Supplementary Information

Aquatic photolysis of strobilurin fungicide kresoxim-methyl: kinetics, pathways, and effects of adjuvants

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Text. S1. SPE method

After the SPE activation with ultrapure water (20 mL) and conditioning with methanol (10 mL), 50 mL of sample was loaded and the eluate was recovered (fraction A). The SPE Column was washed with 1 mL acetonitrile (ACN). The sample was re-dissolved in 1 mL acetonitrile corresponding to a concentration fold of 50.

Text. S2. Reactive intermediates identification

Reactive intermediates were explored using electron paramagnetic resonance spectroscopy analysis (EPR). In this study, 5,5-dimethyl-l-pyrrolidine N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinol (TEMP) were chosen as spin trapping agents for •OH and $^1O_2$, respectively. In each case, the spin trapping agent (0.1 M) was added to the photolytic solutions containing KM. After mixing, samples were taken

into capillariesand inserted into EPR chambers for testing. The instrumental parameters used for sample analysis were as follows: modulation frequency of 100.00 kHz; microwave power of 6.420 mW; microwave frequency of 9.889 GHz; sweep width of 200 G; central field of 3520 G.

Text. S3. Second order rate constant ($k_{^1O_2,KM}$) detection

The second-order rate constants of KM with $^1O_2$ was determined by completion kinetics method according to the following equation. Rose Bengal (RB, 1 μM) was selected as sensitizer of $^1O_2$. Furfuryl alcohol (FFA, 10 μM), with a known rate constant with $^1O_2$, (1.2×10^8 L M^{-1} s^{-1}) was used as a reference chemical in this study. The reaction between FFA and $^1O_2$ was nearly diffusion controlled with 1:1 stoichiometry. During the irradiation, the loss of KM was monitored along with the loss of FFA.

$$k_{^1O_2,KM} = \frac{\ln[KM_t/KM_0]}{\ln[FFA_t/FFA_0]} \times k_{^1O_2,FFA} \quad (1)$$

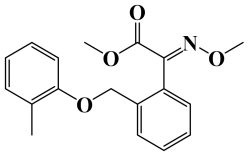
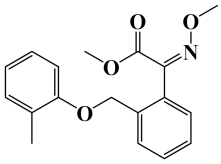
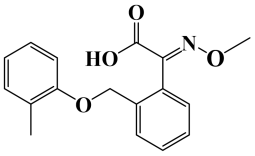
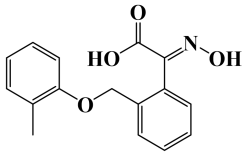
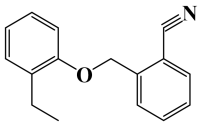
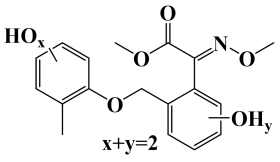
Table. S1. HPLC conditions of three compounds

Chemicals	H_2O	Methanol	0.1% ortho-phospho ric acid	Acetoni--trile	Flow rate (mL/min)	Wavelen--gth (nm)	Retention time (min)
KM	0	0	30	70	1.0	230	8.60
Para-nitr-oanisole	0	35	65	0	1.0	265	5.40
Furfuryl alcohol	0	0	20	80	1.0	270	7.10

Table. S2. The water quality parameters of Zixia Lake in this study.

	TOC (mg/L as C)	Alkalinity (mg/L as $CaCO_3$)	NO3 (mg/L)	Absorbance /UV254nm（1/cm）	pH
Zixia Lake	12.78 ± 0.02	57.6	1.27	0.028	7.9

Table. S3. Major intermediate photoproducts identified in the photodegradation of KM.

Label	RT (min)	Measured exact mass $[M+H]^+$	Theoreti--cal exact mass $[M+H]^+$	Δppm	Formula of neutral structure	Propose structure
KM	3.19	314.1385	314.1387	-0.524	$C_{18}H_{19}NO_4$	
KM isomers	1.60; 2.05; 2.17; 2.96; 6.05	314.1385	314.1387	-0.683	$C_{18}H_{19}NO_4$	
TP1	1.04	300.1233	300.1230	0.951	$C_{17}H_{17}NO_4$	
TP2	1.55	286.1077	286.1074	1.313	$C_{16}H_{15}NO_4$	
TP3	1.44	238.1228	238.1226	1.257	$C_{16}H_{15}NO$	
TP4	1.14	346.1290	346.1285	1.578	$C_{18}H_{19}NO_6$	

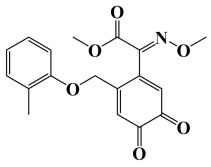
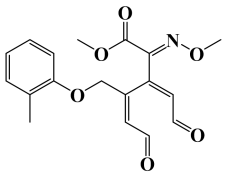
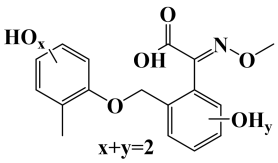
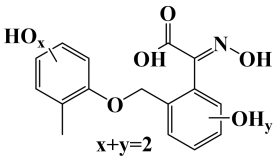
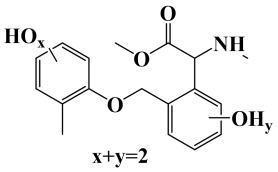
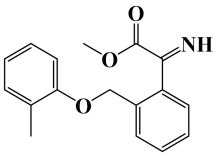
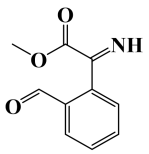
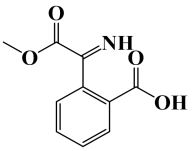
TP5	1.30	344.1132	344.1129	1.035	$C_{18}H_{17}NO_6$	
TP6	1.72	346.1288	346.1285	0.856	$C_{18}H_{19}NO_6$	
TP7	0.85	332.1133	332.1129	1.344	$C_{17}H_{17}NO_6$	
TP8	0.92	318.0977	318.0972	0.446	$C_{16}H_{16}NO_6$	
TP9	1.85	332.1497	332.1492	1.327	$C_{18}H_{21}NO_5$	
TP10	0.58	284.1284	284.1281	0.845	$C_{17}H_{17}NO_3$	
TP11	2.43	192.0658	192.0655	1.668	$C_{10}H_9NO_3$	
TP12	1.27	208.0609	208.0605	1.998	$C_{10}H_9NO_4$	

Table. S4. The acute toxicity (LC50/EC50) and chronic toxicity (ChV) parameters towards aquatic organisms of the photoproducts

Label	LC_{50} (mg L^{-1})		EC_{50} (mg L^{-1})	ChV (mg L^{-1})			Class
	Fish / 96h	Daphnia / 48h	Green Algae / 96h	Fish / 96h	Daphnia / 48h	Green Algae / 96h	
KM and isomers	0.170	0.032	0.011	0.0025	0.0041	0.0049	Aliphatic Amines
TP1	0.251	0.045	0.016	0.0041	0.0056	0.0073	Aliphatic Amines
TP2	0.23	0.042	0.015	0.0037	0.0052	0.0067	Aliphatic Amines
TP3	1.46	1.03	1.9	0.185	0.185	0.808	Meutral Organics
TP4	0.801	0.134	0.057	0.017	0.015	0.024	Aliphatic Amines
TP5	13.4	1.81	1.17	0.536	0.168	0.424	Aliphatic Amines
TP6	5.34	0.772	0.434	0.172	0.077	0.166	Aliphatic Amines
TP7	1.19	0.192	0.086	0.027	0.021	0.036	Aliphatic Amines
TP8	1.09	0.178	0.08	0.025	0.02	0.033	Aliphatic Amines
TP9	35.9	4.48	3.39	1.83	0.384	1.16	Aliphatic Amines
TP10	44.8	27.4	27.6	4.77	3.28	8.53	Meutral Organics
TP11	86.3	93.7	45	30.3	0.742	13.3	Aliphatic Amines
TP12	2.38E-07	0.0000106	0.000503	0.000174	0.00837	0.00293	Aliphatic Amines

Table. S5. The criteria of acute toxicity (LC50/EC50) and chronic toxicity (ChV) (mg/L).

Acute toxicity	Chronic toxicity	Toxicity level
$LC_{50} > 100$ or $EC_{50} > 100$	ChV > 10	Not harmful
$10 < LC_{50} < 100$ or $10 < EC_{50} < 100$	1 < ChV < 10	Harmful
$1 < LC_{50} < 10$ or $1 < EC_{50} < 10$	0.1 < ChV < 1	Toxic
$LC_{50} < 1$ or $EC_{50} < 1$	ChV < 0.1	Highly toxic

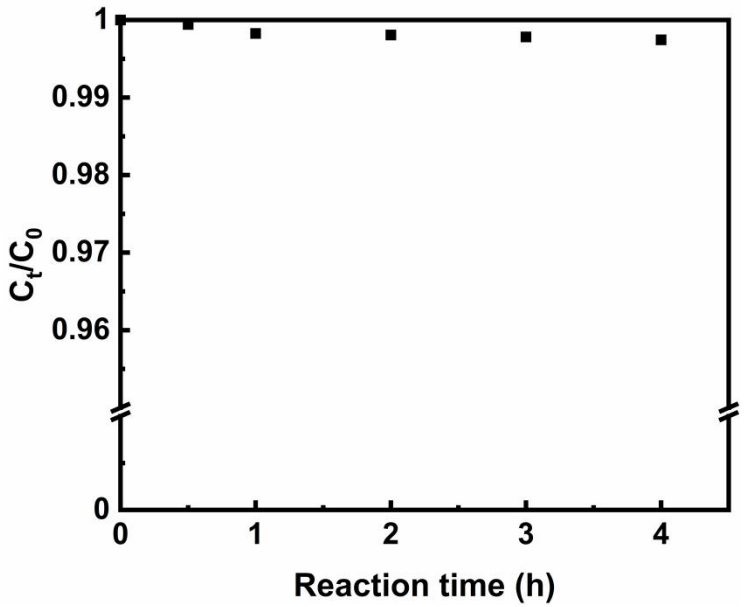


Fig. S1. Dark control experiments of KM in water ([KM] = 10 μM, [phosphate buffer] = 10 mM).

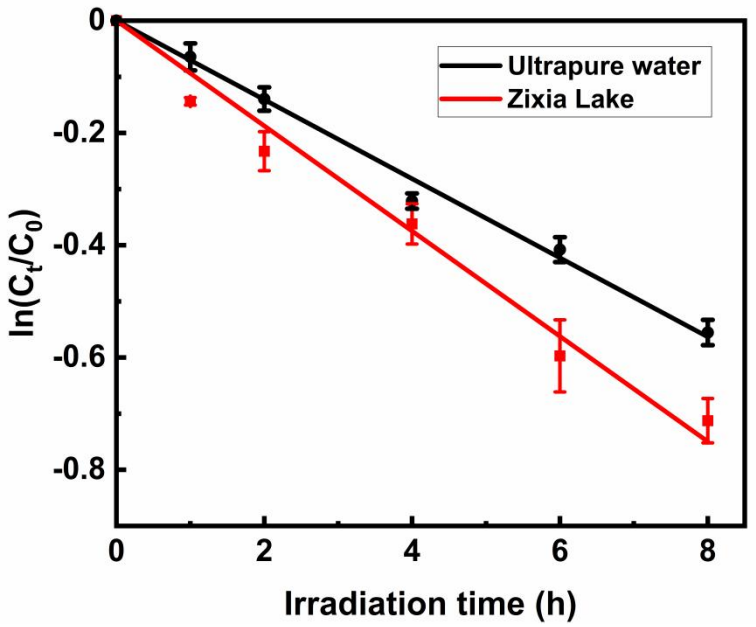


Fig. S2 The photolysis of the KM in natural water and ultrapure water.

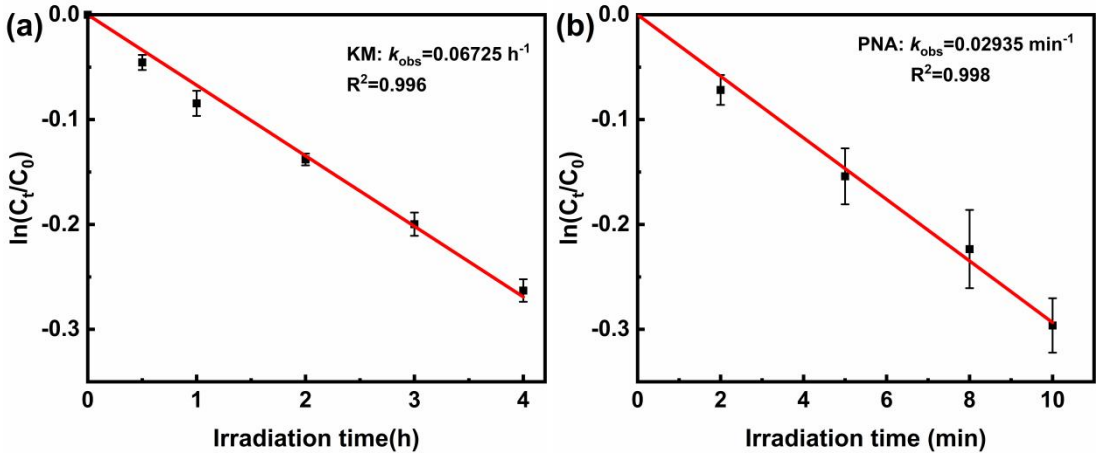


Fig. S3. (a) Photolysis rate constant of actinometer pnitroanisole (PNA) in the presence of pyridine (pyr) ($[PNA]_0$ = 10 μM, $[pyr]_0$ = 10 mM); (b) Photodegradation rate constants of KM ($[KM]_0$ = 10 μM, [phosphate buffer] = 10 mM).

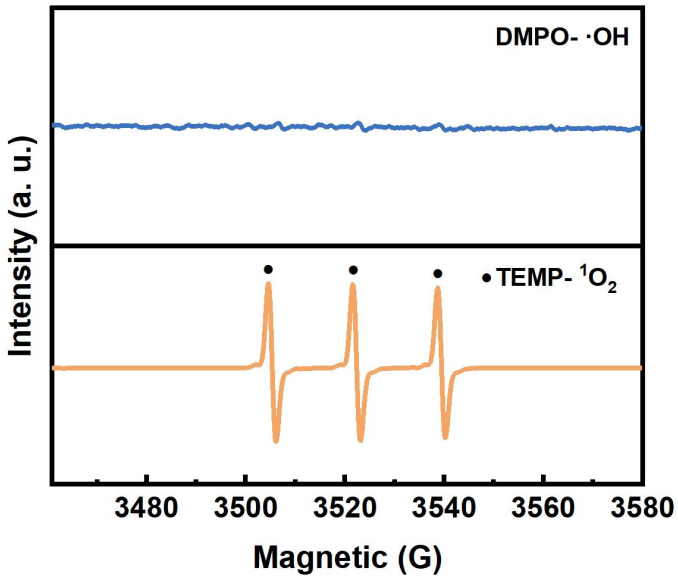


Fig. S4. EPR spectra for the identification of •OH and $^1O_2$ in KM photolysis ($[KM]_0$ = 100 μM).

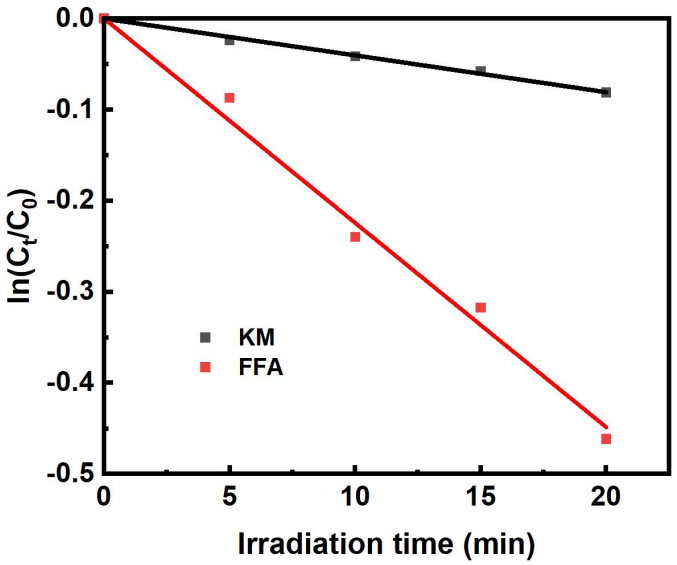


Fig. S5. Measurement of the second-order rate constant ($k_{^1O_2,KM}$) for the reaction of KM with $^1O_2$.

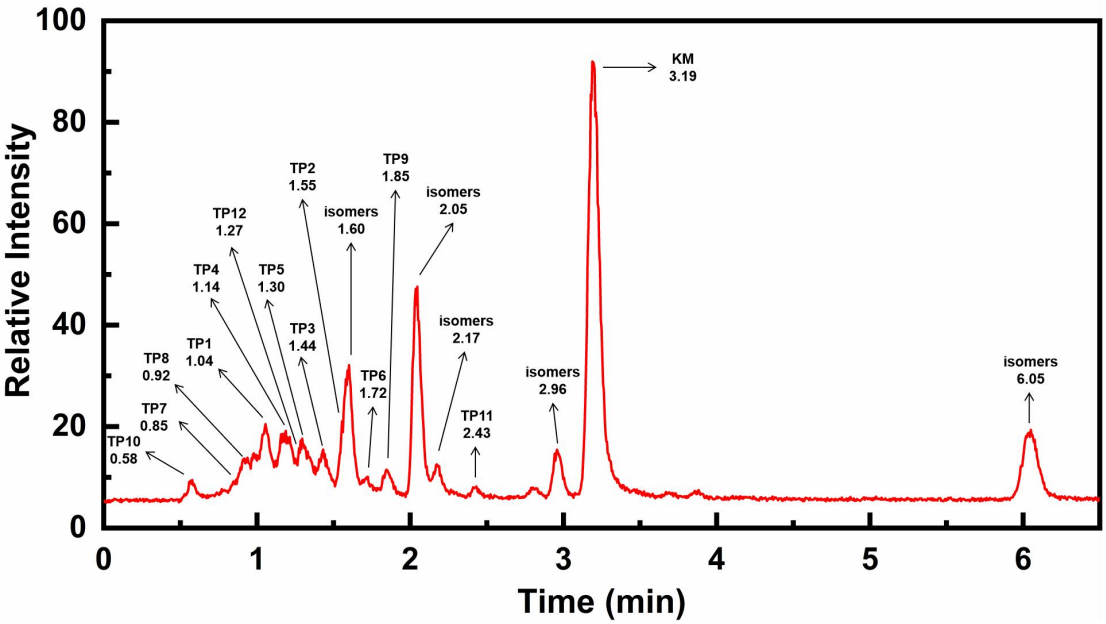


Fig. S6. HR-MS total ion chromatogram (TICs) of KM and some major products in positive mode.

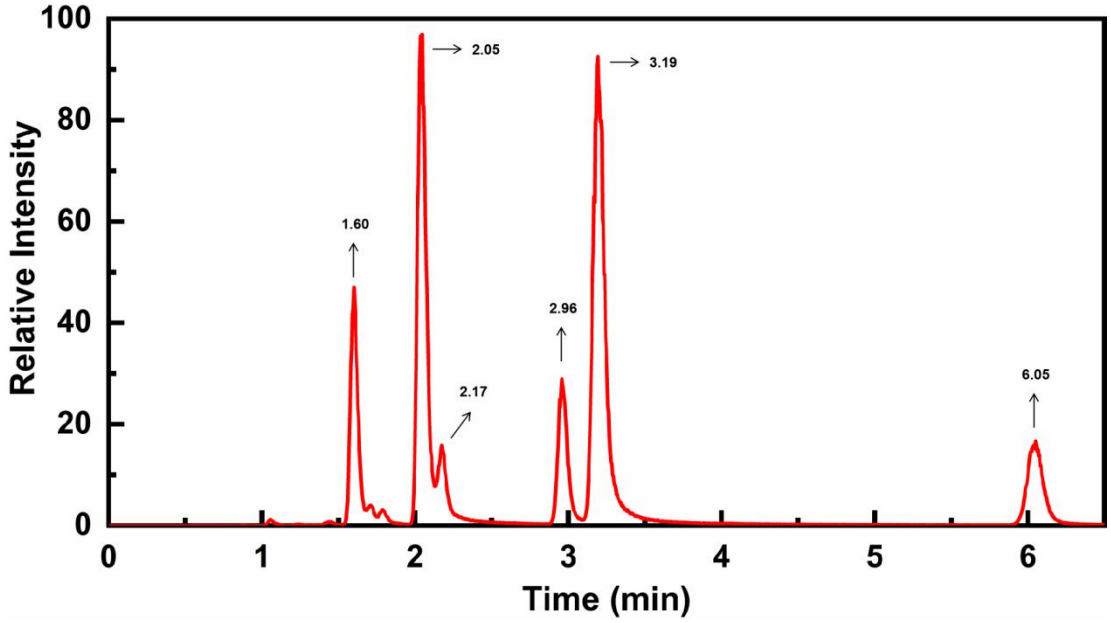


Fig. S7. Extracted diagnostic ion chromatogram at *m/z* 314.1387 at 10 h under simulated sunlight.

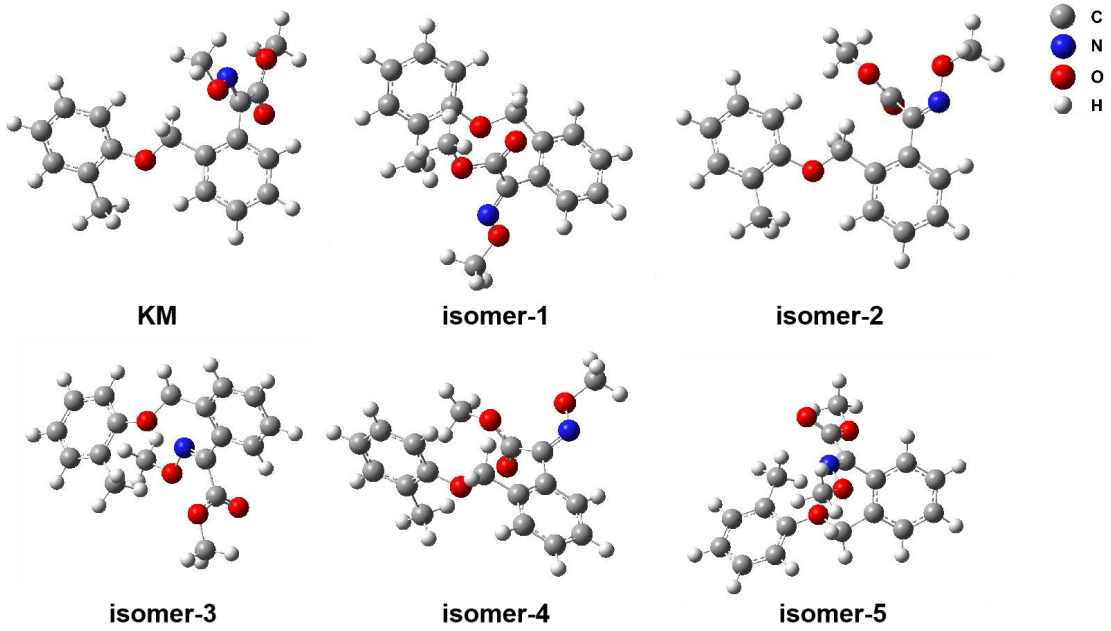


Fig. S8. The speculative three-dimensional structure of the KM and isomers.

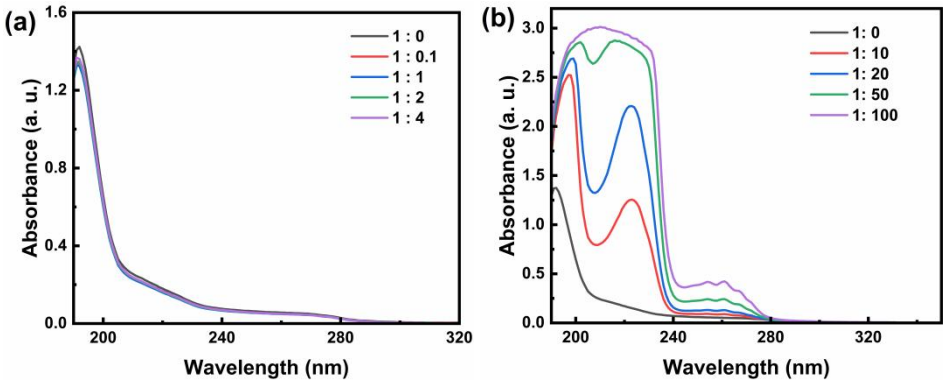


Fig. S9. (a) UV absorption spectrum at different ratios of KM to Tween 20; (b) UV absorption spectrum at different ratios of KM to SDBS.