

# Thermal Degradation of Carbohydrates

## A Review

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Studies on the effect of heat on carbohydrates are reviewed. Attention is centered on thermal degradation of mono-, di-, and polysaccharides in dry systems. Mechanisms leading to the formation of

both volatile and nonvolatile products are discussed. The possible relation between products of thermal degradation of simple carbohydrates and compounds identified in several foodstuffs is pointed out.

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In the course of manufacture and preparation for consumption many foods may be subjected to rather intensive heat treatments. The temperature of exposure may be well over 200°C. in the roasting of coffee and not infrequently in the neighborhood of 150°C. for the roasting, baking, or frying of other foods. Such heat treatments lead to flavor change or development and consequently are of great interest to the food chemist.

The compounds arising from the pyrolysis of the coffee bean provide a good illustration of the complexity of such pyrolytic reactions. In his comprehensive review of coffee flavor, Gianturco (1967) tabulated the results of recent research on this product and listed 103 identified volatile products. More recently Gautschi and his coworkers (1967) identified 20 additional compounds. Maillard reactions (1912) and Strecker degradations (Schonberg and Moubacher, 1952) have usually been considered the most important flavor-producing reactions in such heat processes.

Somewhat simpler systems have been employed to study the effects of heat on carbohydrates. The more recent studies of Greenwood *et al.* (1961) and Bryce and Greenwood (1963) are of particular interest, since they demonstrated that the major volatile products from the pyrolysis of starch, cellulose, sucrose, maltose, and glucose were essentially identical.

Their pyrolyses were carried out at 300°C. for 15 minutes under nitrogen. The identified products were carbon dioxide, acetal, propanal, pentanal, 2-butanone, 2-pentanone, furan, 2-methylfuran, and 2,5-dimethylfuran. More recently, Heyns and Klier (1968) reported that D-erythrose, D-xylose, D-arabinose, L-sorbose, D-glucurono-6,3-lactone, cellobiose, lactose, raffinose, amylose, and amylopectin also yield the same volatile degradation products. Qua and Fagerson (1964) tentatively identified furfural, dihydroxyacetone, acetal, glycolaldehyde, and 5-(hydroxymethyl)-2-furaldehyde (HMF), and noted the presence of six additional volatile products from glucose heated at 250°C. for 1 minute in air. Sugisawa (1966) studied the volatile decomposition products arising from glucose heated at 150°C. for 2.5 hours under nitrogen and found in addition to compounds reported by Greenwood *et al.* (1961) and Bryce and Greenwood (1963) 2-methylpropanal, ethanol, the short-chain fatty acids from methanoic through pentanoic, as well as succinic, levulinic, and furoic acids. Sugisawa and Edo (1964) had earlier shown that glucose heated at 150°C. for 2.5 hours yielded a series of higher oligosaccharides as well as HMF and 1,6-anhydro- $\beta$ -D-glucopyranose (levoglucosan).

The most comprehensive recent study on the identification

of compounds arising from thermal degradation of glucose is probably that of Heyns *et al.* (1966), in which approximately 70 compounds were identified. Gas chromatograms from volatiles trapped at -80°C. showed 130 peaks. Approximately 56 volatile compounds were identified by comparison of gas chromatographic retention times, mass and infrared spectra, and syringe reactions. These authors claim that methyl, isopropyl, and furfuryl alcohols as well as other alcohols and esters reported previously (Sugisawa, 1966) as arising from carbohydrate pyrolysis or from carbohydrate components in materials such as coffee do not arise from D-glucose. Table I contains a compilation of compounds isolated from heated glucose. The compounds identified by Heyns *et al.* (1966) resulted from pyrolysis at 300°C. for 4 hours and also at 500°C. for 3 hours under nitrogen. Also tabulated are references to compounds found in coffee (Gianturco, 1967), bread (Coffman, 1967), and cocoa beans (Bailey *et al.*, 1962). The data in the table are not meant to imply that the compounds found in coffee, bread, and cocoa arose solely from the glucose present, but only to indicate that the thermal degradation of glucose and other carbohydrates could contribute *per se* to the aroma complex of these foods.

Heyns *et al.* (1966) have stated that aromatic hydrocarbons did not form at 300°C. They repyrolyzed the residue obtained at 300°C. at 500°C. for an additional 3 hours to obtain the aromatics reported. Walter and Fagerson (1968), however, were able to identify phenol in their pyrolyzates obtained by heating glucose at 250°C. for 30 minutes under both nitrogen and air.

The possibilities of the decarboxylation of methyl furoic acid at the temperatures employed would contribute to the relatively large amounts of methylfuran usually found in the condensates from these pyrolyses.

Cyclic ketones are of interest, since many of these are associated with characteristic food aromas. Although identified by Heyns *et al.* (1966) in glucose pyrolyzates, 4-hydroxy-2,5-dimethyl-3-(2H)-furanone has been reported by Silverstein (1967) to be an important pineapple flavor component. The formation of this and other cyclic ketones in coffee and from carbohydrates has been discussed by Gianturco (1967) and Hodge (1967a). While 1,6-anhydroglucopyranose has been commonly reported as one of the major nonvolatile primary degradation products from hexoses, Heyns *et al.* (1966) claim that 1,4:3,6-dianhydroglucopyranose is the major nonvolatile component, followed by 1,4-anhydroglucopyranose and HMF. Among the nonvolatile products formed, disaccharides as well as higher saccharides occur (Sugisawa and Edo, 1964).

The presence of inorganic salts may affect the course of thermal degradation of carbohydrates. According to Broido (1966), as little as 0.15% of inorganic impurities can signifi-

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Table I. Volatiles Identified from Heated Glucose

	Reported by <sup>a</sup>	Also Found in <sup>b</sup>		Reported by <sup>a</sup>	Also Found in <sup>b</sup>
Aliphatic aldehydes			2-( <i>trans</i> -1-Propenyl)-furan	1	
Methanal	3	I, II	2-Isopropenylfuran	1	
Ethanal	1, 2	I, II, III	2-Methyl-3(furyl-2)-2-propenefuran	1	
Propanal	1	I, II, III	2-( <i>cis</i> -1-Propenyl)-5-methylfuran	1	
Butanal	1, 2	I, II, III	2-( <i>trans</i> -1-Propenyl)-5-methylfuran	1	
2-Methylpropanal	1, 2	I, II, III	Oxygenated furans		
Pentanal	2	I, II	2-Furfural	1, 3	I, II
2-Methylbutanal	2	II, III	3-Furfural	1	
2-Propenal	1, 2		2-Acetylfuran	1, 3	I
2-Methylpropenal	1	I	3-Methyl-2-furfural	1	
2-Butenal	1		5-Methyl-2-furfural	3	I
2-Pentenal	1		5-Methyl-2-acetylfuran	1, 3	I
1,3-Pentadienal	1		1-(2-Furyl)-propane-1,2-dione	3	I
Aliphatic ketones			Methyl furoic acid	3	
Propanone	1, 2	I, II, III	2-Methyltetrahydrofuran-3-one	1	I
2-Butanone	1, 2	I, II	2-Furoic acid	2	
2-Pentanone	1		Miscellaneous compounds		
3-Pentanone	1, 2		Methanol	2	I, III
2-Hexanone	1		Ethanol	2	I, III
3-Hexanone	1		Methanoic acid	1, 2	I, II
2,3-Butandione	1, 3	II, III	Ethanoic acid	1, 2, 3	I, II
2,3-Pentandione	1	I	Propanoic acid	1, 2	I, II
3-Butene-2-one	1	I	Butanoic acid	1, 2	II
3-Pentene-2-one	1		2-Methylpropanoic acid	1, 2	I, II
3-Methyl-3-butene-2-one	1		Pentanoic acid	2	II
Aromatics			2-Methylbutanoic acid	2	II
Benzene	1	III	Cyclopentanone	1	I
Toluene	1	I, III	3-Methylcyclopentane-1,2-dione	3	I
<i>o</i> -Xylene	1		2-Cyclopenten-1-one	1	
<i>m</i> -Xylene	1		4-Hydroxy-2-pentenoic acid lactone	3	
<i>p</i> -Xylene	1		Nonvolatiles		
Ethylbenzene	1		Levulinic acid	1	
1,3,5-Trimethylbenzene	1		Succinic acid	2	
1,2,4-Trimethylbenzene	1		Tartaric acid	2	
1,2,3-Trimethylbenzene	1		Pyruvic acid	1	
2,3-Benzofuran	1		5-(Hydroxymethyl)-2-furaldehyde	1, 2	
Phenol	3	I	4-Hydroxy-2,5-dimethyl-3-(2 <i>H</i> )-furanone	1	
Furans			Resorcinol	1	
Furan	1, 2, 3	I, III	Hydroquinone	1	
2-Methylfuran	1, 2, 3	I, III	Pyrocatechol	1	
3-Methylfuran	1		1,6-anhydro- $\beta$ -D-glucopyranose	1, 2	
2-Ethylfuran	1		1,4:3,6-dianhydro- $\beta$ -D-glucopyranose	1	
2,5-Dimethylfuran	1	I	Kojibiose	4	
2-Vinylfuran	1		Sophorose	4	
2- <i>n</i> -Propylfuran	1, 3	I	Nigerose	4	
2-Isopropylfuran	1		Laminaribiose	4	
2-Ethyl-5-methylfuran	1		Maltose	4	
2,3,5-Trimethylfuran	1		Cellobiose	4	
2-Isopropyl-5-methylfuran	1		Isomaltose	4	
2-Vinyl-5-methylfuran	1		Gentiobiose	4	
2- <i>n</i> -Propyl-5-methylfuran	1				
2,5-Diethylfuran	1				
2-( <i>cis</i> -1-Propenyl)-furan	1				

<sup>a</sup> 1. Heyns *et al.* (1966). 2. Sugisawa (1966). 3. Walter and Fagerson (1968). 4. Sugisawa and Edo (1964).  
<sup>b</sup> I. Coffee. II. Bread. III. Cocoa bean.

cantly affect the pyrolysis reactions undergone by cellulose. In a more recent report Heyns and Klier (1968) claim that neutral salts have no effect on the composition of pyrolysis products of a number of mono-, oligo-, and polysaccharides including cellulose. Broido (1966) states that thermogravimetric analysis of "ash-free" cellulose indicates that the initial loss of weight is attributable to evaporation of extracellular water. The initial endothermic dip of a differential thermal analysis curve near 100° was also attributable to loss of extracellular water. Some reactions may not be detected by these techniques, since detection is dependent not only upon sensitivity, but also on the speed of transition through a particular temperature interval.

Thermal decomposition of carbohydrates may be initiated at temperatures as low as 100°C. as reported by Murphy

(1962) for cellulose. Glassner and Pierce (1965) observed that acetal and acetone are found, though in relatively small amounts, in cellulose heated at 170°C. As the temperature was increased, volatile products increased in number and concentration.

Puddington (1948) reported that dry starch heated at 180° to 210°C. yielded traces of volatile acids and aldehydes in addition to carbon dioxide, carbon monoxide, and water; since the ratio of concentration of the latter compounds—i.e., CO<sub>2</sub>:CO:H<sub>2</sub>O—did not change with temperature, he concluded that pyrolysis does not involve a separate dehydration reaction.

Puddington (1948) reported that the pyrolysis proceeded more rapidly under reduced pressure, indicating that oxidation was not involved in the degradation. Similar observa-

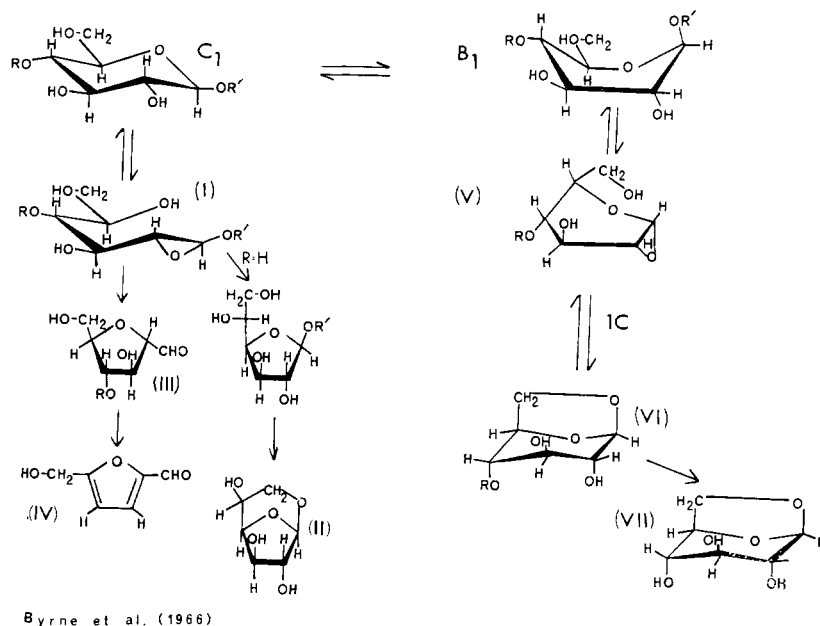


Figure 1. Mechanism of formation of anhydroglucoses and furfurals

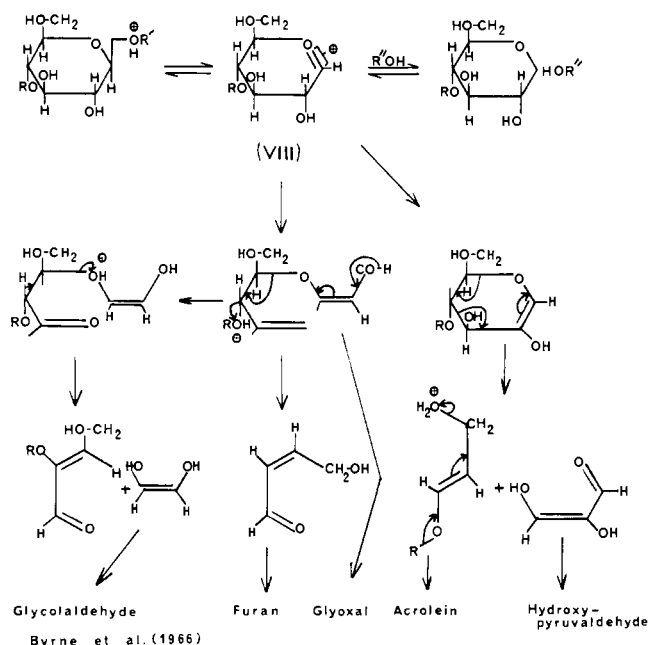


Figure 2. Mechanism of formation of carbonyl compounds

tions were made by Bryce and Greenwood (1963) in their studies with amylopectin, amylose, isomaltose, and glucose as well as by Byrne *et al.* (1966) comparing air and vacuum in the pyrolysis of cellulose. Walter and Fagerson (1968) observed no significant differences in the pyrolysis products from glucose in air or nitrogen. Kato and Takahashi (1967) stated that cellulose was oxidized during pyrolysis even in the absence of air and explain this as occurring via a scission of the glucosidic linkage and hemiacetal bond in the pyranose ring. They state that pyrolytic degradation should be nonoxidative in character. They further reported that in contrast to cellobiose, glucose appears to decompose faster under air than under nitrogen. There is no indication, however, of any qualitative differences in the products formed. Kato and Komarita (1968) found that yields of volatiles from pyrolysis of cellulose are inversely related to the degree of cellulose crystallinity.

The mechanism of carbohydrate pyrolysis has been studied by Hodge (1967a, b), who summarized a general sequence of likely reaction steps as follows:

Enolization of aldoses with the production of the more reactive 2-ketoses; dehydration of ketohexoses, without fission, to HMF, and dehydration of pentoses similarly to 2-furaldehyde; hydrolytic fission of furaldehydes or intermediates leading to furaldehydes to yield, for example, formic acid and levulinic acid from hexoses; fission of 2-ketoses to yield dihydroxyacetone and glyceraldehyde, glycolaldehyde, and four carbon carbonyl compounds; dehydration of the trioses to yield acetol and pyruvaldehyde; dismutation of biose, trioses, and tetroses and their dehydration products to yield lactic aldehyde, pyruvic aldehyde, lactic acid, glycolic acid, acetaldehyde, acetic acid, formaldehyde, formic acid, acetoin, and diacetyl; self- and cross-condensations of aldehydes and ketones containing active hydrogen; reversion of aldoses and ketoses to di-, tri-, and higher oligosaccharides; dimerization of fructose to difructose anhydrides; cyclodehydration of aldoses to glycosans, and then polymerization; enolization and dehydration of the synthetic oligosaccharides.

While there is experimental evidence of many of these reactions, the formation of the large number of furanoids as well as of aromatics such as benzene, xylene, toluene, trimethylbenzene, and phenol is not easily explained by these proposed reaction steps. Byrne *et al.* (1966) have proposed a mechanism for the pyrolysis of cellulose in which two modes are distinguished. In the first, glucose units are pre-ferred as hexose units—i.e., in the form of 1,6-anhydro-β-D-glucopyranose or 1,6-anhydro-β-D-glucofuranose. Two mechanisms are possible for this mode. With the glucose in the normal C1 configuration (Figure 1), ring opening with formation of the 1,2-anhydroglucose unit (I) is favored. From I there may be formed 1,6-anhydro-β-D-glucopyranose (II) or by a different route 2,5-anhydro-D-mannose (III) and thence HMF (IV). The other mechanism starts with the glucose unit in the B1 conformation and leads with chain scission to a 1,2-anhydro-β-D-glucopyranose end unit (V) and thence to a 1,6-anhydro-β-D-glucopyranose and group (VI). A further scission of the chain yields free 1,6-anhydro-β-D-glucopyranose (VII). It is suggested that the change in conformation from the normal C1 to the B1 form governs the rate of formation of levoglucosan.

The second mode (Figure 2) indicated the formation of

carbonium ions (VIII) which arise from chain scission. These may decompose irreversibly to form unsaturated products containing aldehyde and enol groups. These products may yield volatile carbonyl compounds, or may undergo aldol-type condensation with the elimination of water to form ethylene crosslinks between carbon chains and thus ultimately to form a carbon-rich char. Byrne points out the possibility that carbonium ions may also be formed by a random dehydration of cellulose. Kilzer and Broido (1965) have also proposed mechanisms for the pyrolysis of cellulose. It is their opinion that the thermal decomposition of cellulose involves three separate processes, each of which may include one or more reactions. The first is attributed to an intermolecular reaction with loss of water to form a "dehydrocellulose." A second process which competes with the first for native cellulose gives rise to levoglucosan from the rearrangement of 1,4-anhydro- $\alpha$ -D-glucopyranose, which in turn arises from an "unzipping" reaction. The last, an exothermic process, is ascribed to reactions of the "dehydrocellulose" which undergoes carbon-carbon and carbon-oxygen bond ruptures and hydride ion transfers to produce volatile carbon-containing compounds and hydrogen, and intermolecular condensation to produce char. Inorganic impurities enhance the formation and decomposition of "dehydrocellulose" at the expense of the depolymerization reaction (formation of levoglucosan).

Kato (1967) has compared the volatiles produced from cellulose, cellobiose, glucose, and levoglucosan between 250° and 500°C. and found that the relative amounts of furfural and furan from cellulose were higher than those arising from levoglucosans. If most of the pyrolytic degradation proceeded through levoglucosan, the amounts of volatiles from the latter should be higher. Kato's opinion was that the mechanism calling for the formation of volatiles via levoglucosan was not substantiated. Kato agreed with the original proposal of Pakhomov (1957) that cellulose radicals are formed by scission of glycosidic linkages, the radicals being further degraded to the volatile compounds without prior formation of levoglucosan. Relative amounts of the volatile compounds from cellobiose agreed closely with those from glucose, which indicated that after scission of the  $\beta$ -1,4-glycosidic linkage of the cellobiose the glucose moiety was degraded in the same way as glucose.

Kato (1967) has also shown that one of the major volatile compounds, furfural, as well as HMF is fairly thermally stable. When furfural was pyrolyzed at 500°C., about 90% was recovered unchanged. He concludes that the secondary

degradation of both HMF and furfural is of minor importance.

Much work remains to characterize the intermediate reactions further, so that mechanisms may be fully elucidated and in turn lead to some insights into the mode of formation of the rich array of compounds from the thermal degradation of simple carbohydrates and their polymers. Many of these compounds are important because of their aromas or because they are possible reactants, potentiators, or modifiers with other components which may be present in heat-treated food products.

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