Food Chemistry **46** (1993) 343–349

Model reactions on roast aroma formation. XIII. The formation of some uncommon N-heterocyclic compounds and furans after roasting of tryptophan with reducing sugars and sugar degradation products

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(Received 11 March 1992; revised version received and accepted 17 June 1992)

After treatment of D-glucose and D-xylose with tryptophan under the conditions of coffee roasting, 311 volatile compounds were identified. Among others, quinolines, quinoxalines and carbazoles were formed. Their formation is assumed to proceed via alkylated indoles by ring enlargement reactions or intramolecular cyclizations. Another group of compounds formed are bicyclic furans, furfurylamines and N-2-furfuryl-pyrroles, the mass spectra of which are listed. The pathway of tryptophan degradation, as well as the formation of the described products, is discussed.

INTRODUCTION

Recently, we have reported on β-carbolines and indolyl-pyrrolyl-ethanes formed by model reactions of L-tryptophan with selected monosaccharides under the conditions of coffee roasting (Knoch & Baltes, 1992). These compounds were not the only products of the Maillard reaction of tryptophan with sugars. It is well known that amino acids can react with reducing sugars very rapidly in the course of which the latter are decomposed forming highly reactive compounds. So it is no surprise that thermal aromas are composed of a great many compounds in addition to the coloured melanoidins. By analysis of the compounds which were formed by reaction of tryptophan with sugars or selected sugar degradation products, we identified 48 different pyrazines, including cyclopenta-, furyl- and furfurylpyrazines, 4 oxazoles, 24 pyridines, 26 pyrroles, 36 indoles and 16 furanones and pyranones. Additionally, more than 40 aliphatic and alicyclic compounds were identified, most of them being carbonyls. The reactions were performed by roasting tryptophan with D-glucose or D-xylose or some selected furans (2-furfural, 5 methyl-2-furfural) for 10 min. Identical roastings were performed with primary reaction products of tryptophan with sugars. For example, the Amadori rearrangement product (fructose-tryptophan) as well as the corresponding azomethines of the furfurals (N-furfurylidene-trypt amine, N-5-methylfurfurylidene-tryptamine) were roasted in the same manner. Therefore, we obtained a good overview of the compounds formed in this model reaction.

In this paper we report on some quinolines, quinoxalines, carbazoles and furans, most of them not well known as roast aroma compounds. On the other hand, well-known compounds like common pyrazines, pyrroles and pyridines which were the subject of preceding publications (Baltes & Bochmann, 1987*a–e*; Baltes & Mevissen, 1988; Kunert-Kirchhoff & Baltes, 1990*a,b*; Wilken & Baltes, 1990; Reese & Baltes, 1992) are not considered here.

MATERIALS AND METHODS

The preparation of D-fructose-tryptophan, N-2'-furfurylidene-tryptamine, N-(5'-methyl-2'-furfurylidene-tryptamine as well as the roasting procedures and methods of separation and identification of products formed are described in the preceding paper (Knoch & Baltes, 1992).

The synthesis of furanaldimines N-2'-furfurylidene-2-furfurylamine and N-5'-methyl-2'-furfurylidene-2-furfurylamine was carried out by refluxing equimolar amounts (0·01 mol each) of 2-furfural with 2-furfurylamine in 100 ml benzene for 3 h.

Food Chemistry 0308-8146/93/$06.00

The synthesis of N-2'-furfurylidene-5-methyl-2-furfurylamine and N-5'-methyl-2'-furfurylidene-5-methyl-2-furfurylamine were carried out by refluxing equimolar amounts (13·5 mmol each) of 2-furfural or 5-methyl-2-furfural with 5-methyl-2-furfurylamine in 40 ml benzene for 4 h.

5-Methyl-2-furfurylamine was synthesized by stirring 5-methyl-2-furfural (70 mmol), 20 ml conc. ammonia and 20 ml methanol at room temperature for 24 h. After evaporation the aqueous residue was extracted with ether and dried over Na_2SO_4. The ether fraction I (20 ml) was added to lithium aluminium hydride (40 mmol in 50 ml ether) and refluxed for 1 h. The ether fraction II was dried and the ether carefully evaporated. The residue (5-methyl-2-furfurylamine) was instantly used for the preparation of the furanaldimines.

The synthesis of secondary amines N-2'-furfuryl-2-furfurylamine, N-5'-methyl-2'-furfuryl-2-furfurylamine and N-5'-methyl-2'-furfuryl-5-methyl-2-furfurylamine was carried out according to Hahn *et al.* (1954). The furanaldimine (0·3 g), 0·3 g of magnesium turnings for Grignard's reactions and a few small crystals of $HgCl_2$ were refluxed in 100 ml absolute methanol for 2 h. After cooling, the methanol was distilled off. The residue was treated with the same volumes of a $NaHCO_3$ solution and ether. The dried ethereal solution was concentrated.

In the preparation of secondary amines by reduction of Schiff's bases in roasting condensates the ethereal solutions were concentrated to 1 ml and dissolved in 100 ml absolute methanol. For reduction see above.

The synthesis of 2-(2'-furyl)-pyrrole was carried out according to Engel & Steglich (1978) by stirring 2-furoyl chloride with 2-propenylamine (0·1 mol each) in saturated $NaHCO_3$ solution (80 ml) at 0–5°C for 8 h.

RESULTS AND DISCUSSION

As described by Hertz & Shallenberger (1960) roasting of amino acids with reducing sugar produces aromas which are specific for each amino acid. It has become clear (Baltes, 1990) that amino acids react at their amino group via a Strecker degradation with dicarbonyls which were formed simultaneously by sugar decomposition. Aroma compounds formed by this reaction are mostly not amino acid-specific. On the other hand, some amino acids like cysteine or phenylalanine possess further reactive groups which produce specific aroma compounds. An amino acid of this type is tryptophan. Also tryptophan is decomposed by roasting. While the Strecker aldehyde (indolyl-3-acetaldehyde) or succeeding products are scarcely found, the decarboxylation product tryptamine was more prominent. Three main reaction courses of tryptophan can be considered when it is roasted with sugars:

1. Successive decomposition of the side chain. This reaction path yields 3-ethyl-, 3-methylindole and 1H-indole, besides tryptamine and 3-indolyl-acetonitrile. A further new compound is indolyl-2(or 3)-furyl-2-methane on which we have already reported (Knoch & Baltes, 1992)

2. Cyclization to yield β-carbolines on which we have also reported recently (Knoch & Baltes, 1992). These are not only formed by an attack of carbonyls on tryptamine but also directly by decomposition of the Amadori rearrangement product (fructose-tryptophan).

3. Reactions of the side chain. As an example, we have identified some indolylfurylethanes on which we have reported in the preceding paper (Knoch & Baltes, 1992). The corresponding ethylenes are probably formed by dehydrogenation. These compounds are also reaction products of intermediately-formed tryptamine.

Because of the various indoles the aroma impressions of the reaction mixtures formed are unpleasant (faecal).

Quinolines

Among the thermal aroma compounds formed by this reaction we found some quinolines. Quinolines are not conventional roast aroma compounds. Three of them have been found in coffee aroma: quinoline, 3-(or 4)-methylquinoline and 2-hydroxy-3-methylquinoline (Vitzthum & Werkhoff, 1974, 1975; Vitzthium *et al.*, 1975). Imidazolyl-quinolines (IQ-compounds) are well known as strong mutagens which are formed in the course of Maillard reactions in the presence of creatine or creatinine (Nyhammar *et al.*, 1985). They, as well as the 'IQX'-compounds, bear an imidazole ring attached at the benzene residue. In Table 1 the quinolines, carbazoles and quinoxalines identified during our investigations are listed. Besides quinoline, nine of its methyl- and ethyl-substituted compounds are described bearing the alkyl residues in the 2-, 3- and 4-position (i.e. at the N-containing ring). The structures of four of these quinolines were confirmed by standards, the others were identified by spectra published in the literature. In the case of methyl-ethyl quinoline the positions of the alkyl substituents (2 or 3) could not be determined by mass spectrometry. 4-Methylquinoline, being the main product, was also formed by roasting of tryptophan alone, which indicates that it is formed directly from the amino acid by decarboxylation and deamination. Corresponding to its formation we assume ring enlargements of the pyrrole part by incorporation of a methylene group from an alkyl residue. Reactions of this type seem only possible under roast conditions at 220°C. For example, we found an isomerization of pyrrole aldehydes by heating them in an aqueous system at 130–150°C, yielding 3-hydroxy-pyridines (Reese & Baltes, 1992). In Fig. 1 a tentative pathway for the formation of dialkylquinolines is described. The structures of quinolines formed by ring enlargement of indoles depend on the location of the alkyl residues incorporated in the indole ring: correspondingly, a quinoline methylated at the 4-position **1** may be expected when one

Table 1. Quinolines, carbazoles and quinoxalines

Compound	M	RI	*m/z* (relative intensity)	Ref.
5,6,7,8-Tetrahydroquinoxaline	134	1737	134(100) 133(64) 106(25) 119(23) 52(22) 79(14)	L1
2-Methyl-5,6,7,8-tetrahydroquinoxaline	148	1801	148(100) 147(50) 39(23) 79(21) 52(19) 133(12)	L1
1,2,3,4-Tetrahydrocarbazole	171	⟨1802⟩	143(100) 171(37) 170(13) 115(12) 77(11) 144(11) 84(7) 86(6) 168(5)	R
9H-Carbazole	167	⟨1835⟩	167(100) 166(17) 139(13) 168(13) 84(13) 140(10) 69(3)	R
Quinoxaline	130	1898	130(100) 76(88) 103(74) 50(48) 75(18) 51(17)	R
1(2,3 or 4)-Methylcarbazole	181	⟨1909⟩	181(100) 180(77) 90(38) 77(23) 152(13) 63(9)	L2
Quinoline	129	1929	129(100) 102(26) 128(18) 51(13) 76(10) 75(9)	R
2(3 or 4)-Methylcarbazole	181	⟨1945⟩	181(100) 180(73) 90(39) 77(22) 152(13) 63(5)	L2
2-Methylquinoxaline	144	1959	144(100) 117(74) 76(38) 50(27) 77(26) 59(9)	R
2-Methylquinoline-	143	1961	143(100) 144(19) 128(23) 115(22) 76(9) 39(8)	R
2-Ethylquinoline	157	2014	156(100) 157(65) 129(27) 128(16) 130(14) 77(14)	L3
3-Methylquinoline	143	2100	143(100) 115(28) 142(19) 144(10) 89(8) 58(7)	L3
4-Methylquinoline	143	2106	143(100) 115(29) 142(20) 144(11) 89(7) 58(6)	R
2,3-Dimethylquinoline	157	2130	157(100) 156(19) 115(15) 158(10) 142(6) 39(5)	L3
2,4-Dimethylquinoline	157	2135	157(100) 156(10) 115(14) 158(10) 142(7) 77(5)	R
2-Ethyl-(3 or 4)-methylquinoline	171	2174	170(100) 171(59) 143(23) 115(7) 116(5) 144(2)	L4
2-Ethyl-(4 or 3)-methylquinoline	171	2179	170(100) 171(58) 143(22) 115(10) 116(6) 144(4)	L4
4-Ethylquinoline	157	2181	157(100) 156(51) 142(48) 115(16) 129(6) 77(6) 101(4)	L3

Abbreviations used in all tables: RI, modified retention index (van den Dool & Kratz, 1963) on column 1; ⟨RI⟩, modified retention index on column 2; P, proposed structure according to MS data; S, standard synthesized; R, standard available.
[a] Probable *cis/trans* isomeric structure.
L-1, Vitzthum *et al.* (1975); L-2, Hoffman *et al.* (1968); L-3, Draper & McLean (1968); L-4, NBS-MS-Library.

carbon atom of an ethyl residue in the 3-position of indole is incorporated between the 3- and 4-position (reaction pathway 1) or when the pyrrole ring of 3-methylindole is enlarged (reaction pathways 3 and 4). Compound **2** may be formed via reaction pathway 2. Its confirmation requires isotope-marked compounds, the application of which was not possible in connection

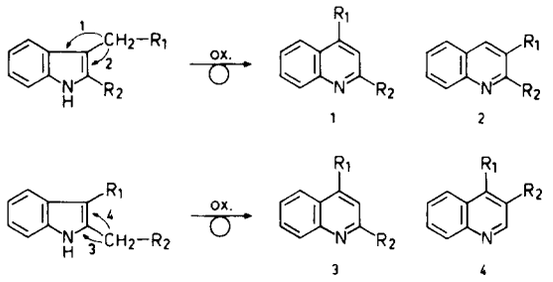

Fig. 1. Tentative mechanism for the formation of quinolines by roasting of tryptophan with sugars (R_1/R_2 = alkyl or H).

with the identification of roast aromas. In the volatiles which we obtained after roasting of tryptophan alone, as well as roasting mixtures of tryptophan with glucose, 2-furfural or 5-methyl-2-furfural, we identified 2,3- as well as 2,4-dimethylquinolines besides two isomeric 2-ethyl-dimethylquinolines. Their formation would require 2,3-diethylindole as precursor, which, by reaction pathway 1 or 2, yield 2-ethyl-3-or 4-methylquinolines.

Carbazoles

As well as quinolines, carbazoles are unusual in roast aromas. But carbazole and some of its methylated derivatives have been identified in cigarette smoke (Hoffman *et al.*, 1968). Investigations relating to comutagenicity, which was thought to be possible because of its similar structure to β-carbolines, were negative (Sugimura *et al.*, 1982).

We have identified, besides tetrahydrocarbazole and carbazole, two methylcarbazoles but the locations of their substituents were not identifiable by mass spectrometry. While carbazole was also identified after roasting of tryptophan alone, the alkylated derivatives were exclusively formed when fructose-tryptophan or sugar/tryptophan mixtures were roasted. By roasting furfurals with tryptophan no carbazole was formed. We assume that carbazoles are formed by cyclization of suitable alkylindoles. Possibly they are formed by a condensation of 2-ethylindolylacetaldehyde and subsequent dehydrogenation (Fig. 2). We observed various intermolecular condensation reactions after roasting mixtures of phenylalanine and glucose (Kunert-Kirchhoff & Baltes, 1990*a*).

Quinoxalines

We have found quinoxalines predominantly in thermal aromas which contained higher concentrations of pyrazines. Pittet *et al.* (1974) suggested that the benzene

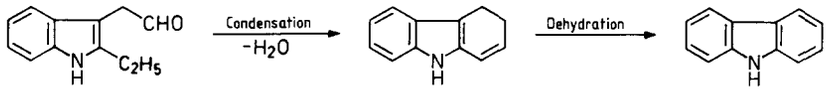

Fig. 2. Tentative mechanism of carbazole formation via intramolecular aldol condensation and dehydrogenation.

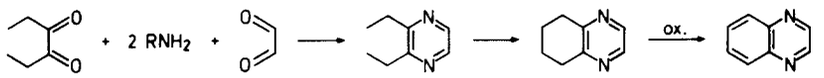

Fig. 3. Proposed mechanism for the formation of quinoxalines by roasting tryptophan with glucose.

part of this molecule is formed by cyclization of pyrazine side chains. We can confirm this theory because we have found tetrahydroquinoline as well as 2,3-diethyl-pyrazine (Reese & Baltes, 1992). These two compounds have also been identified after roasting of a mixture of glucose and tryptophan but not among the thermal aroma compounds after roasting xylose and tryptophan. Therefore, we are of the opinion that hexandione or the corresponding hydroxyketone might be a precursor (Fig. 3).

Furans

Furans are formed by heating of any sugar. Their amounts, as well as their variety, increase with the relative sugar content in the reaction mixture. An overview of furans formed in the course of the Maillard reaction is given by Maga (1979).

In the course of heating tryptophan with sugars some unusual furans are formed. For example, we identified 2,2'-difurfuryl-methane **3** as well as 2,2'-difurfurylethylene **10** and the corresponding ethane **11** after roasting D-xylose with tryptophan. In the case of D-glucose we found additionally methylated derivatives in the 5-position of one or two rings.

Other bicyclic furans formed in these reactions are 2,2'-difurfuryl-amine **9** and N-2'-furfurylidene-2-furfurylamine **8** from the mixtures of xylose/tryptophan as well as the methylated derivatives after reaction of D-glucose. Probably, 2-furfurylamine **6** is an intermediate because we identified simultaneously 2-cyanofuran **7** as well as 5-methyl-2-cyanofuran which are assumed to have been formed from the amines by oxidation.

In order to get an overview of these reactions we roasted mixtures of 2-furfural or 5-methyl-2-furfural with tryptophan. Moreover, we have roasted the corresponding azomethines (2-furfurylidene-tryptamine and 5-methyl-2-furfurylidene-tryptamine). In these reactions we have identified the same bicyclic compounds mentioned above. They are listed in Table 2. With one exception, all structures were confirmed by standards mostly synthesized in our laboratory.

Figure 4 provides a better overview of the compounds formed. We assume that D-glucose as well as D-xylose reacts with tryptophan yielding, by Amadori rearrangement, D-fructose-tryptophan or D-xylulose-tryptophan, respectively, as first reaction products. These compounds are decomposed, forming among

Table 2. Mass spectrometric data of some furan volatiles

Compound	M	RI	*m/z* (relative intensity)	Ref.
2-Cyanofuran	93	1381	93(100) 64(60) 38(55) 39(37) 37(33) 65(32)	R
N-Ethyliden-2-furfurylamine	123	1428	81(100) 53(38) 123(17) 51(2) 52(2)	R
N-2'-Furfurylidenethylamine	123	1443	108(100) 81(97) 123(73) 39(34) 94(32) 53(19)	R
5-Methyl-2-cyanofuran	107	1449	107(100) 52(73) 106(60) 53(43) 51(26) 79(20) 43(18)	L-5
N,N-Di-(2,2'-furfuryl)amine	177	2055	81(100) 109(27) 96(25) 53(21) 82(7) 39(5) 177(3)	S
N-(5-Methyl-2-furfuryl)-2'-furfurylamine	191	2123	95(100) 81(98) 109(50) 43(18) 96(17) 53(16) 191(5)	S
N,N-Di-5,5'-methyl-2,2'-furfurylamine	205	2186	95(100) 123(47) 110(16) 43(15) 96(9) 41(7) 205(2)	S
N-2'-Furfuryliden-2-furfurylamine	175	2201	81(100) 53(20) 175(17) 39(7) 52(6) 51(6) 82(5)	S
N-2-(Furfuryliden)-5-methyl-2-furfurylamine	189	2277	95(100) 43(16) 189(11) 39(10) 41(9) 96(6) 52(6)	S
N-(5-Methyl-2'-(furfuryliden)-2-furfurylamine	189	2305	81(100) 53(41) 51(13) 189(12) 43(12) 52(10) 39(10)	S
N-(5-Methyl-2'-furfuryliden)-5-methyl-2-furfurylamine	203	2403	95(100) 43(11) 203(8) 96(7) 41(5) 160(4) 79(3)	S
1-(2-Furyl)-ethan-1-ol	112	1597	97(100) 112(34) 41(32) 39(31) 43(22) 69(21)	R
Di-2,2'-furylmethane	148	1605	91(100) 148(68) 39(37) 65(24) 53(20) 120(20) 51(16) 119(14)	R
Di-(furyl-3,3')-methane or (Furyl-2)(furyl-3)methane	148	1634	91(100) 148(73) 119(28) 39(19) 118(16) 81(16) 65(16)	L-6
Di-(furyl-3,3')-methane or (Furyl-2)-(furyl-3)methane	148	1658	148(100) 91(67) 119(19) 65(13) 51(11) 39(9)	L-6
2-Furanmethanol	98	1662	98(100) 41(59) 81(49) 97(49) 42(48) 53(38)	R
(Furyl-2)-(5-methylfuryl-2)methane	162	1673	162(100) 91(81) 43(68) 53(37) 119(23) 51(20)	L-7
Di-(furyl-2)ethane	162	1677	81(100) 162(29) 53(28) 39(11) 51(8) 82(5)	L-6
2-Furyl-(5'-methyl-2'-furyl)ethane	176	1745	95(100) 43(11) 176(11) 41(6) 81(5) 39(5)	P
Di-(5-methyl-2-furyl)methane	176	1750	43(100) 176(55) 105(27) 161(19) 95(15) 133(15)	R
Di-(5'-methyl-2-furyl-2'-ethane	190	1812	95(100) 43(16) 190(10) 41(7) 96(6) 39(3)	L-6
Di-(2'-furyl)-1,2-ethylene[a]	160	1984	160(100) 131(47) 103(36) 77(32) 51(31) 78(24) 39(24)	L-8
Di-(2'-furyl)-1,2-ethylene[a]	160	2007	160(100) 131(46) 103(34) 77(34) 51(30) 39(23) 78(23)	L-8
(2'-Furyl)-(5"-methyl-2"-furyl)-1,2-ethylene[a]	174	2057	174(100) 43(48) 131(46) 103(29) 51(29) 77(28) 145(20)	P
(2'-Furyl)-(5"-methyl-2"-furyl)-1,2-ethylene[a]	174	2093	174(100) 131(40) 43(35) 103(22) 145(22) 77(19) 87(18)	P
Di-(5-methyl-furyl-2)-1,2-ethylene[a]	188	2142	188(100) 43(85) 145(78) 115(27) 94(19) 51(18) 187(17) 91(15)	L-6
Di-(5-methyl-furyl-2)-1,2-ethylene[a]	188	2190	188(100) 43(80) 145(75) 115(24) 94(21) 187(16) 51(16) 91(14)	L-6

Abbreviations used in all tables: RI, modified retention index(van den Dool & Kratz, 1963) on column 1; P, proposed structure according to MS data; S, standard synthesized; R, standard available; L-5, Porter & Baldas (1971); L-6; Silwar (1982); L-7, Stoll *et al.*(1967); L-8, Shapiro and Dulan (1983).

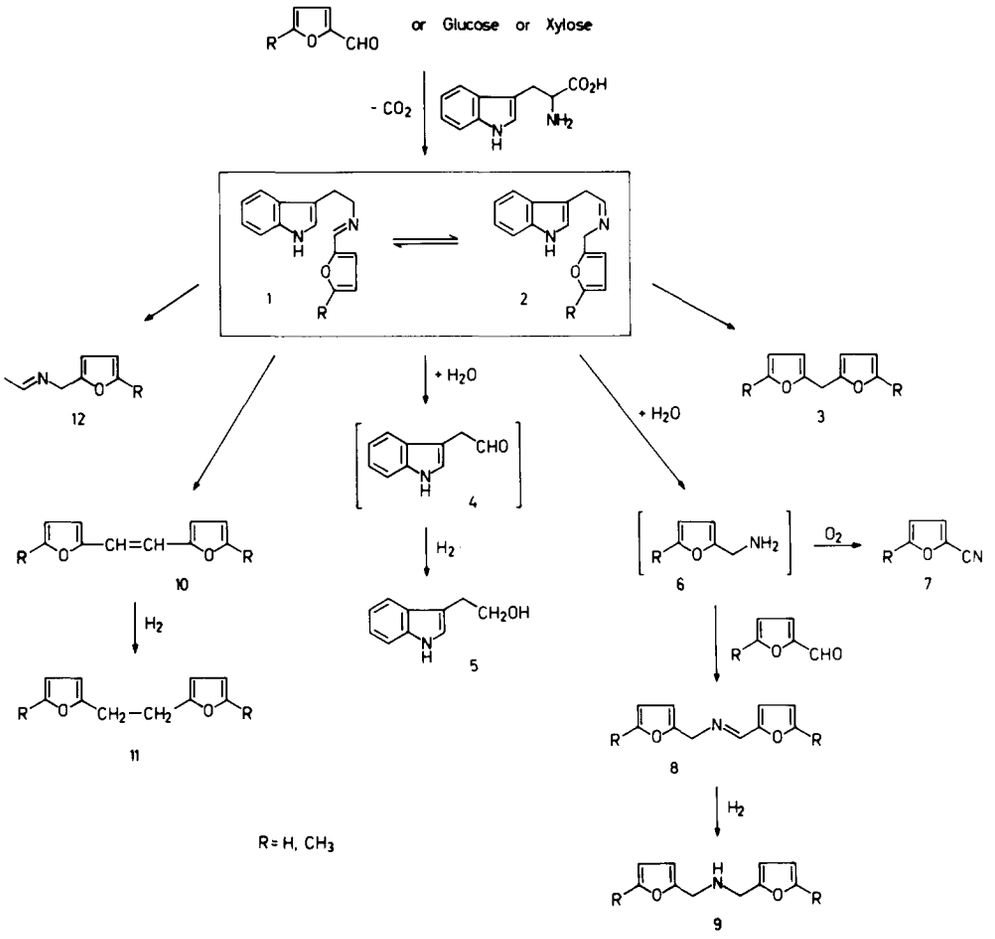

Fig. 4. Overview of furan compounds formed by reaction of glucose or furfurals with tryptophan.

others, 5-methyl-2-furfurylidene- or 2-furfurylidene-tryptophan which are converted by decarboxylation to the corresponding tryptamines **1**. They are also formed by reactions of 5-methylfurfural or furfural with tryptamine. The furfurylidene-tryptamines may exist in tautomeric equilibrium with compound **2**. By hydrolysis **1** and **2** are split to indolylacetaldehyde **4** (which was not identified) and the furfurylamines **6**. Derivatives of **4** and **6** were found. Hydroxyethylindole **5** may have been formed by reduction of **4** while cyanofuran and 5-methyl-2-cyanofuran **7** might have been formed by oxidation of **6**. We have often found, in reactions of this type, that oxidation and reduction reactions are plentiful during roasting. One example is the dehydration of dihydropyrazines yielding pyrazines.

Further reaction products of furfurylamine are the furfurylidene-furfurylamines **8** and, by hydrogen transfer, bisfurfurylidene-amines **9**.

Unclear is the formation pathway of the difurylmethanes **3**, ethylenes **10** and ethanes **11** which were formed as major products, although their concentrations did not reach the quantities of the amines. Feretti & Flanagan (1971) have postulated a condensation reaction of formaldehyde with furans to form difurfurylmethanes. In our opinion, this condensation should also be possible by an attack of 2-furylmethanol on another furan molecule. 2-Furylmethanol, was well as the 5-methyl derivative, was identified in each of our experiments, these being reduction products of the furfurals.

On the other hand, the exclusive formation of the 2'-

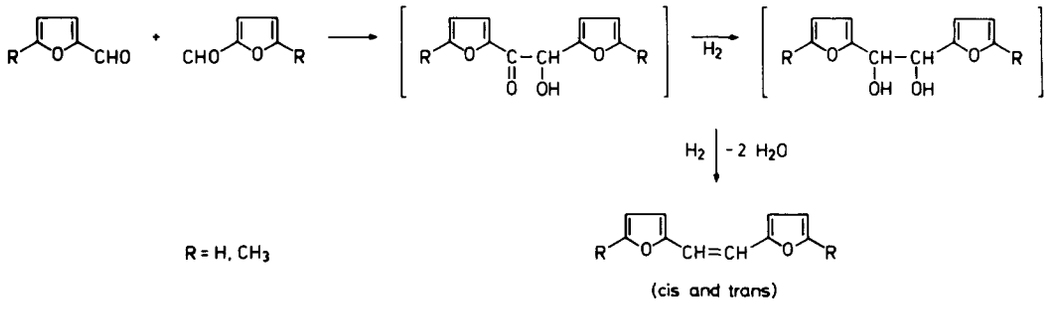

Fig. 5. Possible formation pathway of difurylethylenes and ethanes by benzoin addition.

Table 3. Mass spectrometric data of identified pyrroles with a furan residue

Compound	M	RI	*m/z* (relative intensity)	Ref.
N-(2'-Furfuryl)pyrrole	147	1824	81(100) 147(40) 53(23) 39(7) 117(2)	L-9
N-(5'-Methyl-2'-furfuryl)pyrrole	161	1878	95(100) 161(25) 43(11) 94(8) 96(6) 67(3)	L-9
N-(2'-Furfuryl)-2-methylpyrrole	161	1894	81(100) 161(29) 53(18) 39(3) 82(3) 65(2)	R
N-(5'-Methyl-2'-furfuryl)-2-methylpyrrole	175	1952	95(100) 175(20) 43(15) 81(12) 41(10) 39(8)	L-9
N-(5-Methyl-2'-furfuryl)-2,5-dimethylpyrrole	189	2009	95(100) 189(14) 43(11) 39(9) 94(8) 96(7) 65(4)	L-6
N-(2'-Furfuryl)-2-pyrrolaldehyde	175	2233	81(100) 53(29) 175(28) 39(12) 51(8) 146(2)	R
2-(2'-Furyl)pyrrole	133	2265	133(100) 104(98) 51(39) 39(32) 78(29) 52(21) 66(15)	S
N-(5'-Methyl-2'-furfuryl)-2-pyrrolaldehyde	189	2265	95(100) 43(13) 189(9) 39(8) 96(7) 52(6) 160(2)	L-9
N-(5'-Methyl-2'-furfuryl)5-methyl-2-pyrrolaldehyde	203	2375	95(100) 43(18) 203(9) 96(9) 53(6) 51(5) 160(3)	L-6

Abbreviations used: L-6, Silwar(1982); L-9, Tressl *et al.*(1981).

difuryl-1,2-ethylenes **10** and ethanes **11** was striking because aldehyde groups on any furan ring were not identified. Therefore the aldehyde groups of the furfurals should be taken into consideration as connection points. This should be possible by a benzoin addition which is catalysed by cyanide ions. Possibly, some of the cyanofuran is split to form cyanide at the reaction temperature of 220°C? This reaction pathway is demonstrated in Fig. 5. To our knowledge, neither cyanofuran nor difurylethylenes or ethanes are common reaction products of the Maillard reaction. Products of this type have been described by Silwar (1982) and Shibamoto (1977) in Maillard reactions systems. Like Silwar we have also found *cis-trans* isomers of the ethylenes. Another reference to the existence of furfurylamines is the formation of some N-2'-furyl- and 2'-furfurylpyrroles.

In Table 3 the compounds which have been identified are listed together with their mass spectra. We assume that they are formed according to Rizzi (1974) by a nucleophilic attack of the amine at the 5-position of the furan molecule (Fig. 6). N-2'-Furfurylpyrroles were formed only by reaction of sugars or 2-furfuraldehydes with tryptophan. In this reaction, xylose formed very much higher yields of furfurylpyrroles than glucose. We interpret this difference by a favoured 3-deoxyosone pathway of xylose degradation. Simultaneously, glucose formed higher amounts of 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one which is a prominent product of the 1-deoxyosone pathway (Reese & Baltes, 1992).

Roasting of the N-(2'-furfurylidene)-tryptamines produced no N-2'-furfuryl-pyrroles. Instead, the formation of 3-pyridinoles was registered.

As we have discovered the formation of pyrroles and 3-pyridinoles from furans can proceed simultaneously (Reese & Baltes, 1992) and is a question of reaction conditions. Their formation is demonstrated in Fig. 7. In especially high concentrations they were formed by roasting of the azomethines which obviously formed primarily furans and ammonia while on roasting mixtures of furfurals and trytophan, furfurylamines were formed.

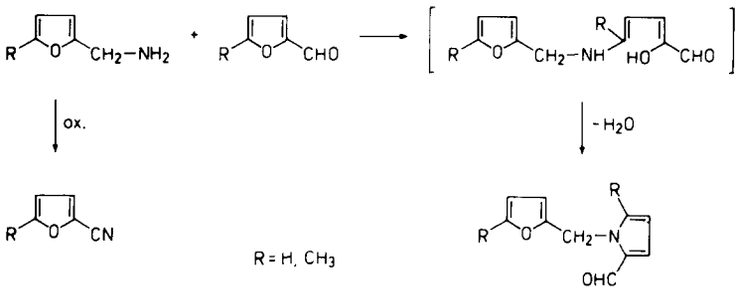

Fig. 6. Assumed formation pathway of furfurylpyrroles.

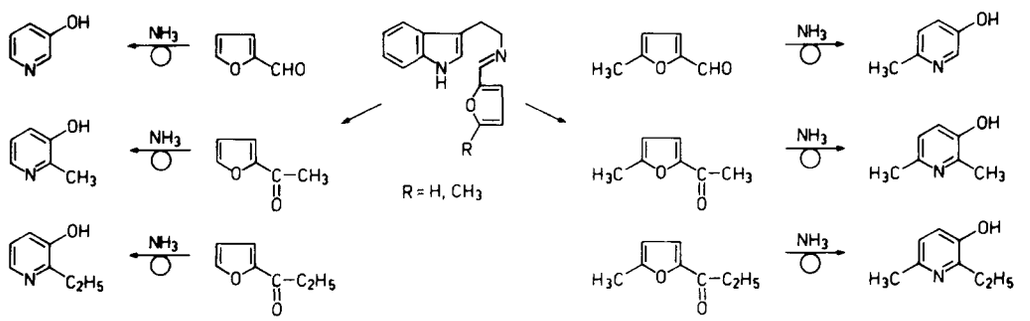

Fig. 7. 3-Pyridinoles formed by roasting of N-furfurylidene-tryptamines.

ACKNOWLEDGEMENT

We gratefully acknowledge the support of the Deutsche Forschungsgemeinschaft.

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