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Indole: A Promising Scavenging Agent for Methylglyoxal and Related Carbonyls in Tryptophan Containing Maillard Model Systems

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Abstract

In situ generation of efficient carbonyl trapping agents from amino acids during food processing can be considered a useful approach to control the accumulation of harmful Maillard reaction products in food. Tryptophan is one such amino acid that can be used to generate carbonyl trapping agents. Indole, the main thermal degradation product of tryptophan, is known to react with simple aldehydes through electrophilic aromatic substitution type reactions mainly at carbon positions 2 and 3 in addition to the ring nitrogen. The ability of indole to scavenge three moles of reactive aldehydes per mole of indole such as formaldehyde, methylglyoxal and phenylacetaldehyde was investigated using model systems containing tryptophan or indole. The model systems were either (a) heated in an aqueous solution in stainless steel reactors at specified time and temperatures and analyzed by qTOF-MS/MS or (b) directly pyrolyzed and analyzed by GC/MS using isotope labelling technique. Unlike the other aldehydes, the initial alcohol formed with phenylacetaldehyde was able to dehydrate and form an stable conjugated system with the indole. In general, indole was able to capture three moles of paraformaldehyde, three moles of methylglyoxal and three moles of phenylacetaldehyde and suppress the formation of 2-amino-1-methyl-6-phenylimidazo(4,5-b)pyridine (PhIP) generated in a model system.

Key words: Tryptophan, indole, carbonyl scavengers, methylglyoxal, formaldehyde, phenylacetaldehyde and PhIP.

1. Introduction

Thermally generated carbonyl compounds in food can play an important role in flavor and aroma formation and also in the generation of toxicants[1]. Trapping of such carbonyl compounds is considered one of the pathways to control the formation of harmful Maillard reaction products. Recently, flavonoids and other phenolic compounds[2] have been suggested as natural scavengers of reactive aldehydes to inhibit the formation of the thermally generated toxicants in food. Availability of other sources of scavenging agents that do not interfere with color and flavor perception[3] can be similarly used in processed food. Among the essential amino acids, tryptophan has been shown to have the highest inhibitory activity towards early and advanced glycation of BSA and highest reduction in the levels of lysine modification compared to the control experiments.[4] During thermal processing of foods tryptophan is also known to degrade into indole and indole derivatives.[5] Furthermore, it scavenge aromatic aldehydes[6] such as benzaldehyde and vanillin and aliphatic aldehydes including sugars[7] through Pictet-Spengler reaction to generate tetrahydro-β-carboline. Tryptophan therefore appears to play a multifunctional role as a carbonyl and free radical scavenger and as an antioxidant and could be a useful replacement to other carbonyl scavenging molecules. Indole, the main volatile thermal degradation product of tryptophan, is also known to react with simple aldehydes through electrophilic aromatic substitution type reactions mainly at carbon position 3 and to a certain extant at carbon position 2 in addition to the ring nitrogen, however, this aspect of tryptophan chemistry and its ability to scavenge three moles of reactive aldehydes per mole of indole, has not been investigated in the context of Maillard reaction. We therefore investigated the in situ generation of indole from tryptophan during the Maillard reaction and its reactivity towards selected Maillard generated

aldehydes or dicarbonyl compounds as a useful approach to control the accumulation of harmful Maillard reaction products in food.

2. Experimental Procedures

2.1 Materials, Reagents, and Equipment. L-tryptophan (99%), L-tryptamine (98%), D-glucose, 2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (98%), 3-methylindole (98%), 2,3-dimethylindole (≥97%), quinoline (98%) and paraformaldehyde were purchased from Sigma-Aldrich chemical company (Milwaukee, WI). The [$^{15}N_2$]tryptophan (98%) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Reactions were carried out in sealed stainless steel reactors heated in a commercial toaster oven (1200 Watts).

2.2 Synthesis of *bis*(tryptophanate)copper (II) complex. The synthesis was carried out according to published procedures. [8] In summary, tryptophan (0.2g) was dissolved in methanol (10 mL) at room temperature in the presence of KOH (0.05g) followed by addition of 0.5 moles of $CuCl_2$. The resulting blue precipitate was filtered, washed with methanol and dried before analysis by ESI/qTOF/MS.

2.3 Sample Preparation. Model systems (see Table 1) were either (a) heated in methanol/water (50%) solutions in a stainless steel reactor at selected temperatures (220^{o}C or 150^{o}C) for 1 or 2h and analyzed by qTOF-MS or (b) directly pyrolyzed at 250 or 300^{o}C and analyzed by GC/MS. All the samples were analyzed in duplicate.

2.4 Py-GC/MS analysis. A Varian CP-3800 gas chromatograph coupled to a Saturn 2000 ion trap detector interfaced to a CDS Pyroprobe 2000 unit through a valved interface (CDS 1500) was used for the desorption of the volatiles from the model systems. For each analysis, approximately 0.5 mg of sample was weighed into a quartz tube, sealed with glass wool and inserted into the pyroprobe and pyrolyzed for 20 s at the desired temperature. The separation was performed using a fused silica DB-5MS column (50-m length x 0.2 mm i.d. x 33 μm film thickness). The GC method used for the analysis of the volatiles was as follows: GC column flow rate was regulated by an electronic flow controller (EFC) and set at a pressure pulse of 70 psi for first 4 minutes then decreased to 33 psi at the rate of 400 psi/min and finally increased to 70 psi at a rate of 1.23 psi/min for the rest of the run. The GC oven temperature was set at −5°C for first 5 min using CO_2 as the cryogenic cooling source and then increased to 50°C at a rate of 50°C/min. Then, the oven temperature was again increased to 270°C at a rate of 8°C/min and kept at 270°C for 5.87 min. The samples were detected by using an ion-trap mass detector. The MS transfer-line temperature was set at 250°C, manifold temperature was set at 50°C, and the ion-trap temperature was set at 175°C. The ionization voltage of 70 eV was used, and EMV was set at 2000 V. The generated data was analyzed using the AMDIS 32 version 2.69 and NIST version 2.0 mass spectral research program.

2.5 Electrospray Ionization/ Quadrupole Time of Flight/ Mass Spectrometric Analysis (ESI/qTOF/MS). The samples were diluted in methanol (90% v/v) before analyzing by ESI/qTOF/MS. The system used was a Bruker Maxis Impact quadrupole time-of-flight mass spectrometer (Bruker Daltonics, Bremen, Germany) operating in positive ion mode. Calibration of the instrument was carried out by using sodium formate clusters. The diluted samples were infused

continuously into the detector. The acquisition parameters for electrospray interface were the following; nebulizer pressure, 0.6 Bar; drying gas, 4.0 l/min, 180 °C; capillary voltage, 4500 V. Scan range was done from *m/z* 90 to 1000. The data were analyzed by Bruker Compass Data Analysis software version 4.2. Tandem mass spectrometry (MS/MS) was carried out in multiple reaction monitoring (MRM) mode using 25 eV collision energy for the ion at $[M+Na]^+ = 311.1154$ and 40eV for the ions at $[M+H]^+ = 225.1126$ and $[M+Na]^+ = 284.0893$.

2.6 Structural Identification. Evidence for the proposed structures of non-volatile reaction intermediates were provided through ESI/qTOF/MS analysis, elemental composition, MS/MS analysis in addition to FTIR and ^{1}H-NMR (see supporting information). Tentative identification of volatile compounds was performed by comparison of their retention times with that of commercial standards and with NIST library search routines in addition to isotope-labeling studies where possible.

3. Results and Discussion

Tryptophan is known to spontaneously scavenge various aldehydes to generate ß-carbolines and tetrahydro-ß-carboline derivatives in food during storage or under commercial or domestic food processing conditions via Pictet-Spengler reaction.[9] Methylglyoxal a well-known and reactive α-dicarbonyl compound can be scavenged by tryptophan to form 1-acetyl-ß-carboline.[10,11] On the other hand, indole derivatives and indole itself which is the major volatile degradation product of tryptophan[5], is also known to undergo electrophilic substitution reaction with carbonyl compounds at C-2 position and to a certain extent at the C-3 and ring nitrogen positions. In addition, the

benzylic position of alkyl substituents of indoles exhibits special reactivity which includes susceptibility to radical or ionic reactions, because of the stabilization provided by the benzylic position due to resonance. However, the ability of indole derivatives and specifically indole to scavenge reactive aldehydes during the Maillard reaction has not been investigated. In order to examine the potential of tryptophan to generate indole derivatives and their ability to scavenge Maillard generated aldehydes various model systems containing tryptophan or indole (see Table 1) were either (a) heated in methanolic aqueous solution in sealed stainless steel reactors and subsequently analyzed by qTOF-MS/MS or (b) directly pyrolyzed and analyzed by GC/MS.

3.1 Proposed mechanism of tryptophan degradation and formation of indole derivatives

The potential of tryptophan containing model systems to generate indole derivatives was verified through both pyrolysis experiments and under heating in an aqueous methanolic solution. Both modes of heating generated indole and its derivatives, however, under pyrolytic conditions the parent indole was the major volatile product of tryptophan containing model systems followed by 3-methylindole. Their structures were verified by comparison of their retention times with those of the commercial standards and through NIST library searches under GC/MS conditions. The mechanism of indole generation from tryptophan is not reported in the literature and it requires breaking of a covalent bond to an aromatic system. The proposed mechanism shown in Figure 1 is based on the observation that tryptophan undergoes thermal decarboxylation to generate tryptamine and tryptamine in turn is degraded into indole and 3-methylindole as evidenced by the presence of both indoles in the heated tryptamine model systems. Furthermore, the importance of decarboxylation step in the generation of indoles was verified when tryptophan was replaced with

bis(tryptophanate)copper (II) complex or when tryptophan was pyrolyzed in the presence of $CuCl_2$, the intensity of the indole peaks increased more than fifty fold due to the catalytic effect of metal salts on the decarboxylation of amino acids.[8] According to Figure 1, tryptamine formed from decarboxylation of tryptophan, can undergo conjugated retro-aldol type reaction to generate 3-methylindole with the loss of methanimine molecule, alternatively, it can lose ammonia to generate 3-ethenyl-2*H*-indole, the acrylamide counterpart of tryptophan. The formation of this intermediate was verified only through its mass spectrum (EI) and through the presence of a single nitrogen atom in the ion at *m/z* 144 when [$^{15}N_2$]tryptophan was used in the model system. Furthermore, the released ammonia was captured as hexamethylenetetramine when tryptophan or [$^{15}N_2$]tryptophan was co-pyrolyzed with paraformaldehyde with the observation of a M+4 peak in the labelled model system in the hexamethylenetetramine peak. The benzylic position in 3-ethenyl-2H-indole is particularly reactive towards addition of water due to the stabilization of the carbocation formed during the addition of water. The resulting alcohol after water addition, undergoes retro-aldol type degradation using the imine moiety as the electron sink instead of a carbonyl and with the loss of acetaldehyde generates indole. Furthermore, tryptamine at *m/z* 161.1069 (6.0 ppm) and 1,2,3,4-tetrahydro-9*H*-pyrido[3,4-b]indole at $[M+H]^+$ 173.1066 (7.3 ppm) were detected in the heated aqueous reaction mixture of tryptophan alone indicating the formation of formaldehyde from tryptamine and its eventual capture by tryptophan via Pictet-Spengler reaction to form the 1,2,3,4-tetrahydro-9*H*-pyrido[3,4-b]indole.

3.2 Scavenging of carbonyl moieties. Selected aldehydes such as formaldehyde, methylglyoxal and phenylacetaldehyde were reacted with indole to confirm the ability of indole to scavenge these aldehydes and identify the specific adducts formed. The selected aldehydes represented common

aldehydes or dicarbonyl compounds formed during the Maillard reaction. All carbonyl compounds were captured through electrophilic substitution reactions at positions C-2, C-3 and the ring nitrogen of indole as shown in Figure 2.

3.3 Formaldehyde represents a simple aldehyde that is usually formed from sugar or tryptamine degradation or as Strecker aldehyde of glycine during the Maillard reaction. When indole was reacted with paraformaldehyde in an aqueous methanolic solution, the expected adduct 2-methylidene-2H-indole was not detected due to the instability of the exocyclic double bond, however its thermal ring-expansion[12] product quinoline was observed at [M+H]+ 130.0651 indicating the capture of formaldehyde. The identity of the peak in the pyrolysis experiment was confirmed through matching of its the retention time with commercial standard and NIST library searches and in the reaction mixture through its elemental composition by qTOF-MS. Furthermore, analysis of the indole/paraformaldehyde methanolic aqueous reaction mixture have indicated that (2*H*-indole-2-yl)methanol can further react with a second mole of formaldehyde to form (3*H*-indole-2,3-diyl)dimethanol as evidenced by the observation of its dehydration product (3-methylidene-3*H*-indol-2-yl)methanol at $[M+H]^+$ = 160.0762 and its further reaction with a third mole of formaldehyde to form (1*H*-indole-1,2,3-triyl)trimethanol at $[M+Na]^+$ = 230.0794 (see Table 2).

On the other hand, indole at [M+H] 118.0645 (9.94 ppm) generated from tryptamine or tryptophan degradation can capture formaldehyde to form quinoline (C_9H_8N) at $[M+H]^+$ 130.0644 (9.8 ppm) after ring expansion as shown in Figure 2 and as verified by library search and by matching the retention time (21.7 min) with the commercial available quinoline standard.

3.4 Methylglyoxal a well-known and reactive α-dicarbonyl compound can be scavenged by tryptophan via Pictet-Spengler reaction to form 1-acetyl-ß-carboline.[10,11] To confirm the ability of indole to scavenge methylglyoxal, the aqueous methanolic mixture was reacted at 150°C for 1.5 h and analyzed by qTOF/MS as indicated in the experimental section. The analysis of the data indicated the ability of indole to capture up to three methylglyoxal moieties at C-3, C-2 and N positions. The initial indole adduct of MG the 1-hydroxy-1-(2*H*-indol-2-yl)propan-2-one $[M+Na]^+$ 212.0676 (see Figure 2) is assumed to form at the C-2 position of indole, this adduct reacted further with another mole of indole to generate 1,2-di(2*H*-indol-2-yl)propan-1-one, the most intense peak in the reaction mixture that was detected in its potassiated $[M+K]^+$ 327.0893 and sodiated forms $[M+Na]^+$ 311.1154. The structure of this adduct was further confirmed through observation in its MS/MS spectrum of the predicted acylium ion at $[M+H]^+$ = 172 generated from the carbonyl moiety and its daughter ion at $[M+H]^+$ = 144 (see Figure 3). Furthermore, the 1,2-di(2*H*-indol-2-yl)propan-1-one reacted further with another mole of indole to eventually form the tri-indolyl derivative at $[M+K]^+$ 444.1486. More importantly, the 1-hydroxy-1-(2*H*-indol-2-yl)propan-2-one at $[M+Na]^+$ = 212.0676 can further scavenge two more molecules of methylglyoxal one at C-3 position to form 1,1'-(2*H*-indole-2,3-diyl)bis(1-hydroxypropan-2-one) at $[M+Na]^+$ = 284.0893 and the other at N to form 1,1',1''-(1*H*-indole-1,2,3-triyl)tris(1-hydroxypropan-2-one) at $[M+Na]^+$ 356.1111 as shown in Figure 2 (see also Table 2). The proposed structure of $[M+Na]^+$ = 284.0893 was further confirmed through analysis of its MS/MS spectrum shown in Figure 3. In addition, ^{1}H-NMR and FTIR spectral data are also provided for the structure of the ion at $[M+Na]^+$ = 212.0676 (see Supporting Information).

3.5 Scavenging of phenylacetaldehyde by indole and tryptophan. To illustrate the potential of tryptophan and indole to capture phenylacetaldehyde; an important precursor of thermally generated carcinogens such as PhIP (2-amino-1-methyl-6-phenylimidazo(4,5-b)pyridine), indole or tryptophan were reacted with phenylacetaldehyde at 220^{o}C in methanol/water for 2h and analyzed by qTOF-MS. The results indicated the formation of various adducts in both systems as major peaks (see Figure 2). Indole reacted with up to three moles of phenylacetaldehyde and in addition, tryptophan containing model system showed Pictet-Spengler adduct of phenylacetaldehyde at $[M+H]^+$ 259.1225 (see Table 2). The mechanism of the adduct formation with phenylacetaldehyde differs slightly from that of MG by the fact that the initial alcohol formed can dehydrate and form an extended conjugated system at $[M+H]^+$ 220.1120. In the case of MG the molecule can stabilize by forming an enediol structure without undergoing dehydration. The initial adduct 2-[2-phenylethenyl]-1*H*-indole at [M+H]+ 220.1120 can react at C-3 position with a second mole of phenylacetaldehyde to form 2,3-bis[(2-phenylethenyl]-1*H*-indole at $[M+Na]^+$ 380.1626 which can dehydrate and form the ion at $[M+H]^+$ 322.1590. Finally, the indole nitrogen can capture a third mole of phenylacetaldehyde to form 1,2,3-tris[(2-phenylethenyl]-1*H*-indole at [M+H]+ 424.2066 (see Table 2).

3.6 Scavenging of phenylacetaldehdye in PhIP generating model systems. To confirm the ability of indole to scavenge phenylacetaldehyde the important precursor of PhIP in a model system, a mixture of creatinine, serine and phenylalanine (1:1:1 molar ratio) was heated at 220^{o}C for 2h in a water methanol solution to generate PhIP. In this mixture, the formation of PhIP was confirmed through the observation of a peak at $[M+H]^+$ = 225.1126 ($C_{13}H_{13}N_4$; 6 ppm error) consistent with the elemental composition of PhIP and through its MS/MS profile (loss of CH_3 and

231 CH_2N_2) as shown in Figure 3. When indole was added to this mixture prior to the heating, not only
232 the ion at $[M+H]^+$ = 225.1126 disappeared but also two of the indole/phenylacetaldehyde adducts
233 observed above at [M+H]+ 424.2066 and at $[M+Na]^+$ 380.1626 appeared, indicating the ability of
234 indole to scavenge phenylacetaldehyde formed in the model system and supress the formation of
235 PhIP.
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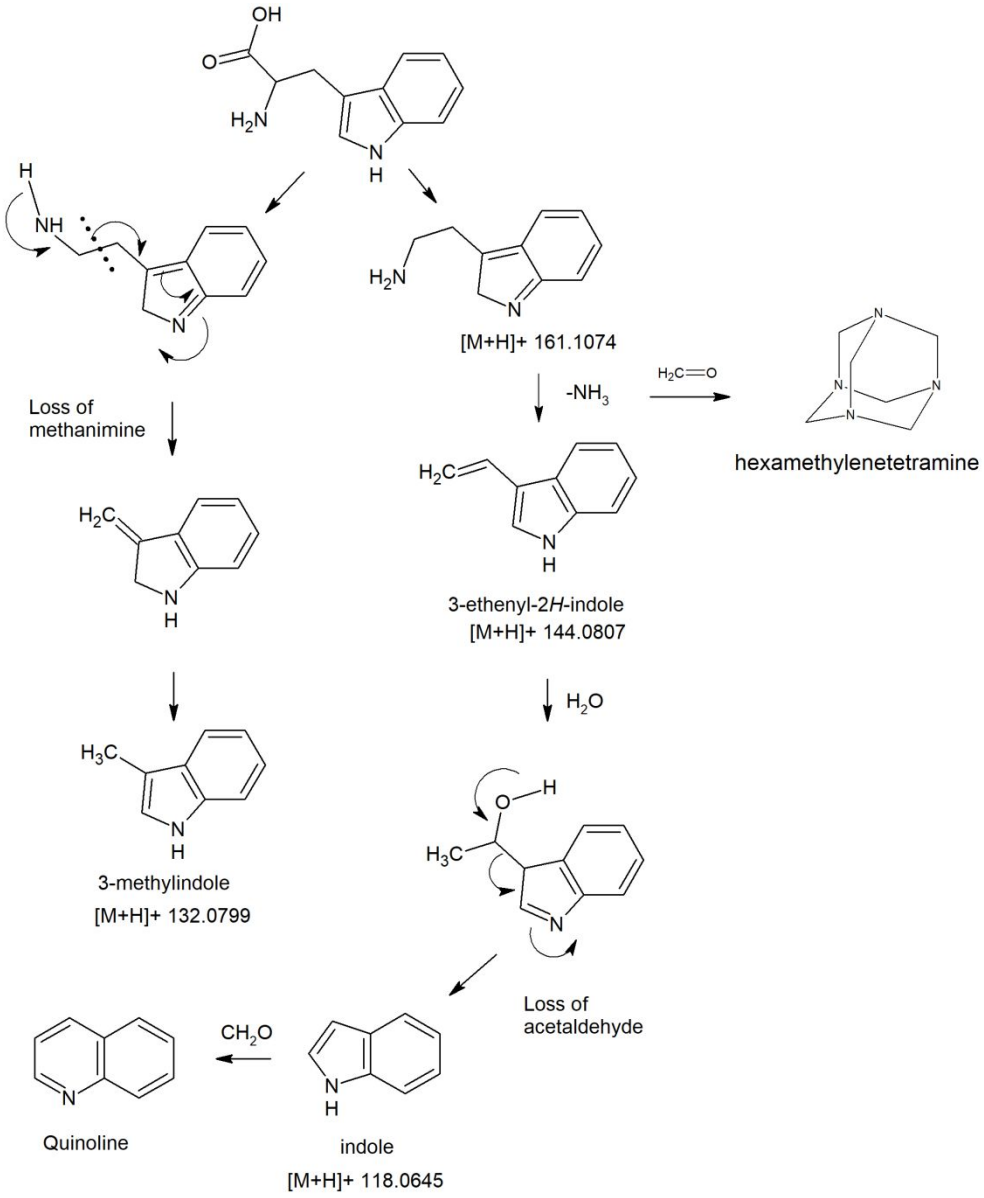
Table 1 Composition of model systems

Models systems analyzed by Py-GC/MS[a]	**Model systems analyzed by qTOF/MS**[b]
Tryptophan	Tryptophan
Tryptamine or Tryptophan[$^{15}N_2$]	Tryptamine
Tryptophan/glucose	Tryptophan/glucose
Tryptophan/paraformaldehyde	Tryptophan/phenylacetaldehyde
Tryptophan[$^{15}N_2$]/paraformaldehyde	Indole/phenylacetaldehyde
Tryptamine/paraformaldehdye	Indole/methylglyoxal
Indole/paraformaldehyde	Indole/paraformaldehyde
Bis(tryptophanate)copper (II)	Creatinine/serine/phenylalanine[c]

[a] All model systems were prepared in a 1:2 molar ratio and pyrolyzed via GC/MS at 250 or 300°C.
[b] The model systems were prepared at 1:1 molar ratio, analyzed by qTOF-MS after heating in water/methanol between 150 to 220°C for 1 to 2 h.
[c] The model system was prepared at 1:1:1 molar ratio, analyzed by qTOF-MS after heating in water/methanol at 220°C for 2 h.

Table 2. Elemental composition of carbonyl-indole adducts and degradation products of tryptophan shown in Figures 1 & 2

Ion	Elemental composition	Error (ppm)	Model system
$[M+K]^+$ 444.1486	$C_{27}H_{23}KN_3O$	1.7	Indole/methylglyoxal
$[M+K]^+$ 327.0893	$C_{19}H_{16}KN_2O$	1.13	Indole/methylglyoxal
$[M+Na]^+$ 311.1154	$C_{19}H_{16}N_2NaO$	1.18	Indole/methylglyoxal
$[M+H]^+$ 289.1329	$C_{19}H_{17}N_2O$	4	Indole/methylglyoxal
$[M+Na]^+$ 356.1111	$C_{17}H_{19}NNaO_6$	0.26	Indole/methylglyoxal
$[M+Na]^+$ 284.0893	$C_{14}H_{15}NNaO_4$	3.1	Indole/methylglyoxal
$[M+Na]^+$ 212.0679	$C_{11}H_{11}NNaO_2$	4	Indole/methylglyoxal
$[M+K]^+$ 228.042	$C_{11}H_{11}KNO_2$	3	Indole/methylglyoxal
$[M+Na]^+$ 401.1474	$C_{22}H_{22}N_2NaO_4$	0.8	Indole/methylglyoxal
$[M+Na]^+$ 342.1303	$C_{17}H_{21}NNaO_5$	4.2	Indole/methylglyoxal
$[M+H]^+$ 220.1112	$C_{16}H_{14}N$	6	Tryptophan or Indole/Phenylacetaldehyde
$[M+Na]^+$ 260.102	$C_{16}H_{15}NNaO$	12	Indole/Phenylacetaldehyde
$[M+Na]^+$ 242.0932	$C_{16}H_{13}NNa$	6	Indole/Phenylacetaldehyde
$[M+Na]^+$ 344.1405	$C_{24}H_{19}NNa$	3	Indole/Phenylacetaldehyde
$[M+H]^+$ 424.2066	$C_{32}H_{26}N$	0.18	Tryptophan /Phenylacetaldehyde
$[M+Na]^+$ 446.1857	$C_{32}H_{25}NNa$	6.2	Tryptophan /Phenylacetaldehyde
$[M+Na]^+$ 380.1626	$C_{24}H_{23}NaNO_2$	0.12	Tryptophan /Phenylacetaldehyde
$[M+H]^+$ 322.1596	$C_{24}H_{20}N$	0.08	Tryptophan /Phenylacetaldehyde
$[M+Na]^+$ 344.1389	$C_{24}H_{19}NNa$	7.6	Tryptophan /Phenylacetaldehyde
[M+H]+ 259.1225	$C_{18}H_{15}N_2$	3.9	Tryptophan/Phenylacetaldehyde
$[M+Na]^+$ 183.0907	$C_{10}H_{12}N_2Na$	4.8	Tryptophan or Tryptamine
$[M+H]^+$ 118.0645	C_8H_8N	9.9	Tryptophan
$[M+H]^+$ 173.1066	$C_{11}H_{13}N_2$	7.3	Tryptophan
$[M+Na]^+$ 166.0621	$C_{10}H_9NNa$	7	Tryptophan
$[M+H]^+$ 132.0799	$C_9H_{10}N$	10.8	Tryptophan
$[M+H]^+$ 144.0807	$C_{10}H_{10}N$	4.3	Tryptophan
$[M+H]^+$ 161.1074	$C_{10}H_{13}N_2$	2.9	Tryptamine or Tryptophan
$[M+K]^+$ 199.0634	$C_{10}H_{12}KN_2$	1.8	Tryptamine
$[M+H]^+$ 160.0762	$C_{10}H_{10}NO$	0.2	Tryptamine
$[M+H]^+$ 130.0651	C_9H_8N	4.4	Tryptamine or Tryptophan or tryptophan or Indole/Formaldehyde
$[M+Na]^+$ 230.0794	$C_{11}H_{13}NNaO_3$	0.37	Indole/ formaldehyde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O
H2N
N
H
H
NH
N
H2N
N
[M+H]+ 161.1074
-NH3
H2C=O
N
N
N
hexamethylenetetramine
Loss of
methanimine
H2C
N
H
3-ethenyl-2H-indole
[M+H]+ 144.0807
H2O
H3C
N
H
3-methylindole
[M+H]+ 132.0799
O
H
H3C
N
Loss of
acetaldehyde
CH2O
N
H
indole
[M+H]+ 118.0645
N
Quinoline

Figure 1

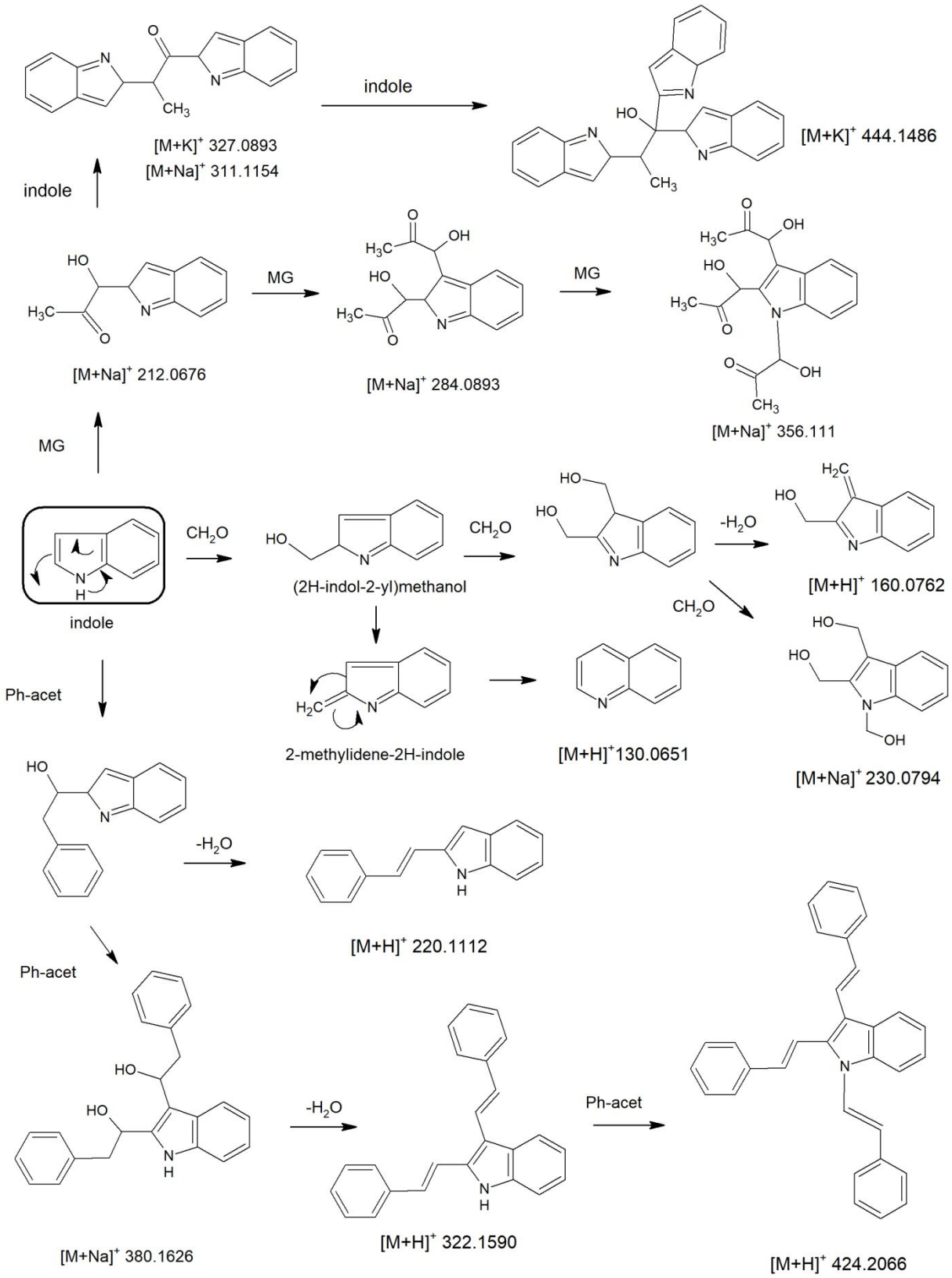
indole
[M+K]+ 327.0893
[M+Na]+ 311.1154
[M+K]+ 444.1486
MG
[M+Na]+ 212.0676
[M+Na]+ 284.0893
[M+Na]+ 356.111
CH2O
(2H-indol-2-yl)methanol
-H2O
[M+H]+ 160.0762
Ph-acet
2-methylidene-2H-indole
[M+H]+130.0651
[M+Na]+ 230.0794
[M+H]+ 220.1112
[M+Na]+ 380.1626
[M+H]+ 322.1590
[M+H]+ 424.2066

Figure 2

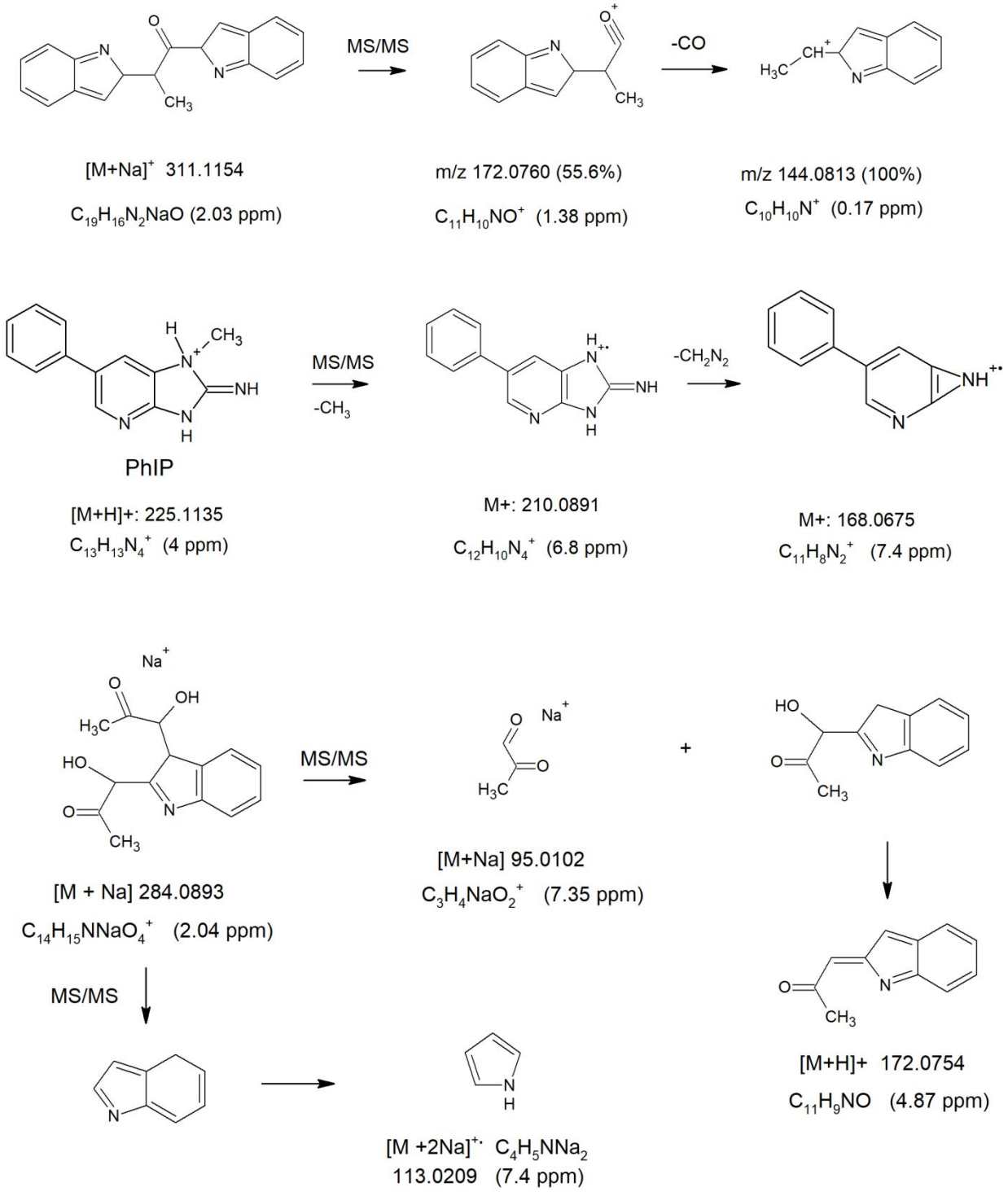
MS/MS
-CO
[M+Na]+ 311.1154
C19H16N2NaO (2.03 ppm)
m/z 172.0760 (55.6%)
C11H10NO+ (1.38 ppm)
m/z 144.0813 (100%)
C10H10N+ (0.17 ppm)
MS/MS
-CH3
-CH2N2
PhIP
[M+H]+: 225.1135
C13H13N4+ (4 ppm)
M+: 210.0891
C12H10N4+ (6.8 ppm)
M+: 168.0675
C11H8N2+ (7.4 ppm)
MS/MS
[M + Na] 284.0893
C14H15NNaO4+ (2.04 ppm)
[M+Na] 95.0102
C3H4NaO2+ (7.35 ppm)
+
MS/MS
[M+H]+ 172.0754
C11H9NO (4.87 ppm)
[M +2Na]+· C4H5NNa2
113.0209 (7.4 ppm)

Figure 3

TOC figure

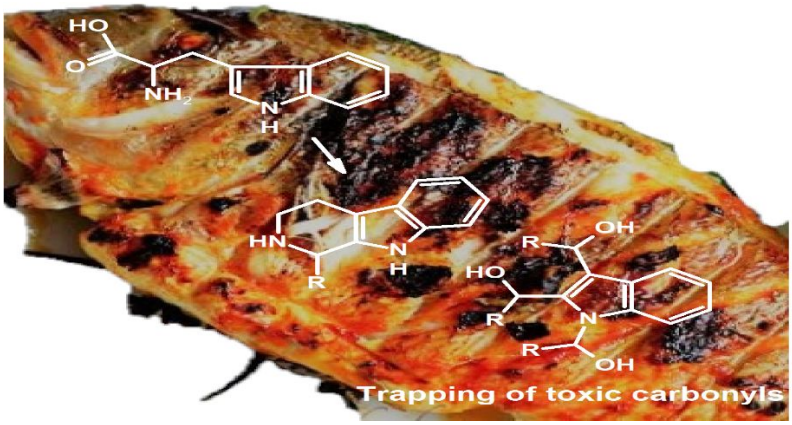

Figure captions

Figure 1. Proposed mechanism of formation of indole and 3-methyl-indole from tryptophan based on both Py-GC/MS (Library search and retention times) and qTOF/MS data (elemental composition).

Figure 2. Proposed mechanism of scavenging of methylglyoxal (MG), formaldehyde and phenylacetaldehyde (Ph-acet) by indole.

Figure 3. MS/MS fragments generated from the ions at $[M+Na]^+ = 311.1154$, $[M+H]^+ = 255.1131$ and $[M+Na]^+ = 284.0893$