SUPPLEMENTARY MATERIALS

Autoxidation of melatonin at excited state: mechanism proposal for formation of N^1-acetyl-N^2-formyl-5-methoxykynuramine

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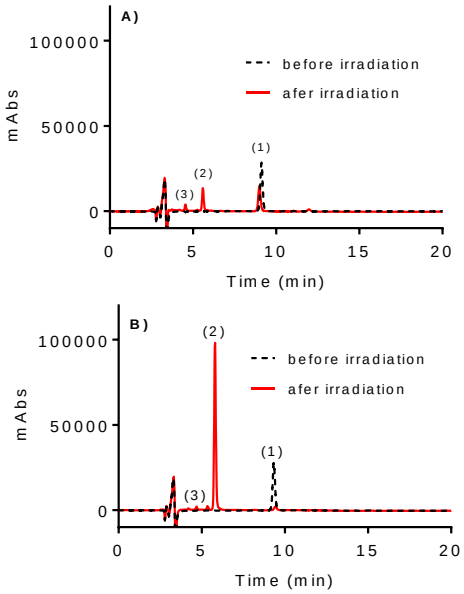

Fig. S1. **Chromatograms before and after autoxidation of melatonin**.

(A) pH 7.0 and (B) pH 10.0. The reaction conditions were: Melatonin 100 mM, UVC (12 W) irradiation for 60 minutes. Peaks (1) melatonin, (2) AFMK, and (3) hydroxy-melatonin.

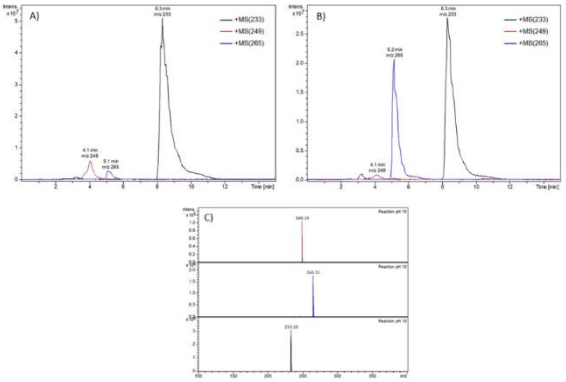

Fig. S2. **LC-MS chromatograms of melatonin before and after autoxidation.**

The monitored molecular ion $(M+H)^+$ were 233 (melatonin), 249 (hydroxylated melatonin), and 265 (AFMK). (A) reaction conducted at pH 7.0, (B) reaction conducted at pH 10.0, and (C) Peaks of the molecular ions.

Table S1. Electronic energies and ZPE (in Hartree) of Melatonin (Ground and 1st Excited States).

Molecular System	GS/GS	EE/GS	EE/EE	ZPE
I	-764.40903	-764.25057	-764.26052	0.2747
II	-764.21167	-764.18203	-764.18059	0.2750
III	-763.91312	-763.77386	-763.78498	0.2687
IV	-763.75844	-763.71560	-763.71550	0.2612

Molecular systems obtained at [PBE0 / TD-PBE0-GD3(BJ)/6-311++G(3df,2p) level of theory using IEFPCM(water) to describe the solvent effect.

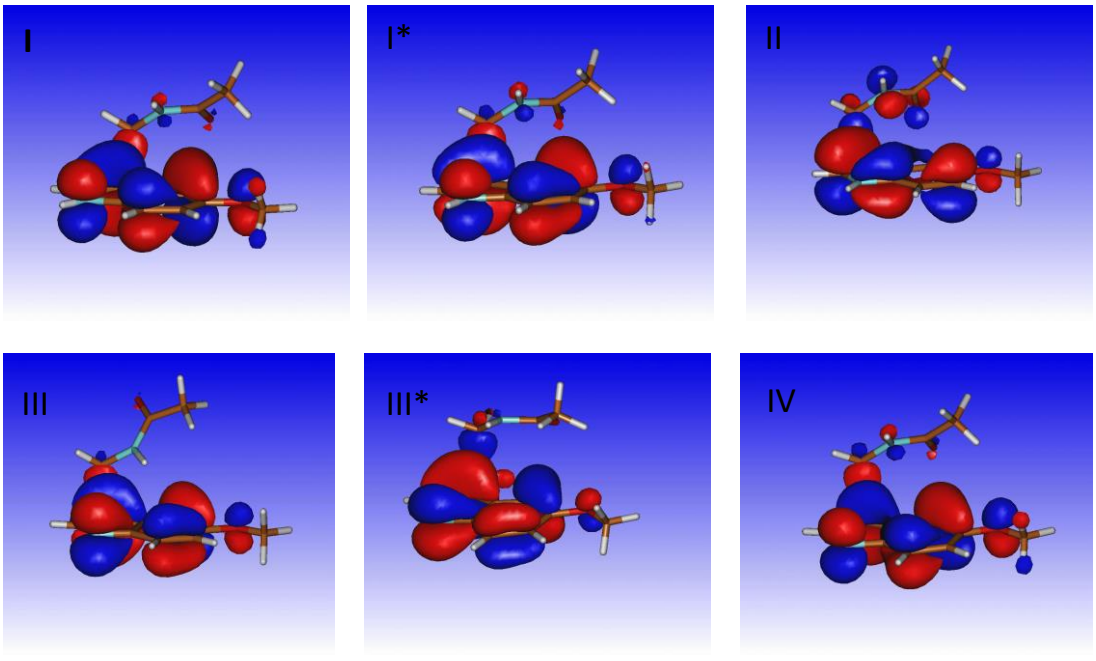

Fig S3. Frontier molecular orbitals of the studied species.

(I) Ground state melatonin, (I) electronically excited melatonin, (II) ground state melatonin cation radical, (III) ground state deprotonated melatonin, (III*) electronically excited deprotonated melatonin, (IV) ground state melatonin radical.*

Table S2. Cartesian Coordinates (in Å) of the ground state of the molecular system (I).

Atom	x	y	z
C	-2.095	-0.497	-0.276
C	-0.757	-0.220	-0.624

C	-0.248	1.024	-0.323
C	-1.049	2.008	0.304
C	-2.354	1.734	0.638
C	-2.880	0.465	0.346
C	1.037	1.639	-0.510
C	0.885	2.951	0.020
N	-0.324	3.188	0.501
C	2.263	1.012	-1.047
H	1.658	3.711	0.046
H	-0.174	-0.988	-1.120
H	-2.976	2.479	1.122
H	-3.907	0.251	0.611
H	2.006	0.256	-1.793
H	2.892	1.763	-1.533
C	3.111	0.339	0.049
O	-2.518	-1.739	-0.593
C	-3.852	-2.085	-0.266
H	-3.987	-3.111	-0.600
H	-4.020	-2.027	0.812
H	-4.565	-1.435	-0.783
H	3.976	-0.128	-0.422
H	3.469	1.090	0.754
N	2.397	-0.664	0.799
H	1.957	-0.396	1.664
C	2.158	-1.898	0.318
O	2.590	-2.268	-0.770
C	1.324	-2.798	1.188
H	1.098	-2.366	2.163
H	0.386	-3.011	0.671
H	1.851	-3.744	1.325

Obtained at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

Table S3. Cartesian Coordinates (in Å) of the ground state of the molecular system (II).

Atom	x	y	z
C	-2.024	-0.712	-0.284
C	-0.740	-0.298	-0.596
C	-0.359	1.012	-0.305
C	-1.297	1.891	0.288
C	-2.585	1.477	0.599
C	-2.943	0.169	0.311
C	0.857	1.752	-0.488
C	0.608	3.014	-0.014
N	-0.674	3.103	0.453
C	2.146	1.231	-1.031

H	1.264	3.871	0.022
H	-1.095	3.932	0.835
H	-0.056	-1.000	-1.060
H	-3.301	2.151	1.057
H	-3.944	-0.161	0.553
H	1.949	0.488	-1.810
H	2.711	2.040	-1.503
C	3.040	0.596	0.036
O	-2.324	-2.007	-0.592
C	-3.618	-2.476	-0.279
H	-3.648	-3.517	-0.594
H	-3.816	-2.419	0.795
H	-4.389	-1.915	-0.818
H	3.945	0.196	-0.423
H	3.334	1.352	0.768
N	2.396	-0.483	0.748
H	1.737	-0.243	1.471
C	2.436	-1.762	0.332
O	3.114	-2.126	-0.625
C	1.603	-2.737	1.120
H	1.064	-2.274	1.947
H	0.882	-3.204	0.445
H	2.252	-3.523	1.508

Obtaimed at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

Table S4. Cartesian Coordinates (in Å) of the ground state of the molecular system (III).

Atom	x	y	z
C	-2.027	-0.713	-0.245
C	-0.699	-0.290	-0.557
C	-0.346	1.009	-0.295
C	-1.309	1.890	0.248
C	-2.606	1.486	0.548
C	-2.962	0.170	0.300
C	0.875	1.760	-0.467
C	0.588	3.040	-0.031
N	-0.702	3.099	0.386
C	2.177	1.244	-0.942
H	1.222	3.912	0.006
H	-1.146	3.934	0.743
H	-0.020	-1.007	-1.003
H	-3.326	2.177	0.969
H	-3.964	-0.160	0.532
H	2.024	0.496	-1.723

H	2.767	2.057	-1.370
C	3.014	0.603	0.182
O	-2.262	-1.984	-0.522
C	-3.553	-2.525	-0.246
H	-3.502	-3.568	-0.545
H	-3.775	-2.451	0.819
H	-4.315	-2.005	-0.830
H	3.960	0.274	-0.251
H	3.227	1.343	0.953
N	2.380	-0.527	0.810
H	1.913	-0.396	1.692
C	2.382	-1.757	0.256
O	2.913	-1.977	-0.828
C	1.696	-2.839	1.042
H	1.211	-2.473	1.947
H	0.953	-3.321	0.405
H	2.436	-3.594	1.315

Obtained at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

Table S5. Cartesian Coordinates (in Å of the ground state of the molecular system (IV).

Atom	x	y	z
C	-2.160	-0.777	-0.332
C	-0.946	-0.264	-0.754
C	-0.556	1.015	-0.325
C	-1.422	1.777	0.533
C	-2.639	1.231	0.938
C	-3.008	-0.037	0.511
C	0.582	1.839	-0.537
C	0.311	3.000	0.192
N	-0.876	2.994	0.838
C	1.827	1.501	-1.292
H	0.966	3.866	0.261
H	-0.323	-0.865	-1.411
H	-3.303	1.793	1.589
H	-3.955	-0.450	0.836
H	1.587	0.882	-2.165
H	2.300	2.411	-1.675
C	2.867	0.763	-0.448
O	-2.472	-2.035	-0.792
C	-3.682	-2.608	-0.357
H	-3.735	-3.596	-0.812
H	-3.710	-2.713	0.732
H	-4.549	-2.019	-0.680

H	3.716	0.439	-1.055
H	3.251	1.434	0.328
N	2.277	-0.408	0.158
H	1.297	-0.345	0.395
C	2.943	-1.535	0.437
O	4.146	-1.679	0.210
C	2.124	-2.641	1.052
H	1.065	-2.395	1.134
H	2.237	-3.541	0.445
H	2.518	-2.861	2.046

Obtained at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

Table S6. Cartesian Coordinates (in Å) of the ground state of O_2.

Atom	x	y	z
O	0.000	0.000	0.598
O	0.000	0.000	-0.598

Obtained at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

Table S7. Cartesian Coordinates (in Å) of the ground state of the O_2^- (GS).

Atom	x	y	z
O	0.000	0.000	0.662
O	0.000	0.000	-0.662

Obtained at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

Table S8. Cartesian Coordinates (in Å) of the 1st EE of the molecular system (I)

Atom	x	y	z
C	-2.083	-0.488	-0.286
C	-0.762	-0.226	-0.638

C	-0.228	1.034	-0.335
C	-1.018	2.032	0.300
C	-2.324	1.769	0.639
C	-2.860	0.495	0.344
C	1.042	1.615	-0.521
C	0.917	2.952	0.021
N	-0.274	3.220	0.504
C	2.268	0.981	-1.054
H	1.715	3.689	0.040
H	-0.179	-0.994	-1.138
H	-2.945	2.514	1.128
H	-3.890	0.291	0.613
H	2.012	0.215	-1.793
H	2.904	1.726	-1.544
C	3.108	0.313	0.058
O	-2.542	-1.730	-0.594
C	-3.879	-2.053	-0.253
H	-4.030	-3.081	-0.583
H	-4.039	-1.991	0.828
H	-4.591	-1.398	-0.768
H	3.976	-0.162	-0.404
H	3.464	1.067	0.764
N	2.378	-0.683	0.806
H	1.932	-0.405	1.667
C	2.131	-1.920	0.325
O	2.573	-2.298	-0.765
C	1.277	-2.811	1.188
H	1.069	-2.390	2.174
H	0.327	-2.989	0.676
H	1.776	-3.776	1.306

Obtained at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

Table S9. Cartesian Coordinates (in Å) of the 1st EE of the molecular system (II).

Atom	x	y	z
C	-2.060	-0.643	-0.256
C	-0.713	-0.291	-0.596
C	-0.301	1.022	-0.297
C	-1.214	1.931	0.257
C	-2.536	1.609	0.559
C	-2.946	0.250	0.301
C	0.938	1.717	-0.478
C	0.739	3.044	-0.034

N	-0.539	3.127	0.396
C	2.205	1.148	-0.971
H	1.417	3.879	0.014
H	-0.954	3.971	0.765
H	-0.063	-1.031	-1.045
H	-3.222	2.327	0.988
H	-3.955	-0.048	0.547
H	2.009	0.385	-1.730
H	2.824	1.928	-1.424
C	3.038	0.495	0.153
O	-2.355	-1.934	-0.540
C	-3.659	-2.390	-0.244
H	-3.691	-3.437	-0.542
H	-3.870	-2.306	0.826
H	-4.409	-1.824	-0.805
H	3.962	0.115	-0.282
H	3.292	1.243	0.905
N	2.366	-0.593	0.812
H	1.783	-0.388	1.606
C	2.305	-1.832	0.281
O	2.884	-2.122	-0.762
C	1.516	-2.848	1.060
H	0.975	-2.418	1.902
H	0.809	-3.336	0.388
H	2.204	-3.612	1.432

Obtained at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

Table S10. Cartesian Coordinates (in Å) of the 1st EE of the molecular system (III).

Atom	x	y	z
C	-2.071	-0.509	-0.271
C	-0.710	-0.235	-0.607
C	-0.208	0.996	-0.310
C	-1.058	1.964	0.299
C	-2.398	1.699	0.630
C	-2.899	0.459	0.344
C	1.089	1.626	-0.500
C	0.955	2.888	-0.021
N	-0.329	3.079	0.455
C	2.303	0.975	-1.058
H	1.672	3.692	0.025
H	-0.665	3.943	0.856
H	-0.132	-1.014	-1.091

H	-3.018	2.455	1.097
H	-3.925	0.223	0.588
H	2.013	0.249	-1.821
H	2.936	1.721	-1.545
C	3.153	0.264	0.002
O	-2.469	-1.717	-0.584
C	-3.812	-2.131	-0.308
H	-3.875	-3.153	-0.669
H	-4.000	-2.098	0.764
H	-4.517	-1.497	-0.845
H	3.980	-0.243	-0.496
H	3.571	0.998	0.691
N	2.424	-0.702	0.791
H	2.139	-0.448	1.722
C	2.084	-1.916	0.322
O	2.365	-2.274	-0.818
C	1.333	-2.810	1.270
H	1.134	-2.346	2.236
H	0.386	-3.097	0.809
H	1.914	-3.721	1.425

Obtained at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

Table S11. Cartesian Coordinates (in Å) of the 1st EE of the molecular system (IV).

Atom	x	y	z
C	-2.022	-0.060	-0.315
C	-0.657	-0.073	-0.731
C	0.116	1.029	-0.339
C	-0.436	2.146	0.300
C	-1.804	2.200	0.602
C	-2.577	1.023	0.329
C	1.504	1.343	-0.535
C	1.669	2.655	-0.013
N	0.534	3.134	0.496
C	2.529	0.413	-1.048
H	2.595	3.216	0.035
H	-0.244	-0.942	-1.228
H	-2.245	3.043	1.121
H	-3.624	1.013	0.606
H	2.096	-0.223	-1.825
H	3.375	0.955	-1.483
C	3.078	-0.499	0.072
O	-2.710	-1.196	-0.646

C	-4.073	-1.250	-0.296
H	-4.440	-2.219	-0.633
H	-4.209	-1.167	0.787
H	-4.644	-0.455	-0.787
H	3.708	-1.269	-0.376
H	3.695	0.092	0.751
N	2.057	-1.145	0.861
H	1.603	-0.569	1.555
C	1.322	-2.181	0.378
O	1.644	-2.787	-0.650
C	0.184	-2.625	1.252
H	-0.263	-1.794	1.801
H	-0.579	-3.100	0.637
H	0.546	-3.361	1.980

Obtained at PBE0-GD3(BJ)/6-311++G(2d,p) using IEFPCM(water) to describe the solvent effect.

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