

Glucocorticoids in Freshwaters: Degradation by Solar Light and Environmental Toxicity of the Photoproducts

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Table S1. NUTRIENT BROTH FOR BIOLUMINESCENT BACTERIA ASSAY (final volume 500 mL, pH=7).

NaCl	g	15
Peptone	g	2.5
Yeast extract	g	1.5
Glycerol	mL	1.5
HEPES	M	0.01

Table S2. JAWORSKI'S CULTURE MEDIUM FOR ALGAL GROWTH INHIBITION ASSAY.

(Ca(NO ₃) ₂ ·4H ₂ O	g L ⁻¹	20
KH ₂ PO ₄	g L ⁻¹	12.4
MgSO ₄ ·7H ₂ O	g L ⁻¹	50
NaHCO ₃	g L ⁻¹	15.9
EDTAFNa	g L ⁻¹	2.25
EDTANa ₂	g L ⁻¹	2.25
H ₃ BO ₃	g L ⁻¹	2.48
[(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O]	g L ⁻¹	1
MnCl ₂ ·4H ₂ O	g L ⁻¹	1.4
cyanocobalamin	g L ⁻¹	0.04
biotin	g L ⁻¹	0.04
thiamine	g L ⁻¹	0.04
NaNO ₃	g L ⁻¹	80
NaH ₂ PO ₄ ·2H ₂ O	g L ⁻¹	36

Table S3. OPTIMIZED MRM CONDITIONS FOR THE HPLC-ESI-MS/MS ANALYSIS.

Target ^a	Parent peak ^b (m/z)	MRM product ions (m/z)	Dwell time	Fragmentor Energy (V)	Collision Energy (V)
CORT	419	359.4	50	91	0
		329.4	50	91	8
HCORT	421.5	331.4	50	91	12
		297.3	50	91	36
PRED	417	357.3	50	81	0
		327.3	50	81	8
PREDLO	419	329.3	50	116	12
		295.3	50	116	32
BETA	451.5	361.4	50	106	12
		307.3	50	106	32
DEXA	451.5	361.4	50	91	12
		307.3	50	91	32
TRIAM	493.5	413.4	80	133	16
		59	80	133	24

^a retention time (min): CORT 3.84; H-CORT 4.61; PRED 3.52; PREDLO 4.59; BETA 6.33; DEXA 6.33; TRIAM 6.72. ^b [M+AcO]⁻ adduct.

Table S4. FRAGMENTATION OF PHOTOLYTIC PRODUCTS OF CORT ([M+1]⁺=361)

Fragment	HPLC-ESI-MS/MS							
	28,94		28,47		31,92		27,25	
	m/e	Int%	m/e	Int%	m/e	Int%	m/e	Int%
[M+1] ⁺	361,16	10	377,28	0	375,4	0	379,31	0
[M+1] ⁺ -H ₂ O	343,11	100	359,13	70			361,33	100
[M+1] ⁺ -H ₄ O ₂	325,10	70	341,04	100				
[M+1] ⁺ -CO ₂					330,75	15		
[M+1] ⁺ -CH ₂ O ₂	315,10	10						
[M+1] ⁺ -CH ₄ O ₂	313,07	22						
[M+1] ⁺ -H ₆ O ₃	307,09	40	323,13	30				
[M+1] ⁺ -CH ₄ O ₃			313,19	20				
[M+1] ⁺ -C ₂ H ₆ O								
[M+1] ⁺ -C ₃ H ₂ O								
[M+1] ⁺ -C ₃ H ₆ +H ₂ O								
[M+1] ⁺ -C ₅ H ₄								

[M+1] ⁺ -C ₃ H ₆ O										
[M+1] ⁺ -C ₂ H ₆ O ₂	299,10	38								
[M+1] ⁺ -CH ₄ O ₃						311,16	20			
[M+1] ⁺ -CH ₆ O ₃	295,12	24								
[M+1] ⁺ -C ₂ H ₂ O ₃						301,06	100			
[M+1] ⁺ -C ₂ H ₄ O ₃	285,06	26								
[M+1] ⁺ -C ₃ H ₈ O ₂										
[M+1] ⁺ -C ₂ H ₆ O ₃	283,11	40	299,08	22						
[M+1] ⁺ -C ₃ H ₈ O ₃						283,37	100			
[M+1] ⁺ -CH ₆ O ₄			295,14	40						
[M+1] ⁺ -C ₂ H ₈ O ₄			281,05	22						
[M+1] ⁺ -C ₂ H ₁₀ O ₃	279,12	22								
[M+1] ⁺ -C ₂ H ₆ O ₄	267,10	38								
[M+1] ⁺ -C ₆ H ₆ O ₂						265,18	80			
[M+1] ⁺ -C ₂ H ₈ O ₄	265,11	34								
[M+1] ⁺ -C ₂ H ₁₂ O ₅								281,28	30	
[M+1] ⁺ -C ₉ H ₆										
[M+1] ⁺ -C ₈ H ₆ O										
[M+1] ⁺ -C ₁₂ H ₁₃										
[M+1] ⁺ -C ₁₀ H ₁₂ O ₂								215,48	60	

Table S5. FRAGMENTATION OF PHOTOLYTIC PRODUCTS OF HCORT ([M+1]⁺=363)

Fragment	HPLC-ESI-MS/MS									
	32,13		28,91		32,11		28,02		29,31	
	m/e	int%	m/e	Int%	m/e	Int%	m/e	Int%	m/e	Int%
[M+1] ⁺	303,2	0	362,9	1	377,3	0%	379,2	2	361,1	4
[M+1] ⁺ -CH ₃					363,08	10				
[M+1] ⁺ -OH										
[M+1] ⁺ -H ₂ O	285,06	100	345,17	40			361,12	10	343,07	100
[M+1] ⁺ -H ₃ O ₂										
[M+1] ⁺ -H ₄ O ₂	267,13	60	327,12	100			343,11	100	325,06	70
[M+1] ⁺ -CH ₂ O ₂	256,95	20			331,11	24				
[M+1] ⁺ -H ₆ O ₃	249,21	20	309,13	80			325,09	70	307,11	52
[M+1] ⁺ -CH ₂ O ₃									299,06	40
[M+1] ⁺ -CH ₄ O ₃					3131,4	20	315,16	22		
[M+1] ⁺ -H ₈ O ₄							307,11	28		
[M+1] ⁺ -CH ₆ O ₃			297,11	30						

[M+1] ⁺ -CH ₃ O ₄	239,07	40				
[M+1] ⁺ -CH ₆ O ₄			281,09	28	297,09	62
[M+1] ⁺ -H ₁₀ O ₅					289,14	10
[M+1] ⁺ -C ₂ H ₆ O ₃						283,07 40
[M+1] ⁺ -C ₂ H ₅ O ₄	225,09	10				
[M+1] ⁺ -C ₂ H ₈ O ₄			267,12	30		
[M+1] ⁺ -C ₂ H ₈ O ₅			251,16	12		265,1 44
[M+1] ⁺ -C ₃ H ₄ O ₂						
[M+1] ⁺ -C ₃ H ₇ O ₄	211,08	6				
[M+1] ⁺ -C ₃ H ₈ O ₄					283,12	30
[M+1] ⁺ -H ₁₂ O ₆					279,17	28
[M+1] ⁺ -C ₃ H ₆ O ₆						239,11 20
[M+1] ⁺ -CH ₁₄ O ₆					265,14	6
[M+1] ⁺ -C ₂ H ₁₆ O ₆					251,12	12
[M+1] ⁺ -C ₃ H ₁₈ O ₆					237,18	8
[M+1] ⁺ -C ₄ H ₂₀ O ₆					223,10	12
[M+1] ⁺ -C ₅ H ₄ O						
[M+1] ⁺ -C ₅ H ₆ O				295,07	22	
[M+1] ⁺ -C ₅ H ₇ O ₂						
[M+1] ⁺ -C ₇ H ₁₀ O				267,10	100	

Table S6. FRAGMENTATION OF PHOTOLYTIC PRODUCTS OF BETA ([M+1]⁺=393)

Fragment	HPLC-ESI-MS/MS					
	30,8		30,0		26,7	
	m/e	Int%	m/e	Int%	m/e	Int%
[M+1] ⁺	392,90	0	407,33	0	411,37	0
[M+1] ⁺ -HF	373,03	100			393,50	20
[M+1] ⁺ -CH ₂ O					381,37	100
[M+1] ⁺ -H ₃ FO	355,10	50				
[M+1] ⁺ -H ₅ FO ₂	337,09	20				
[M+1] ⁺ -CHFO ₂			343,41	20		
[M+1] ⁺ -CH ₃ FO ₂			340,99	80		
[M+1] ⁺ -H ₇ FO ₃	319,12	12				
[M+1] ⁺ -C ₃ H ₆ O ₂					337,17	50
[M+1] ⁺ -C ₂ H ₂ O ₃			333,23	100		
[M+1] ⁺ -C ₂ H ₇ FO ₄	279,14	10				

Table S7. FRAGMENTATION OF PHOTOLYTIC PRODUCTS OF DEXA ([M+1]⁺=393)

Fragment	HPLC-ESI-MS/MS					
	31,7		30,9		26,9	
	m/e	Int%	m/e	Int%	m/e	Int%
[M+1] ⁺	379,33	0	392,98	0	411,40	0
[M+1] ⁺ -H ₂ O	361,13	25				
[M+1] ⁺ -HF	359,22	100	372,99	100		
[M+1] ⁺ -CH ₂ O					381,33	100
[M+1] ⁺ -H ₃ FO	341,30	60	355,07	50		
[M+1] ⁺ -H ₄ O ₂					375,17	15
[M+1] ⁺ -H ₅ FO ₂	323,41	20	337,08	30		
[M+1] ⁺ -CH ₄ O ₂					363,13	40
[M+1] ⁺ -H ₆ O ₃					357,49	15
[M+1] ⁺ -CH ₆ O ₃					345,17	20
[M+1] ⁺ -CH ₅ FO ₂			325,05	10		
[M+1] ⁺ -H ₇ FO ₃			319,10	18		
[M+1] ⁺ -CH ₅ FO ₃	295,34	15	309,06	10		
[M+1] ⁺ -CH ₇ FO ₃					325,32	25
[M+1] ⁺ -H ₉ FO ₄			301,15	6		
[M+1] ⁺ -C ₂ H ₇ FO ₃	280,99	20				
[M+1] ⁺ -CH ₇ FO ₄	277,30	40	291,13	10		

Table S8. FRAGMENTATION OF PHOTOLYTIC PRODUCTS OF PRED ([M+1]⁺=359)

Fragment	HPLC-ESI-MS/MS											
	29,49		32,6		28,0		31,9		28,6		26,0	
	m/e	Int%	m/e	Int%	m/e	Int%	m/e	Int%	m/e	Int%	m/e	Int%
[M+1] ⁺	358,80	1	299,01	1	317,39	0	373,38	0	375,13	0	377,07	2
[M+1] ⁺ -H ₂ O	341,01	100	281,02	100	299,25	60	355,50	40	357,08	100	358,99	100
[M+1] ⁺ -CO			271,02	60								
[M+1] ⁺ -CH ₂ O											347,03	4
[M+1] ⁺ -H ₄ O ₂	323,08	44	263,11	68	281,35	40	337,43	10	339,01	80	341,06	14
[M+1] ⁺ -CH ₂ O ₂	313,04	46	253,02	40			327,43	45				
[M+1] ⁺ -CH ₄ O ₂					269,45	25					329,03	2
[M+1] ⁺ -H ₆ O ₃	305,01	30							321,09	42	323,08	4
[M+1] ⁺ -C ₂ H ₂ O ₂			240,93	2								
[M+1] ⁺ -C ₂ H ₄ O ₂									315,03	40	317,10	20
[M+1] ⁺ -CH ₄ O ₃	295,08	32					309,33	70	311,04	82		
[M+1] ⁺ -CH ₆ O ₃									308,94	4		
[M+1] ⁺ -C ₂ H ₂ O ₃							299,25	60				

Figure S1. Tap water solutions fortified with 50 µg L⁻¹ of each GCs and kept in the dark at room temperature for a monitoring period of 3 hours for PRED (□) and PREDLO (+), 5 hours for BETA (×), DEXA (Δ) and TRIAM(○), 16 hours for CORT (◇) and HCORT(*).

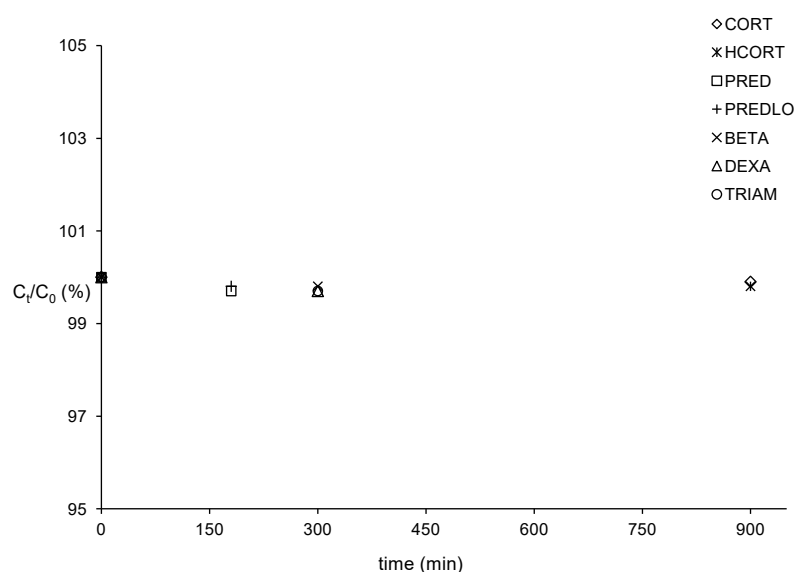


Figure S2. HPLC-UV chromatogram of BETA (black line) in presence of the maximum amount of photoproducts (red line) (a); photodegradation profile of BETA and evolution profile of the generated photoproducts verified by HPLC-UV (b) (90 minutes irradiation).

