Research Article

Journal of MASS SPECTROMETRY

Received: 20 December 2009 Accepted: 15 March 2010 Published online in Wiley Interscience: 9 April 2010

(www.interscience.com) DOI 10.1002/jms.1741

Photodegradation kinetics and byproducts identification of the Aflatoxin B_1 in aqueous medium by ultra-performance liquid chromatography–quadrupole time-of-flight mass spectrometry

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A photodegradation study of Aflatoxin B_1 (AFB_1) in water solution was performed under UV irradiation at different AFB_1 initial concentrations and UV irradiation intensities. The effect of UV intensity on the AFB_1 photodegradation ratio is dominative, when compared with AFB_1 initial concentration. The photodegradation of AFB_1 was proved to follow first-order reaction kinetics ($R^2 \geq 0.99$). Three photodegradation products, i.e. P_1 ($C_{17}H_{14}O_7$), P_2 ($C_{16}H_{14}O_6$) and P_3 ($C_{16}H_{12}O_7$), were identified on the basis of low mass error and high matching property by ultra-performance liquid chromatography–quadrupole time-of-flight mass spectrometry (UPLC–Q-TOF MS), and the degradation pathway was proposed. This study first reports the appearance of these photodegradation products and the proposed degradation pathway in aqueous media.

Keywords: AFB_1; photodegradation; UV; aqueous media; UPLC–Q-TOF MS

Introduction

Aflatoxins, a group of highly toxic, mutagenic and carcinogenic compounds, are secondary metabolites of *Aspergillus flavus* and *A. parasiticus*, which are found worldwide in air and soil to infest both living and dead plants and animals.[1] Among the various aflatoxin species, Aflatoxin B_1 (AFB_1) is the most potent teratogen, mutagen and hepatocarcinogen, which is classified as a Group 1 carcinogen by the International Agency for Research in Cancer (IARC).[2,3] Aflatoxins occur in many countries, especially in tropical and subtropical regions, where conditions of temperature and humidity are optimum for the growth of the molds and for the production of the toxin. Many agricultural commodities and important crops, especially peanuts and peanut-based foods, are susceptible to such contamination. Preventing the contamination of food by the toxigenic fungi, the most rational and economical approach to avoid the potential hazards, is not always possible under certain agronomic storage practices. Therefore, removal or inactivation in salvaging food and feedstuff already contaminated with toxic fungal metabolites is a major concern.[1]

Various physical, chemical and biological approaches are available for the detoxification of aflatoxins.[1,4,5] UV irradiation has been discovered for many years as an effective physical method to destroy aflatoxins for its photosensitive property.[6] Recently, advanced photochemical transformation has emerged as a powerful method for degrading and transforming the photosensitive materials into harmless substances.[7–9] But, what the photodegradation products are and whether they are harmless substances become the major apprehensiveness of this advanced photochemical detoxification method. Although thin-layer chromatography has revealed the appearance of new photodegradation products, and UV and IR spectroscopy have revealed decreases in the characteristic absorption of the aflatoxins in analysis performed after the UV irradiation of aflatoxins,[10–13] knowledge of the nature of these UV-induced aflatoxin degradation products was previously rather limited, and the exact nature of the resulting photodegradation products of AFB_1 remains unknown. Quadruple time-of-flight (Q-TOF) mass spectrometers have been suggested as suitable analytical tools for the identification of metabolites[14,15] and degradation products of harmful trace materials present in drinking water[16] or pesticide residues in foods.[17]

In our earlier work, the photodegradation products of AFB_1 in acetonitrile solution were identified.[18] The aim of this article is to study the photodegradation behavior and the products in water solution, provides clues to the study of the photodegradation mechanism of AFB_1 and the assessment of safety issues of UV method applied in AFB_1 decontamination. Q-TOF MS was used here to identify the photodegradation products and the pathway of UV degradation of AFB_1.

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Experimental

Materials

AFB_1 (2,3,6α,9α-tetrahydro-4-methoxycyclopenta [*c*] furo [2,3 : 45] furo [2,3-*h*] chromene-1,11-dione; purity >98%) was obtained from Fermentek (Jerusalem, Israel). High-performance liquid chromatography (HPLC)-grade acetonitrile and benzene were purchased from Sigma (St Louis, MO, USA).

For the UPLC–Q-TOF MS studies, deionized water (18-MΩ cm^{-1} resistivity) was obtained from a Milli-Q SP Reagent Water system (Millipore, Bedford, MA, USA) and prefiltered through a 0.2-µm membrane. Acetonitrile was Optima LC–MS-grade from Fisher Scientific (Fremont, CA, USA).

Standard stock solutions (200 mg/l) of AFB_1 were prepared in benzene–acetonitrile (98:2 *v*/*v*) and stored at 4 ± 2 °C in a refrigerated dark room (stability of stock and standard solutions under these conditions was checked and demonstrated for at least 3 months). Immediately before use, 0.5 ml of standard stock solutions were placed in glass tubes and dried under a jet of nitrogen. Working solutions of AFB_1 with initial concentrations of 0.2, 2 and 5 ppm were prepared by adding 500, 50 and 20 ml of water solution (pH 7.0), respectively.

Photodegradation procedure

For degradation experiments, water solutions of pure AFB_1 were placed in quartz vessels and irradiated at 4 ± 2 °C under an ultraviolet lamp (NatureGene Corp., Medford, NJ, USA) at different intensities. The intensity reaching the sample surface was measured by means of a UV intensity detector (Beijing Normal University Photoelectric Instrument Factory, Beijing, China).

Meanwhile, control experiments in the dark (blank experiments) under the same conditions were carried out in parallel for comparison without the application of light or AFB_1. At selected time intervals, samples were collected and quantitatively analyzed directly by UPLC–Q-TOF MS for the amount of the compound of interest remaining in the solution after irradiation based on external calibration.

Instrumental analysis and quantification

UPLC was performed on a Waters Acquity UPLC system (Milford, MA, USA) equipped with a binary solvent-delivery system and an autosampler. Chromatography was performed on a 10 cm × 2.1 mm, 1.7-µm particle, Waters Acquity C_{18} column. The injection volume was 2 µl. The mobile phase was a gradient prepared from acetonitrile (component A) and 0.1% formic acid aqueous solution (component B). Elution started with 8% A for 0.1 min and then the proportion of A was increased linearly to 30% at 10 min and then to 100% at 15 min and brought back to 8% A at 15.1 min. Total run time, including conditioning of the column prior to the initial conditions, was 17 min. The flow rate was 500 µl min^{-1}.

Mass spectrometry was performed on a Waters Synapt Q-TOF system (Milford, Massachusetts, USA). Compounds were analyzed in the positive-ion (PI) mode. The optimized conditions were: desolvation gas 500 l/h at a temperature of 420 °C, cone gas 50 l/h, source temperature 120 °C and capillary and cone potentials 3000 and 30 V, respectively. The Q-TOF instrument was operated in the wide pass quadrupole (V) mode, and data were collected between *m*/*z* 50 and 1000, with a scan accumulation time of 0.2 s. The MS–MS experiments were performed using a collision energy of 25 or 30 eV, which was optimized for each compound. To ensure accuracy and reproducibility, all analyses were acquired using an independent reference spray via the Lock Spray interface; Tyr-Gly-Gly-Phe-Leu was used as lock mass (*m*/*z* 556.2771) under positive-ion conditions. The Lock Spray frequency was set at 6 s, meaning that every 5 s flow from the Lock Spray was introduced into the mass spectrometer for 1 s, thus giving the software the possibility of performing ongoing correction of the exact mass of the analyte. Data for the reference compound were averaged over ten spectra per minute. The accurate mass and composition of the precursor and fragment ions were calculated using the MassLynx 4.1 software supplied with the instrument. The software has a feature that calculates all possible elemental composition from the accurate mass; then, by using previous knowledge, such as low i-FIT (Norm), type and number of atoms, various impossible formulae can be further ruled out. Therefore, Q-TOF system is a powerful tool for forming hypotheses about the identity of an unknown compound. Final identification can then be performed on the basis of accurate measurement of the mass of the parent ions and the fragments obtained in MS–MS experiments.

Calculation methods and reproducibility

The experiments were made at least in triplicate and the analytical methods were applied at least in triplicate. The calculation and statistical methods used are available in the program Origin8.0.

Results and Discussion

Effect of initial concentration on degradation of AFB_1

The effect of initial concentration on the degradation of AFB_1 by UV irradiation is presented in Fig. 1(a). The initial concentrations of AFB_1 were 0.2, 2.0 and 5.0 ppm, and there are no detectable changes shown in blank experiment with different concentrations (results exemplified by that pertaining to an initial concentration of 0.2 ppm shown in Fig. 1(a)). Therefore, the declines observed in the degradation curve arise from the photodegradation process. It can be seen that there is no significant difference in the three degradation curves, indicating that the effect of the initial concentration in the selected range on the AFB_1 photodegradation is nearly inexistent, which is in agreement with the feature of the first-order kinetics model.[19]

Effect of UV intensity on degradation of AFB_1

Significant changes among each degradation curves of AFB_1 at different UV intensities are presented in Fig. 1(b). The initial concentration of AFB_1 was 2 ppm, and UV intensities corresponding to the curves are shown in Fig. 1(b) as an inset. Quantitative recoveries from blank experiments sampled over the entire exposure period of simulated UV irradiation showed that AFB_1 did not undergo dark reaction; thus, the decline observed in the degradation curve should be attributed to the photodegradation process. Therefore, photodegradation rate of AFB_1 is strongly affected by UV intensity.

Photodegradation kinetic of AFB_1

The plot of $\ln(C_t/C_0)$ *versus* irradiation time for AFB_1 at different initial concentrations and UV irradiation intensity is given in Fig. 2, and the deduced parameters are listed in Table 1. The linear relationship between $\ln(C_t/C_0)$ and irradiation time indicate that the degradation followed a first-order kinetics ($R^2 \geq 0.99$),

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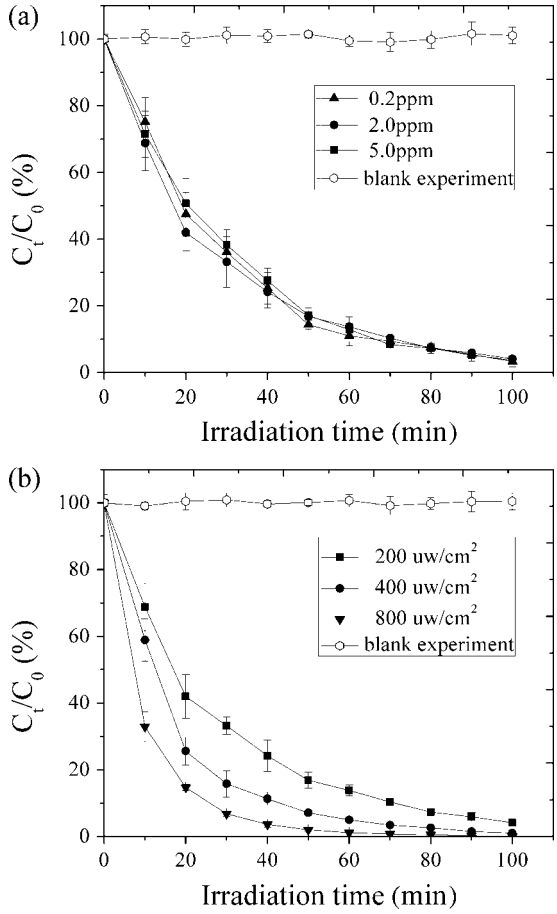

Figure 1. Photodegradation curve of AFB_1 at (a) various initial concentrations and (b) different UV irradiation intensities.

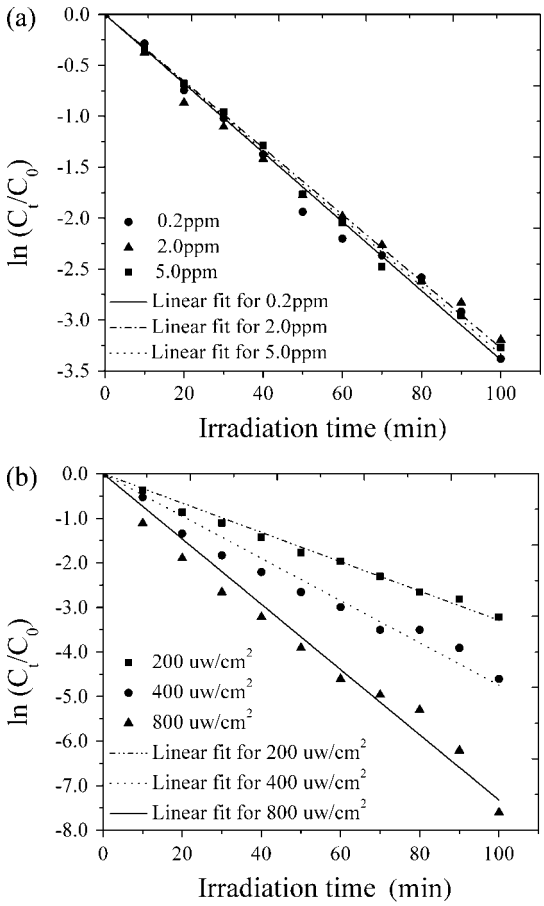

Figure 2. Kinetics of the photodegradation of AFB_1 at (a) various initial concentrations and (b) different UV irradiation intensities.

given by the equation $C_t = C_0e^{-kt}$ where C_0 and C_t are the concentrations at times 0 and t, t is the irradiation time and k is the first-order rate constant. The half-life $t_{1/2}$ of AFB_1, the time required for its concentration to fall to half its initial value, is related to the rate constant by the equation: $t_{1/2} = \ln 2/k$. It can be observed from Table 1 that the values of k and $t_{1/2}$ are nearly the same for different initial AFB_1 concentrations and they have no connection with the AFB_1 initial concentration. However, the values of k and $t_{1/2}$ in Table 1 show obvious changes under different UV intensities, and the AFB_1 photodegradation rate was lower following the order: 800 > 400 > 200 μw/cm^2 illustrating a strong dependence on the intensity of UV irradiation.

Time development of the formation of photodegradation products of AFB_1

To study the time development of the formation of AFB_1 photodegradation products and simultaneously identify their structure, the solution irradiation at the intensity of 400 μw/cm^2 was sampled periodically and the samples were analyzed by UPLC–Q-TOF MS. It is apparent from Fig. 3(a) that AFB_1 is degraded within 100 min, leading to the formation of the three new compounds denoted 'P_1', 'P_2' and 'P_3', which were not detected in the blank experiment and the ultraviolet absorption spectra of these three compounds are similar to that of AFB_1. Thus, these three new compounds were considered as photodegradation products of AFB_1. It can also be noted that the presence of the first, second and the third new photoproducts, P_1, P_2 and P_3, can be detected at 10, 20 and 40 min, respectively, and the response of P_3 is much lower than that of P_1 and P_2.

Identification of photodegradation products of AFB_1

P_1, P_2 and P_3 had a retention time of 6.9, 7.5 and 3.8, respectively, showing an order of polar character $P_3 > P_1 > P_2 > AFB_1$ (shown in Fig. 3). There were no available standards with which to match UPLC-diode array detector (DAD) retention times, so the photodegradation products were identified by UPLC–Q-TOF MS.

UPLC–MS analysis suggested that P_1 (molecular mass m/z 331.0812), P_2 (m/z 303.0868) and P_3 (m/z 317.0659) were the products of photodegradation of AFB_1; for component AFB_1, m/z = 313.0709 was in a good agreement with the molecular mass of the parent compound (AFB_1). Accurate masses, molecular formulas, mass error (mDa and ppm), double-bond equivalents (DBE) and i-FIT (Norm) value (the likelihood that the isotopical pattern of the elemental composition matches a cluster of peaks in the spectrum) of these four protonated molecules are shown in Table 2 using the elemental composition tool incorporated in the MassLynx 4.1 software. The specifications of the Synapt Q-TOF state a maximum mass error of 5 ppm for the range of masses discussed in this article. In this work, the accurate mass and molecular formula of the parent ion were used as another mass lock to verify the precision of the Synapt Q-TOF system. As is apparent from Table 2, the experimental mass of the parent (AFB_1) ion given

Table 1. Kinetic parameters of AFB_1 at different initial concentrations and UV intensities

Initial concentration (ppm)/UV intensity ($\mu w/cm^2$)	Equation	R^2	k (min^{-1})	$t_{1/2}$ (min)
0.2 ppm	$\ln(C_t/C_0) = -0.03391t$	0.99680	-0.03391 ± 0.0006	20.5
2.0 ppm	$\ln(C_t/C_0) = -0.03274t$	0.99695	-0.03274 ± 0.0006	21.2
5.0 ppm	$\ln(C_t/C_0) = -0.03336t$	0.99885	-0.03336 ± 0.0003	20.8
200 $\mu w/cm^2$	$\ln(C_t/C_0) = -0.03291t$	0.99693	-0.03291 ± 0.0005	21.1
400 $\mu w/cm^2$	$\ln(C_t/C_0) = -0.04745t$	0.99001	-0.04745 ± 0.0014	14.6
800 $\mu w/cm^2$	$\ln(C_t/C_0) = -0.07325t$	0.99316	-0.07325 ± 0.0018	9.5

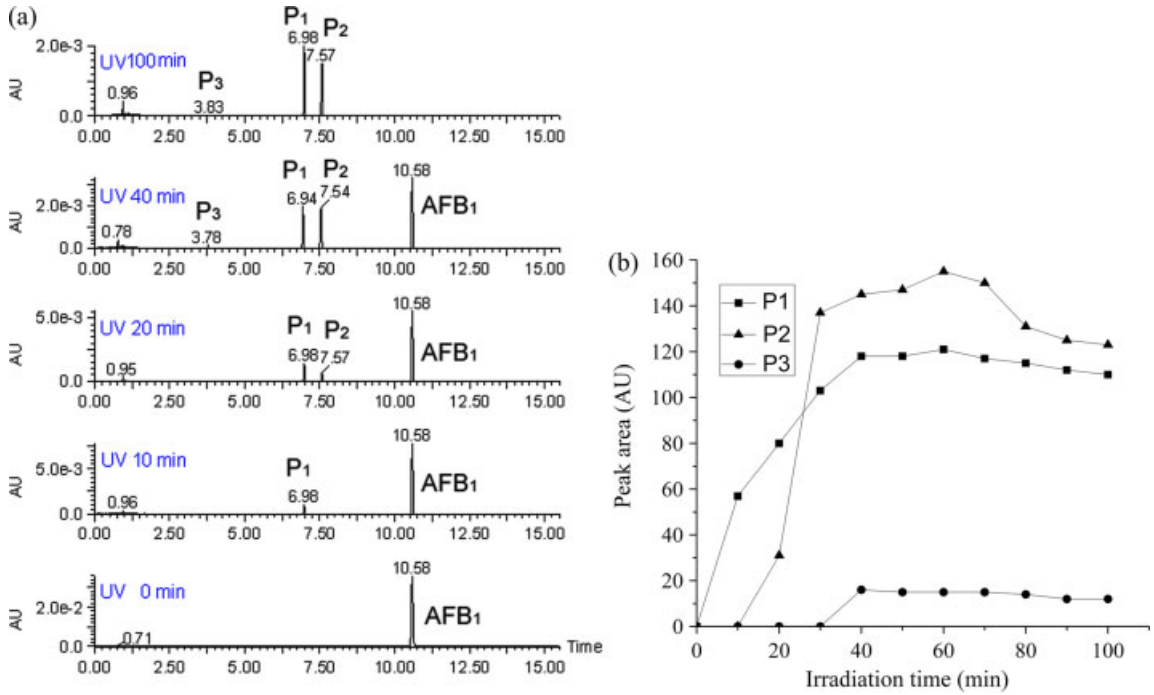

Figure 3. (a) Kinetics of formation of the photodegradation products of AFB_1. (b) Curves showing the evolution of AFB_1 photodegradation products P_1, P_2 and P_3 with increasing UV irradiation time.

by the Synapt Q-TOF system is 313.0709, which is 0.3 mDa less than the theoretical mass, 313.0712, and the molecular formula proposed, $C_{17}H_{13}O_6$, is the same as the theoretical molecular formula. The mass errors of the three photodegradation products were all below 5 ppm and their i-FIT (Norm) values were all 0, which indicated at least 95% confidence in the accuracy of the suggested composition.

In separate MS–MS in Q-TOF mode, the ions of these four compounds were used as precursor compounds, and the ion-filtering function of the quadrupole permitted only ions of *m/z* 331, 303, 317 and 313 to pass to the collision cell, where 30 eV was applied for 331, 303 and 317, and 25 eV was applied for 313. Thus, the MS–MS spectra, the fragmentation formation and the corresponding parameters (mass error, DBE, i-FIT, etc.) of these precursor compounds were obtained and shown in Fig. 4 and Table 2, respectively. The structural formulas of these degradation products were proposed based on the molecular formula calculated from the accurate mass and the MS–MS fragmentation formation supplied by the Q-TOF mode and elucidated by the tool Massfragment incorporated in the MassLynx 4.1 software to verify how much they matched the corresponding fragment information (matching information shown in Fig. 4 as an inset).

The photodegradation pathway of AFB_1 in water solution was proposed based on the identified structural formulas of these photodegradation products and shown in Fig. 5. It can be deduced that a photoaddition reaction induced by water might occur in the C(8)–C(9) bond that produces P_1 from AFB_1, and a photoreduction reaction in the O(1)–C(14) bond and a photoelimination reaction in the C(4)–O(12) bond combined lead to the reaction from P_1 to P_2, while a photoelimination reaction alone in the C(12)–O(13) bond forms P_3 from P_1. Nevertheless, the quantity of P_2 is much more than P_3, which may be due to the competition between the reaction from P_1 to P_2 and the reaction from P_1 to P_3.[20,21] The C(8)–C(9) bond and the O(1)–C(14) bond are two active sites of AFB_1[4] and are easy to be reduced to more stable saturated bonds in photochemistry reaction; thus, these three photoreduction or photoaddition products would be more stable than their parent compound, which is in agreement with Fig. 3(a).[20,22–24] These photochemical principles have been used here to propose the photodegradation pathway of AFB_1, but the photochemical elucidation of the proposed photodegradation pathway of AFB_1 needs to be proved further in future study.

This photodegradation study on AFB_1, a trace toxin in food, points out the good possibilities of Q-TOF MS to identify

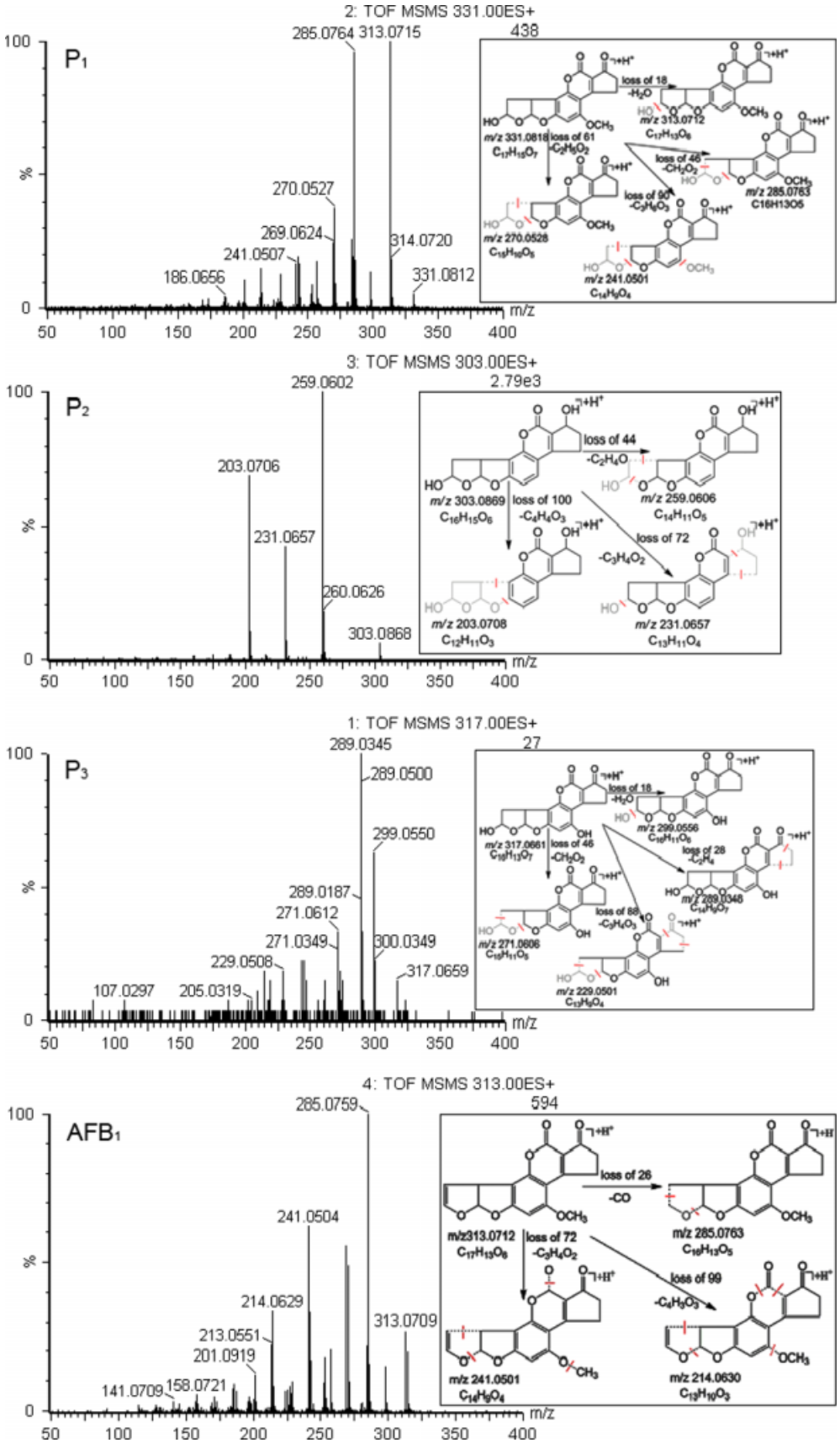

Figure 4. TOF MS–MS spectra and proposed fragmentation of degradation products in the presence of UV irradiation. Proposed fragmentations are shown as an inset.

Table 2. Q-TOF MS accurate mass elemental composition of the AFB_1 photodegradation products[a]

Compound precursorion	Experimental mass (*m/z*)	Theoretical mass (*m/z*)	Mass error		DBE	Molecular formula	i-FIT (Norm)
			mDa	ppm			
P_1	331.0812	331.0818	−0.6	−1.8	10.5	$C_{17}H_{15}O_7$	0
	313.0715	313.0712	0.3	1.0	11.5	$C_{17}H_{13}O_6$	0
	285.0764	285.0763	0.1	0.4	10.5	$C_{16}H_{13}O_5$	0
	270.0527	270.0528	−0.1	−0.4	11.0	$C_{15}H_{10}O_5$	0
	241.0507	241.0501	0.6	2.5	10.5	$C_{14}H_9O_4$	0
P_2	303.0868	303.0869	−0.1	−0.3	9.5	$C_{16}H_{15}O_6$	0
	259.0602	259.0606	−0.4	−1.5	9.5	$C_{14}H_{11}O_5$	0
	231.0657	231.0657	0.0	0.0	8.5	$C_{13}H_{11}O_4$	0
	203.0706	203.0708	−0.2	−1.0	7.5	$C_{12}H_{11}O_3$	0
P_3	317.0659	317.0661	−0.2	−0.6	10.5	$C_{16}H_{13}O_7$	0
	299.0550	299.0556	−0.6	−2.0	11.5	$C_{16}H_{11}O_6$	0
	289.0345	289.0348	−0.3	−1.0	10.5	$C_{14}H_9O_7$	0
	271.0612	271.0606	0.6	2.2	10.5	$C_{15}H_{11}O_5$	0
	229.0508	229.0501	0.7	3.1	9.5	$C_{13}H_9O_4$	0
AFB_1	313.0709	313.0712	−0.3	−0.9	11.5	$C_{17}H_{13}O_6$	0
	285.0759	285.0763	−0.4	−1.4	10.5	$C_{16}H_{13}O_5$	0
	241.0504	241.0501	0.3	1.2	10.5	$C_{14}H_9O_4$	0
	214.0629	214.0630	−0.1	−0.5	9.0	$C_{13}H_{10}O_3$	0

[a] The elemental composition report was obtained using single-mass analysis of 5 mDa with DBE between −1.5 and 50.0, monoisotopic masses, odd and even electron ions and element limits from 0 to 20 for C, H and O.

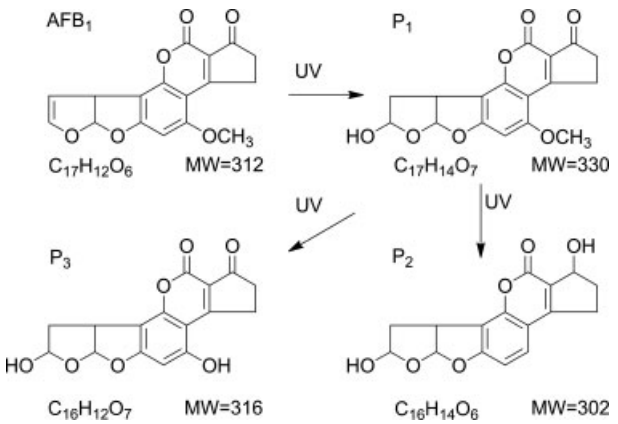

Figure 5. Photodegradation pathway of AFB_1 proposed on the basis of the results from this study.

non-target molecules such as photodegradation products of photosensitive trace materials another time. Published literature on the subject, chemical database and websites are very useful to unambiguously identify compounds, combined with the Q-TOF MS. The main problem of this technique is the lack of libraries that allow us to search a possible structure for a given elemental composition within the equipment software. That would be a very good feature for the identification work.

Conclusions

The photochemical behavior of AFB_1 in aqueous solution has been investigated in this study. The effect of UV intensity on the AFB_1 photodegradation ratio is dominative, when compared with AFB_1 initial concentration. The photodegradation of AFB_1 was proved to follow the first-order reaction kinetics well.

Three photodegradation products of AFB_1 were observed and identified by UPLC–Q-TOF MS for the first time. The photodegradation pathway of AFB_1 was proposed, which is supported by the elementary reaction mechanisms of photochemistry.

The power of UPLC–Q-TOF MS is displayed here another time for the identification of the trace materials and their degradation products. Measurement of an accurate mass for product ions and Elemental Composition tool and MassFragment tool software incorporated in the software MassLynx 4.1 supplied with the instrument offer easier and more precise identification and elucidation of the structures of photodegradation products.

Acknowledgements

The work is supported by the National Key Technology R&D Program in the 11th Five year Plan of China (Contract No: 2009BADB9B08) and the National High Technology Research and Development Program (863 Program) of China (Contract No: 2010AA101504).

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