde (XXXII) has a burnt coffee note (Shibamoto 1983).



XXIX. XXX. XXXI. XXXII.

The sensory properties of some of the other sulfur containing heterocyclic compounds are presented in Table 3.2. These compounds, like the thiazoles and thiophenes, typically are formed via the reaction of sulfur containing amino acids with intermediates of the browning reaction. An alternative mechanism involves the initial formation of H_2S from the sulfur-containing amino acids and then the reaction of the H_2S with browning intermediates (Sakaguchi and Shibamoto 1978). Some of