Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information for

Evaluation of the Effect of *Moringa peregrina* bark on the Crystal Habit and Size of Calcium Oxalate Monohydrate Crystals in Different Stages of Crystallization using Experimental and Theoretical Methods†

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1. SAMPLING

Sample	*Moringa peregrina* bark
Date/time	19/Sep/2019/ 11.00 AM
Place	Al-Waariya in (Almudabi) in north AL-Sharqiya governorate, Sultanate of Oman (22° 32´ 13° N and 58° 27´21°)
Number & size	6 trees located on the slopes of Al Waariya valley or by the constructed road. The height ranged from 2 to 5 m
Drying method	Natural 35°C
Storage method before grinding	Paper bag
Storage method after grinding.	Glass container

Table S1. Sampling of *Moringa peregrina* bark

Figure S1. *Moringa peregrina* tree in Al Waariya valley

2. **LC-MS**

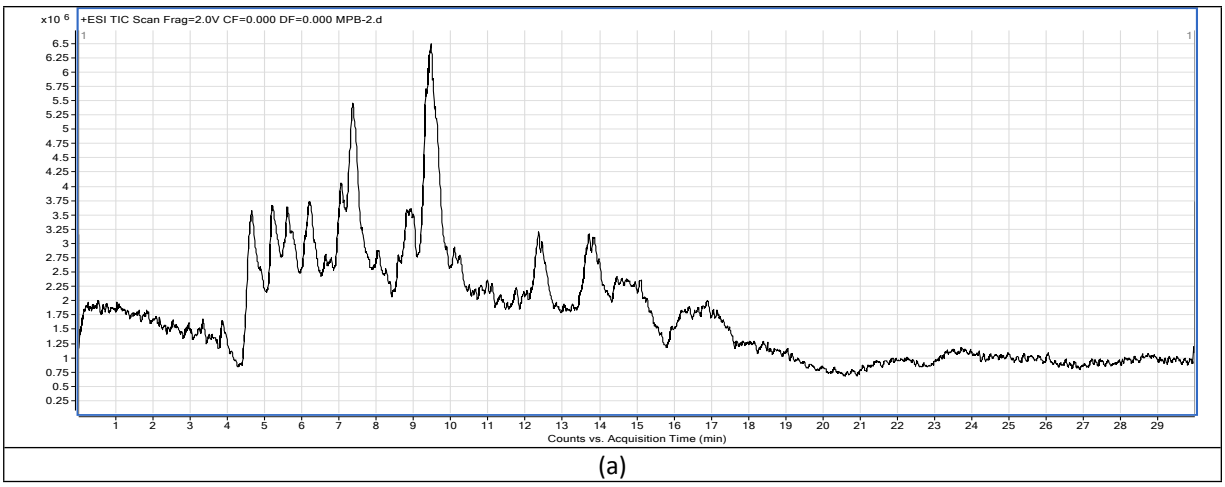
LC-MS analysis of the 7.5 mg ml^{-1} bark extract was carried out using Agilent Technologies Triple Quad LC/MS system, equipped with 6460 Triple Quad MS Detector, a High Performance Autosampler (G4226A), Quaternary Pump (G4204A), Diode Array Detector (DAD) (G4212A) and Thermostatted Column Compartment (G1316C) under ESI positive as well as negative conditions using the column Waters Resolve 5µm Spherical C18, 3.9X150mm, Part No: WAT085711.

Mobile phase: Containing 0.1% formic acid (v/v) in water (A) and 0.1% formic acid (v/v) in acetonitrile (B) used in isocratic elution with 70% A

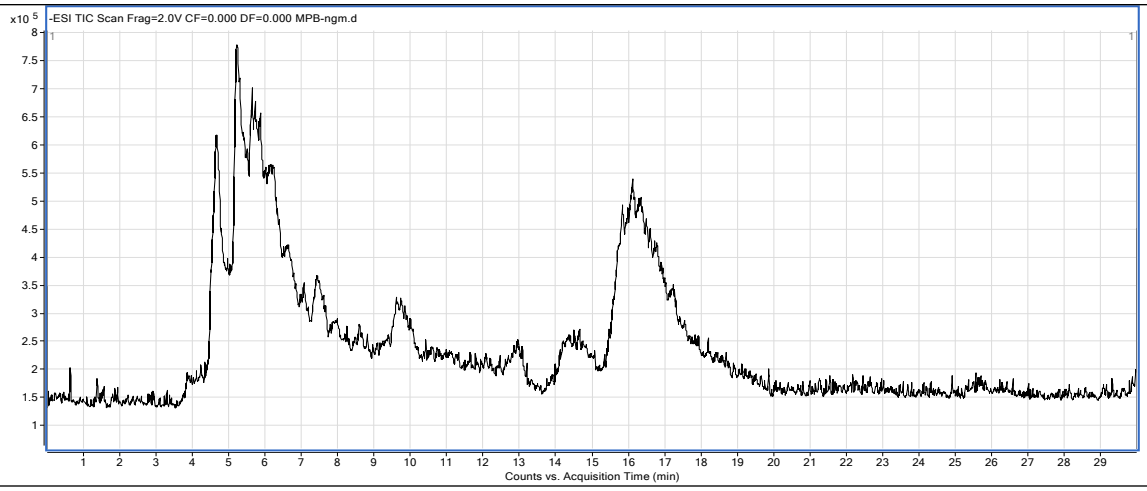
Column used: Waters Resolve 5µm Spherical C18, 3.9X150mm, Part No: WAT085711, Column temperature: 25^{o}C, Injection volume: 20 µL, Flow rate: Flow: 0.200 ml/min, Eluent monitoring: ESI-MS under positive ion and negative ion mode scanned, Time filter width: 0.07 min, Gas temperature: 300^{o}C, Gas flow rate: 5L/min, Nebulization: At 50 psi, Gas used: Nitrogen, Scan Time 150 min, Data acquisition: Agilent Mass Hunter

The wavelengths set for the DAD UV-visible set-up were 254 nm, 282 nm and 370 nm.

Chromatograms:



(a)



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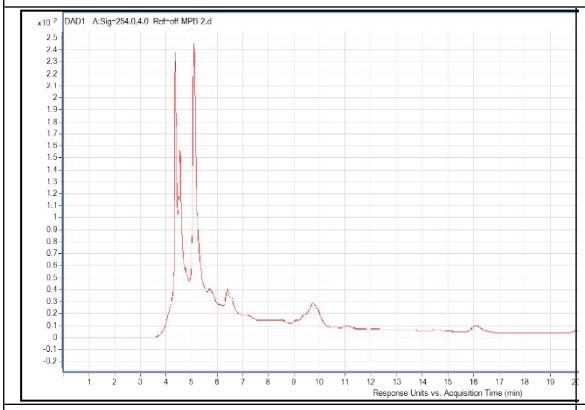
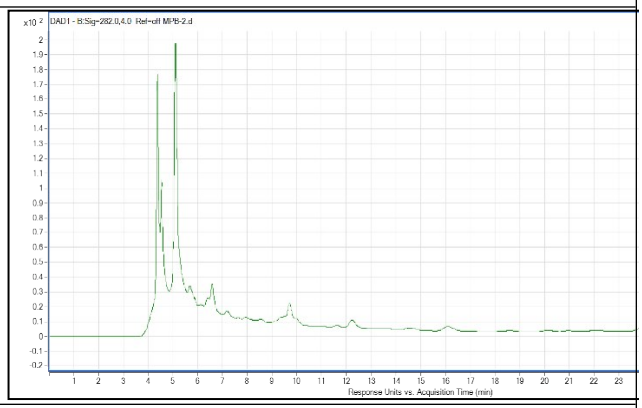
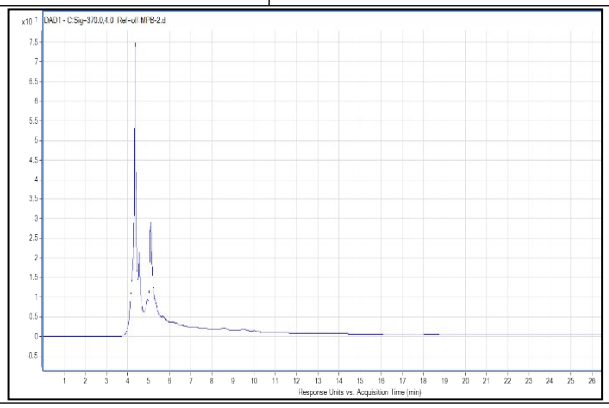


λ = 254 nm



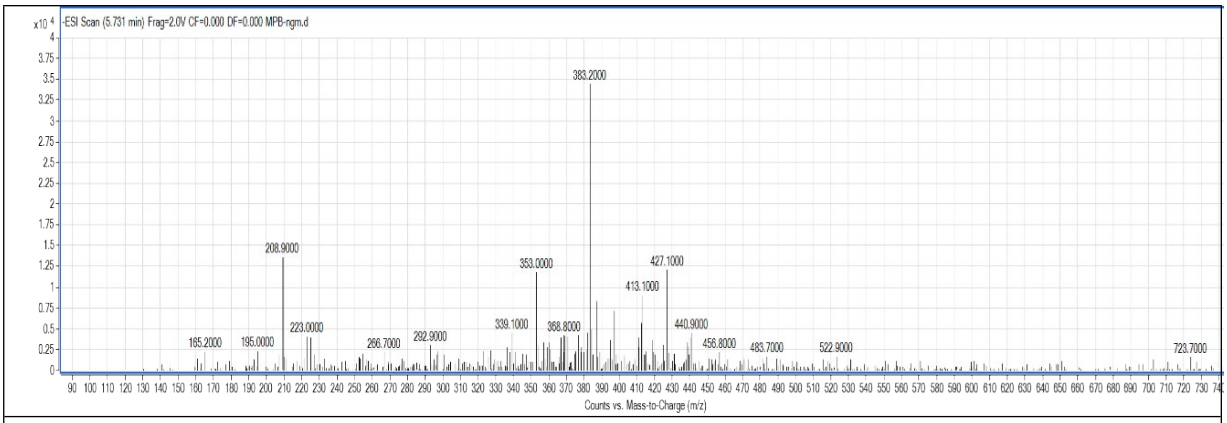
λ = 282 nm



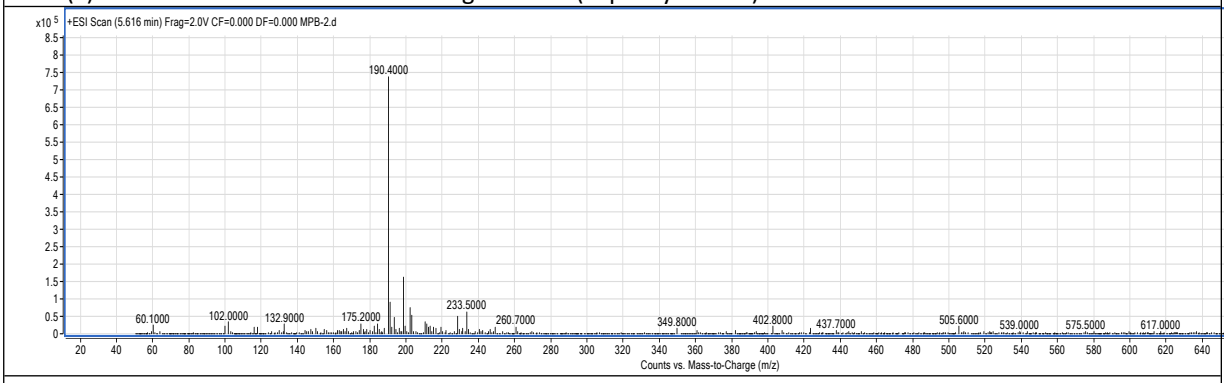
λ = 370 nm

(c)

(i) Time = 5.73 min : Vicenin 2 (% purity = 14.5%)

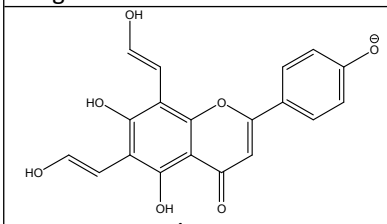


(ii) Time = 5.61 min: Neochlorogenic acid (% purity = 8.2%)

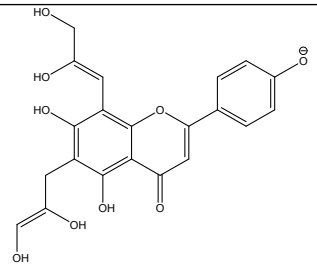


(d)

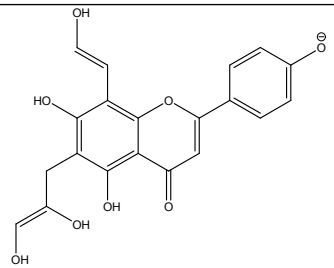
Fragments of vicenin 2



m/z = 383

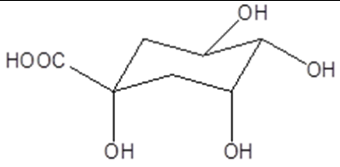


m/z = 413



m/z = 353

Fragments of neochlorogenic acid



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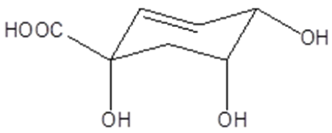


m/z =173

(e)

Figure S2. LCMS Analysis of *M. peregrina* bark extract (a) ESI Positive: Chromatogram (b) ESI Negative Chromatogram (c) UV Data against time in minutes (d) Assigned Mass Spectra (e) Fragments of assigned molecules

3. TURBIDITY MEASUREMENTS

Table S2A. Turbidity (NTU) vs Time (min)

	A			B			C		
Time	1 mg/ml	2 mg/ml	0 mg/ml	1 mg/ml	2 mg/ml	0 mg/ml	1 mg/ml	2 mg/ml	0 mg/ml
10	0.70	0.41	1.82	0.79	0.31	1.69	0.34	0.19	1.54
20	1.35	0.73	4.50	1.58	0.84	4.94	2.06	0.33	5.84
30	2.08	1.43	7.00	2.10	1.58	7.35	1.73	1.29	5.96
40	3.61	1.71	8.08	3.68	1.89	8.93	2.59	2.01	7.60
50	4.25	3.82	12.51	4.57	4.22	13.70	4.17	3.75	12.77
60	2.56	0.95	6.77	2.73	1.05	7.90	2.18	1.03	6.33
70	2.69	1.44	7.01	2.84	1.31	8.40	2.25	2.46	6.71
80	2.80	1.38	6.50	2.99	1.52	7.35	2.64	1.93	6.64
pH	5.80	5.70	5.72	5.68	5.40	5.70	5.83	5.58	5.68

Table S2B. Average Turbidity (NTU) vs Time (min)

Time	1 mg/ml	2 mg/ml	0 mg/ml
10	0.61	0.35	1.68
20	1.66	0.63	5.09
30	1.97	1.43	6.77
40	3.29	1.87	8.20
50	4.33	3.93	12.99
60	2.49	1.01	7.00
70	2.59	1.74	7.37
80	2.81	1.61	6.83

Av pH	5.77	5.56	5.70

4. CHARACTERIZATION OF CALCIUM OXALATE MONOHYDRATE

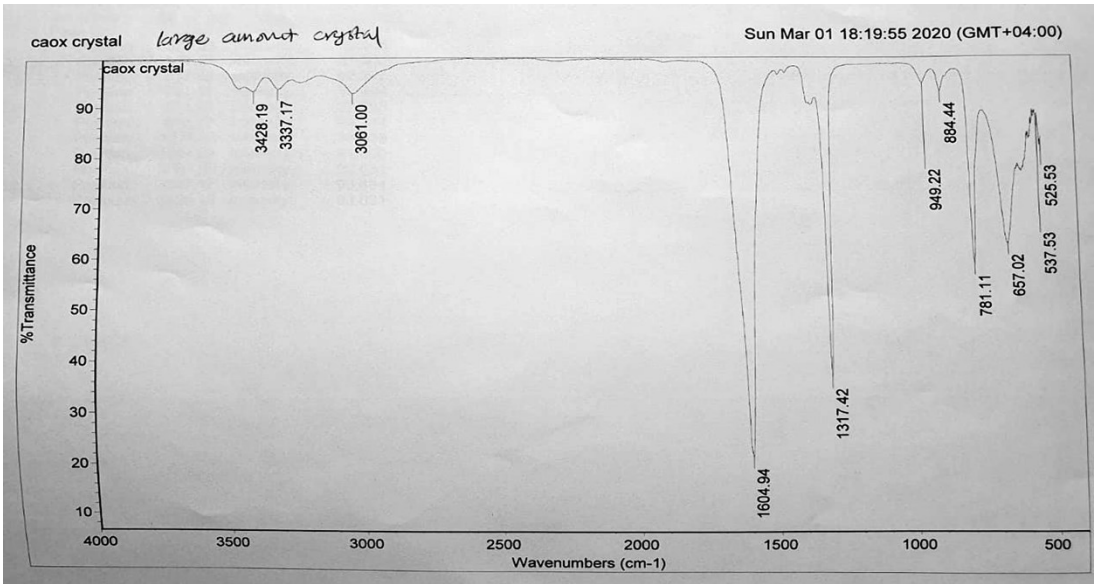


Figure S3. FT-IR of Calcium Oxalate Monohydrate

Table S3. FT-IR peaks of Calcium Oxalate Monohydrate
Region: 4000.00 400.00; Absolute threshold: 99.624

Sensitivity: 60

Position cm^{-1}	Intensity	Position cm^{-1}	Intensity
525.53	79.868	1317.42	36.336
537.53	84.902	1604.94	21.000
657.02	62.232	3061.00	92.631
781.11	58.404	3337.17	93.484
884.44	92.793	3428.19	93.031
949.22	94.444		

IR peaks for COM crystal: 3428 cm^{-1}, 3061 cm^{-1} (Symmetric and asymmetric O-H stretching), 1605 cm^{-1}, 1317cm^{-1} (C=O, C-O stretch), 949.36, 884 cm^{-1} (C-Cstretch), 781 cm^{-1}, 657 cm^{-1} (out of plane O-H bending and C-H bending)

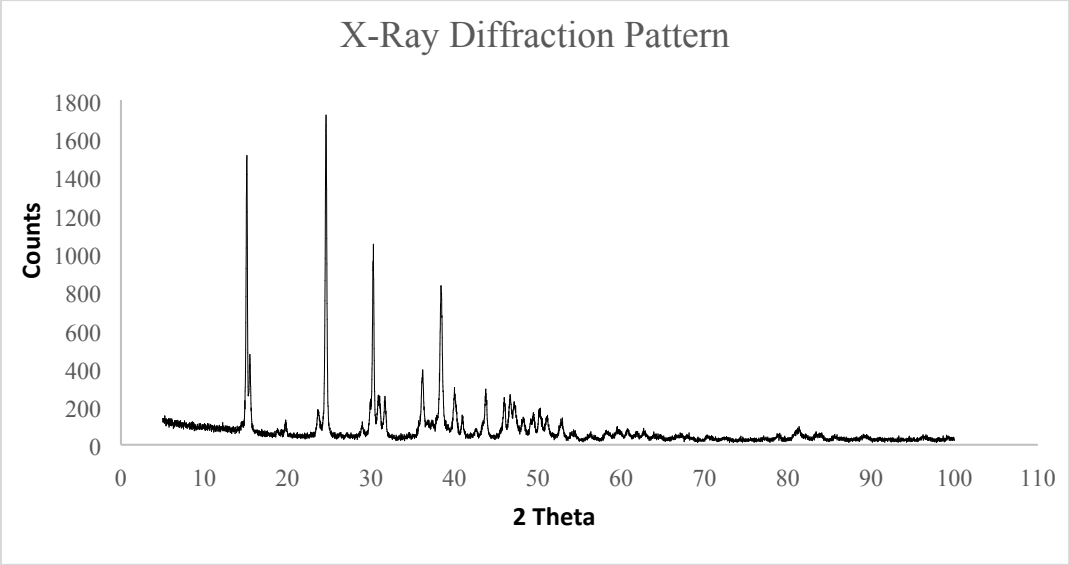


Figure S4. Powder X-Ray Diffraction: pattern of calcium oxalate monohydrate crystals

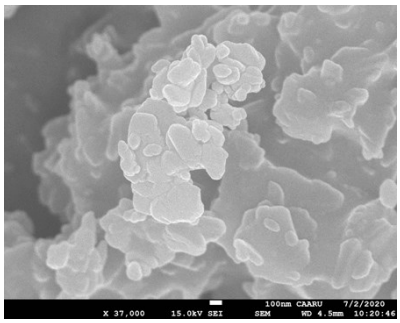


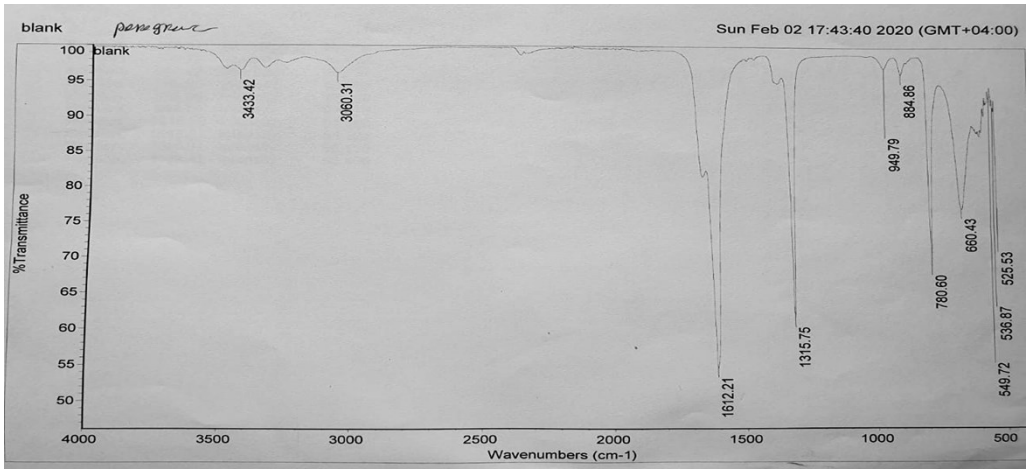
Figure S5. SEM of calcium oxalate monohydrate crystals

Table S4. Lengths of some COM crystals as measured from SEM

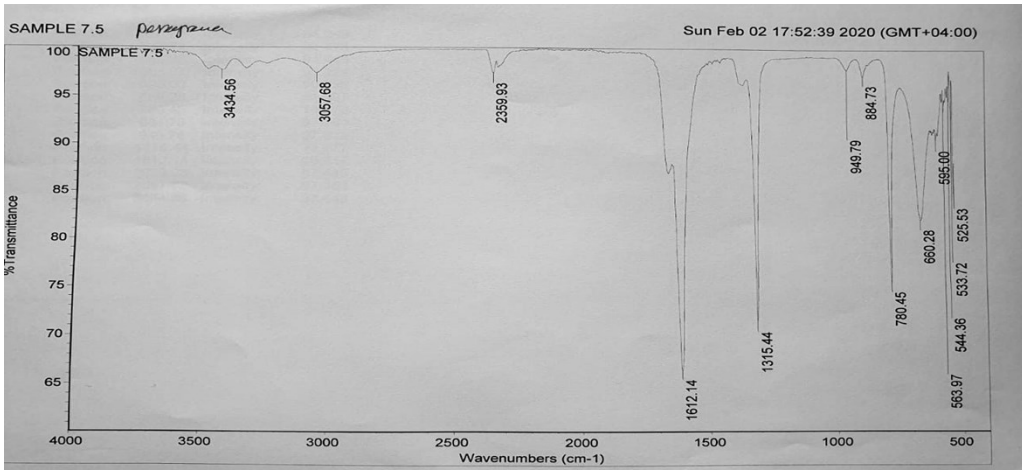
Length in nm		
247.409	448.951	119.109
269.884	221.43	387.432
387.03	250.121	265.75
282.965	239.449	243.745
453.399	307.968	505.172
423.57	329.969	198.306
135.805	475.162	198.459
213.797	353.039	181.426
305.089	417.274	348.253
525.113	137.828	437.774
280.771	188.327	286.081

306.518	148.026

5. CHARACTERIZATION OF PRECIPITATE UNDER VARIOUS CONDITIONS



(a)



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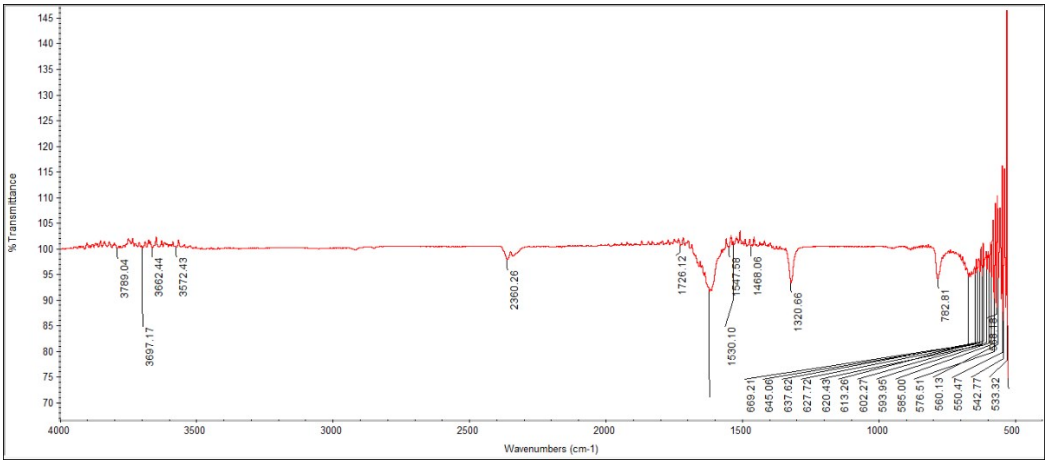

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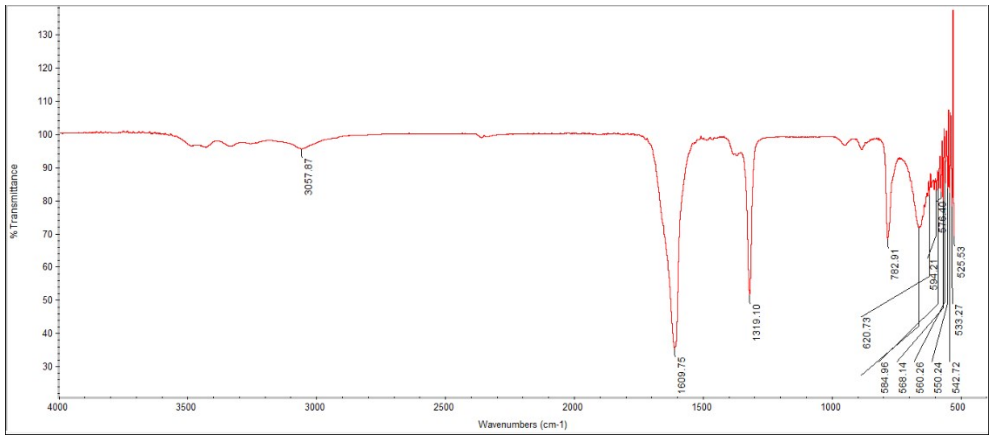
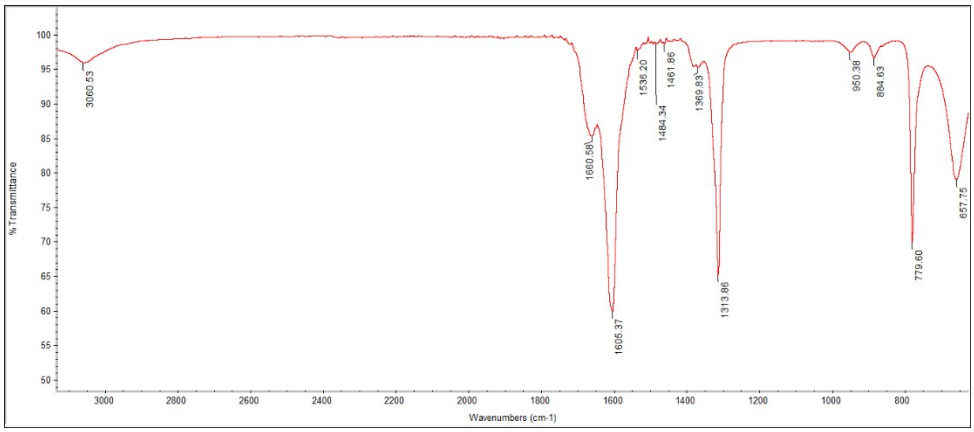


(d)



(e)

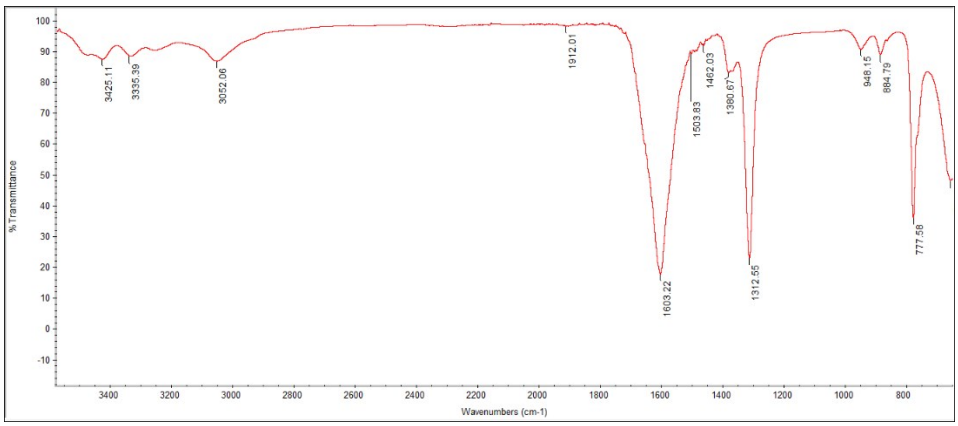


Figure S6. FT IR Spectra of precipitates of different suspensions (a) Control suspension 1 (b) with *M. Peregrina* bark extract 7.5 mg/ml suspension 1 (c) Control Suspension 2 (d)) with *M. Peregrina* bark extract 7.5 mg/ml suspension 2 (e) Control Suspension 3 (f)) with *M. Peregrina* bark extract 7.5 mg/ml suspension 3

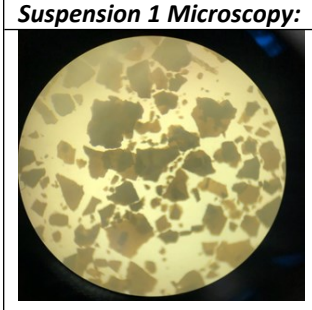
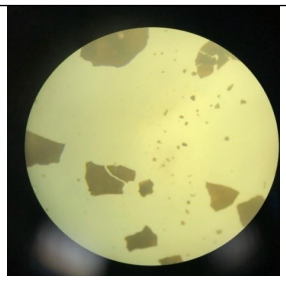
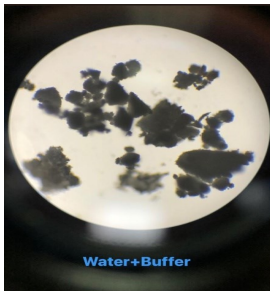
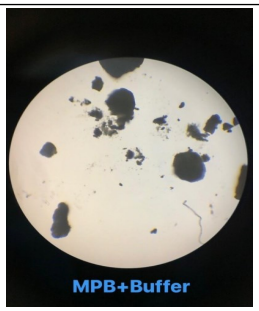
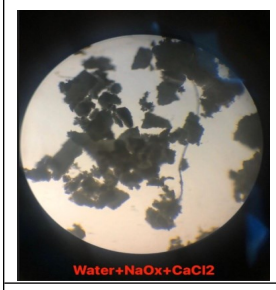
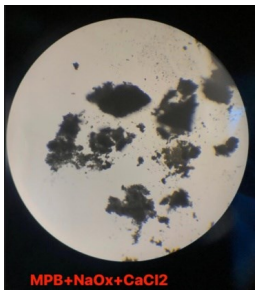
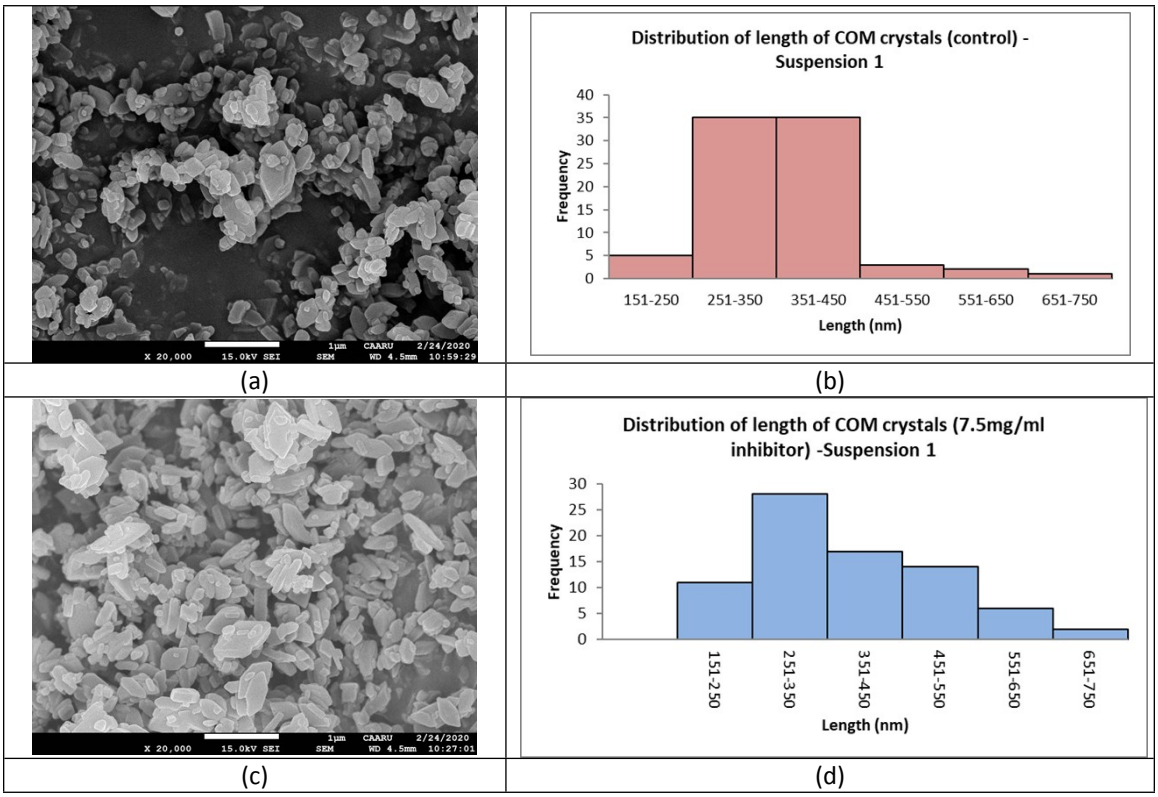
Suspension 1 Microscopy:		***Suspension 2 Microscopy***	
			
(i)Control	(ii) *M. peregrina* bark (7.5 mg/ml)	(i) Control	*(ii) M. peregrina* bark (7.5 mg/ml)
Suspension 3 Microscopy			
			
(i)Control	(ii) *M. peregrina* bark (7.5 mg/ml)		

Figure S7. Microscopy Images of precipitates formed in various suspensions



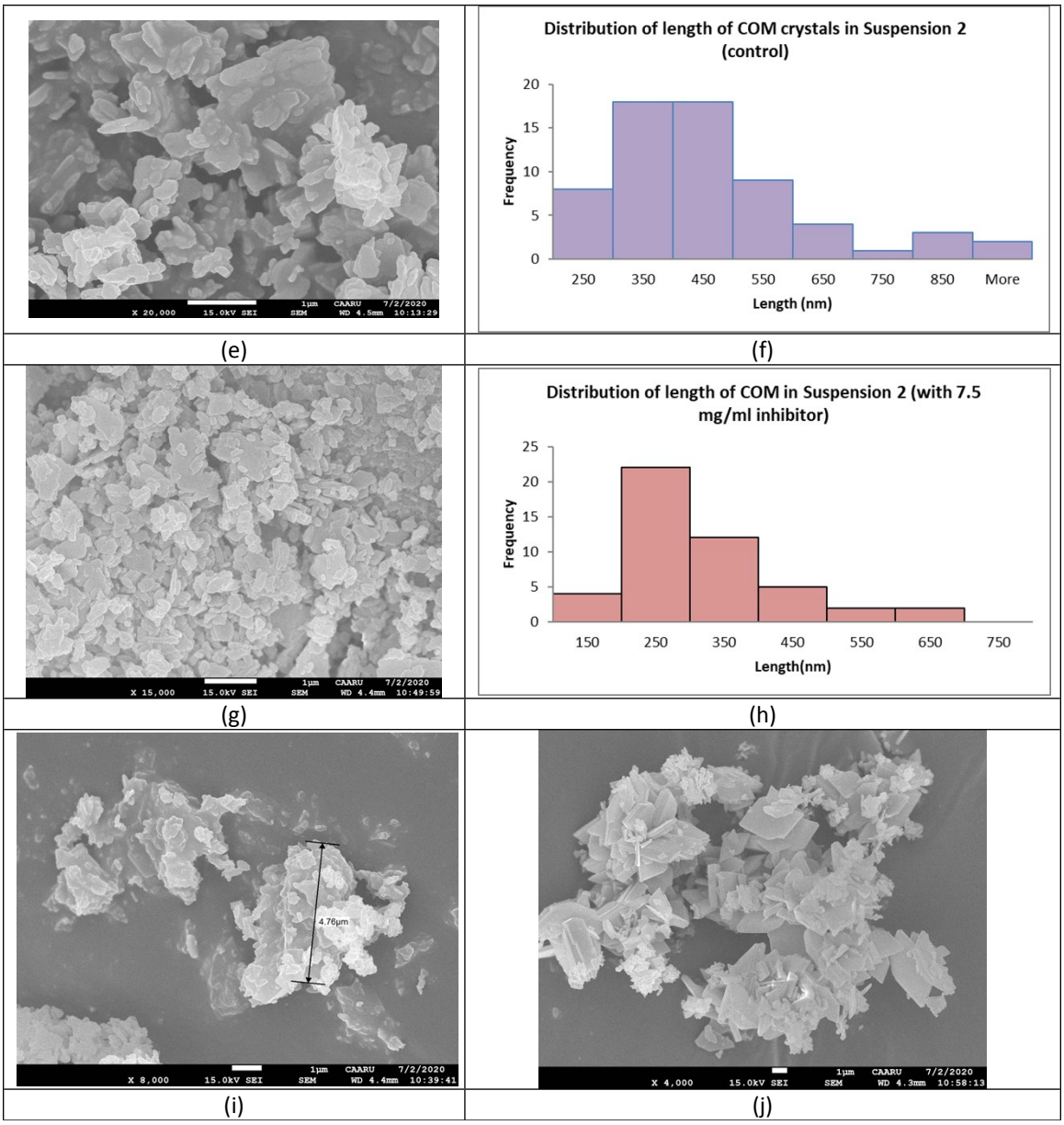
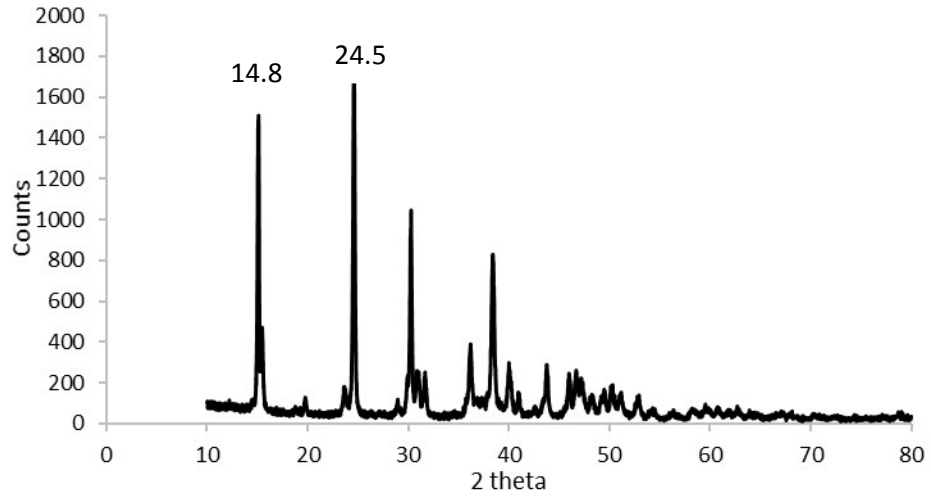
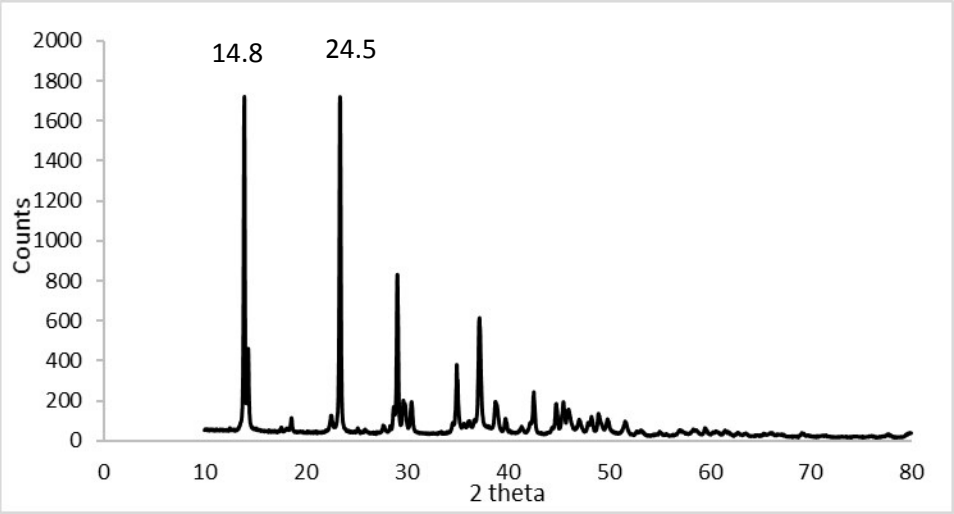


Figure S8. ***SEM Suspension 1*****:** (a) Crystals and (b) Histogram of length of crystals of control of suspension 1. (c) Crystals and (d) Histogram of length of crystals of suspension 1 with *M. peregrina* bark extract. ***SEM Suspension 2*****:** (e) Crystals and (f) Histogram of length of crystals of control of suspension 2. (g) Crystals and (h) Histogram of length of crystals of suspension 2 with *M. peregrina* bark extract. ***SEM Suspension 3*** (i) Crystals of control of suspension 3 (j) Crystals of suspension 3 with *M. peregrina* bark extract.



A.



B.

Figure S9. Powder X-ray Diffraction pattern of A. calcium oxalate monohydrate crystals and B. Crystals grown in Suspension 3 (with inhibitor, M. *peregrina* bark). The spectra have been normalized by equalizing the peaks at 24.5° in both cases.

Table S5. Descriptive statistics of the lengths of the crystals formed under various conditions

	Suspension 1 (Control)	Suspension 1 (*M. peregrina*)	Suspension 2 (Control)	Suspension 2 (*M. peregrina*)
Mean	345.6	378.4	420.8	263.6
Standard Error	9.7	14.7	25.4	16.9
Median	351.0	348.5	378.6	217.8
Mode	367.0	610.0	809.5	216.1
Standard Deviation	87.2	130.2	201.4	116.0
Sample Variance	7612.2	16942.2	40568.9	13456.9
Kurtosis	4.6	-0.2	7.1	2.3
Skewness	1.5	0.6	2.2	1.5
Range	528.0	549.0	1207.4	519.5
Minimum	190.0	161.0	154.2	120.0
Maximum	718.0	710.0	1361.6	639.4
Sum	27996.0	29513.0	26512.5	12390.3
Count	81	78	63	50

6. STRUCTURAL ANALYSIS

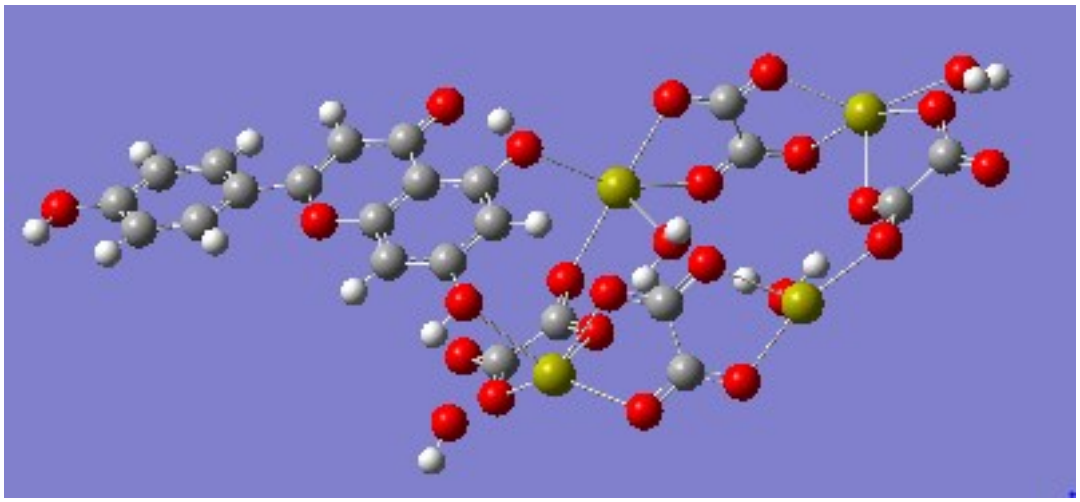


Figure S10. Optimized geometry of complex formed between COM and apigenin through two sites of calcium coordination

Table S6. Coordinates of optimized geometries of the complexes formed between stone unit, apigenin and neochlorogenic acid at B3LYP/6-31G* level of theory

COM-Apigenin-chelation complex NImag=0 HF=-5479.0500233				COM-Apigenin-bridging on Calcium NImag=0 HF=-5479.0326969			
6	-1.846477	-2.48917	0.60237	6	2.94456	-3.191641	-0.362249
6	-1.920105	-2.33301	-0.97313	6	3.12962	-3.092582	1.218734
8	-0.862743	-1.93735	1.164891	8	1.780712	-3.001068	-0.805916
8	-0.905681	-1.90075	-1.56365	8	2.104594	-2.784741	1.887698
8	-2.790716	-3.10672	1.16008	8	3.984189	-3.399436	-1.043057
8	-3.043035	-2.59295	-1.51465	8	4.292453	-3.275663	1.665738
20	-4.770275	-3.30259	-0.07269	20	5.985934	-2.999813	0.074552
20	0.492528	-0.51101	-0.24396	20	0.455533	-1.736437	0.62645
8	2.865446	3.888119	1.105071	8	-3.17535	1.161872	2.628293
8	1.278903	1.622801	0.353063	8	-0.838712	-0.206139	1.865977
6	-3.50462	2.846892	0.921957	6	2.007999	3.061926	-1.113845
6	-3.985546	3.78211	-0.26412	6	2.391433	4.272695	-0.16286
6	1.646382	3.934549	1.076269	6	-2.249181	1.789183	2.146813
6	0.860614	2.800845	0.336046	6	-0.91364	1.039778	1.771317
8	-2.736169	3.342972	1.778522	8	0.802972	2.938277	-1.429948
8	-3.363061	4.868229	-0.39786	8	1.429812	4.932348	0.306892
8	-3.858198	1.626974	0.85517	8	2.934671	2.236611	-1.397202
8	-4.900599	3.329174	-1.00293	8	3.618561	4.420407	0.095504
8	0.858066	4.840721	1.573536	8	-2.208118	3.049588	1.820639
8	-0.220302	3.167483	-0.26886	8	0.027042	1.776436	1.295419
20	-5.295697	1.026989	-0.91759	20	4.902836	2.507192	-0.176015
20	-1.340278	4.952632	0.800556	20	-0.637686	3.798311	0.24803
8	-5.832046	-1.20188	-0.1482	8	6.073733	-0.657745	0.412831
8	-6.910285	-3.55834	-0.97261	8	7.806175	-2.079868	-1.08019
6	-6.942025	-1.1876	-0.835	6	6.874819	-0.007579	-0.347333
6	-7.717007	-2.53982	-0.9249	6	8.07544	-0.818379	-0.949957
8	-7.337909	-0.14276	-1.39669	8	6.744403	1.220378	-0.607487
8	-8.935011	-2.5277	-0.90807	8	9.112609	-0.224705	-1.194925
8	-3.548094	0.108884	-2.2699	8	4.202768	0.967686	1.459996
1	-3.435869	-0.86583	-2.33511	1	4.863262	0.241902	1.291925
1	-2.677912	0.425584	-1.92892	1	3.323863	0.572099	1.263704
8	-1.507652	0.90472	-0.5818	8	1.789689	0.209982	0.206713
1	-2.179626	0.944385	0.13453	1	2.104843	0.617445	-0.629011
1	-1.078753	1.820683	-0.57643	1	1.182423	0.901254	0.633451
8	-5.976117	-5.21721	0.748405	8	8.038435	-4.223297	0.32987
1	-6.32643	-5.66178	1.531963	1	8.699107	-4.580407	0.93808
8	-0.232758	7.076636	0.937362	8	-2.934063	4.934044	0.322886
1	0.045035	7.873809	0.466848	1	-3.323353	5.778275	0.594988

1	0.579539	6.577235	1.220335	1	-3.050837	4.281074	1.08074
1	-6.741004	-4.9167	0.188255	1	8.47097	-3.526434	-0.230716
8	1.718806	-1.80642	1.457007	8	-1.414026	-1.660438	-1.015839
1	1.048692	-2.19022	2.055176	6	-1.922574	0.660645	-1.316854
6	3.005008	-1.96212	1.872807	6	-2.325514	-0.645954	-1.088629
6	4.034328	-1.60882	0.956199	6	-2.894199	1.673255	-1.278392
6	3.820406	-1.13296	-0.41361	8	-2.436371	2.963421	-1.410341
8	2.692701	-0.97518	-0.93805	1	-3.120096	3.608977	-1.133618
6	3.287948	-2.44133	3.139346	1	-0.880584	0.914624	-1.483118
1	2.493695	-2.70176	3.831652	1	-1.988984	-2.516532	-0.958925
6	4.624518	-2.57398	3.549908	6	-4.248987	1.406763	-1.093479
6	5.669366	-2.22963	2.695883	6	-3.691576	-0.964603	-0.89696
1	6.709759	-2.32198	2.990356	6	-4.624145	0.078449	-0.905393
6	5.355668	-1.75701	1.423057	1	-4.992713	2.195364	-1.061241
6	6.264825	-1.00303	-0.63829	6	-4.127495	-2.334001	-0.676118
6	5.017366	-0.84334	-1.16032	6	-6.398198	-1.446871	-0.491284
1	4.884215	-0.45198	-2.16014	6	-5.539829	-2.509583	-0.48147
8	6.429308	-1.45645	0.635728	1	-5.908454	-3.516795	-0.340131
8	4.825828	-3.04553	4.803426	8	-5.950854	-0.175758	-0.709777
1	5.776883	-3.07779	4.993931	8	-3.302182	-3.285919	-0.677514
6	7.537923	-0.72598	-1.30743	6	-7.849421	-1.500994	-0.296746
6	7.602403	-0.55978	-2.70539	6	-8.65966	-0.397602	-0.617021
6	8.728603	-0.61322	-0.56887	6	-8.472038	-2.657279	0.215249
6	8.801808	-0.2822	-3.33998	6	-10.037527	-0.448703	-0.447265
1	6.706788	-0.66707	-3.30828	1	-8.205675	0.505279	-1.007969
6	9.935541	-0.33276	-1.19725	6	-9.844756	-2.716147	0.388952
1	8.705537	-0.73521	0.507755	1	-7.875022	-3.516225	0.502638
6	9.978826	-0.16352	-2.58678	6	-10.638751	-1.609381	0.055246
1	8.852785	-0.16014	-4.41671	1	-10.648771	0.413406	-0.706043
1	10.845714	-0.24004	-0.60835	1	-10.322608	-3.603357	0.790639
8	11.124621	0.110672	-3.26253	8	-11.978392	-1.724601	0.24625
1	11.864462	0.172347	-2.63753	1	-12.416035	-0.896737	-0.00854

COM-Neochlorogenic acid chelation complex
NImag=0
HF=-5822.8530569

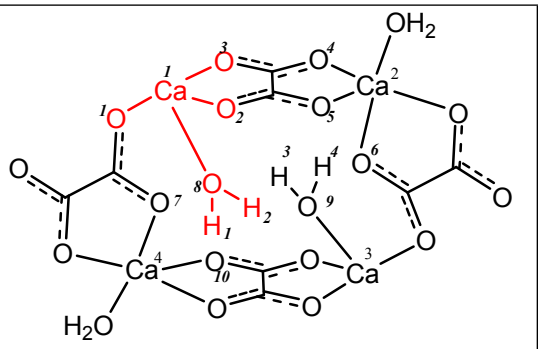
6	-4.38436	-2.80057	0.027875
6	-5.09361	-2.16411	-1.23759
8	-3.1263	-2.8549	-0.02484
8	-4.38577	-1.95315	-2.25051
8	-5.11753	-3.14649	0.989351
8	-6.31608	-1.84167	-1.09974
20	-7.27042	-2.24617	1.031809
20	-2.10171	-1.54942	-1.77532

8	1.327282	0.934754	-2.29156
8	-1.30916	0.338032	-2.97985
6	-3.20166	3.01439	0.960182
6	-3.94645	4.221765	0.251388
6	0.482526	1.847073	-2.2794
6	-1.02562	1.465017	-2.52167
8	-1.94691	3.025676	0.968372
8	-3.21036	5.039421	-0.36384
8	-3.93119	2.053972	1.363928
8	-5.20282	4.211158	0.303296
8	0.67889	3.075853	-2.00002
8	-1.88644	2.311123	-2.09747
20	-6.22607	2.15997	0.795028
20	-1.09984	4.179942	-0.88532
8	-7.13413	0.052731	1.583975
8	-9.24119	-1.53814	2.00262
6	-8.26737	0.635329	1.857956
6	-9.49082	-0.28557	2.226464
8	-8.38577	1.878289	1.774714
8	-10.5103	0.233953	2.639933
8	-5.86008	0.939962	-1.24101
1	-6.28481	0.069754	-1.41182
1	-4.90278	0.725309	-1.30142
8	-3.12891	0.386597	-0.67918
1	-3.22658	0.698048	0.250199
1	-2.79838	1.180455	-1.18176
8	-9.09951	-3.81124	0.821018
1	-9.6267	-4.28884	0.166238
8	1.07087	5.087874	-0.3874
1	1.631007	5.332553	0.362584
1	1.531855	4.380392	-0.89369
1	-9.6883	-3.15777	1.274322
8	-0.83065	-3.62363	-1.05268
1	-1.41267	-3.91996	-0.32513
8	0.330695	-1.42199	-1.76298
1	0.786595	-0.56072	-2.05229
6	1.123622	-2.29257	-1.07217
6	0.491623	-3.47699	-0.65333
6	1.191593	-4.42636	0.077444
6	2.456241	-2.06396	-0.76358
6	2.529397	-4.18957	0.397691
1	3.079126	-4.92801	0.973787
1	2.914494	-1.1354	-1.08901

6	3.181904	-3.01658	-0.01897
1	0.696672	-5.342	0.388832
6	4.585678	-2.82963	0.346065
1	5.032938	-3.62528	0.94015
6	5.38519	-1.79271	0.037016
1	5.057686	-0.9415	-0.55111
6	6.786408	-1.77423	0.505545
8	7.325799	-2.6449	1.165038
8	7.403653	-0.63881	0.098869
6	8.774364	-0.44509	0.510704
6	9.732251	-1.29599	-0.33456
6	9.043206	1.054619	0.368766
1	8.873238	-0.76288	1.550637
6	11.19408	-0.95526	0.019094
1	9.547805	-2.35227	-0.11014
6	10.4958	1.406992	0.698584
1	8.851631	1.36289	-0.66342
1	8.372363	1.612138	1.026706
6	11.45752	0.545702	-0.14009
1	11.84733	-1.50973	-0.67535
1	12.49931	0.777639	0.116626
1	11.30514	0.821017	-1.18872
8	9.49135	-1.00761	-1.71096
1	9.84019	-1.74418	-2.23453
8	11.40818	-1.40034	1.358849
1	12.28921	-1.10415	1.637078
8	10.66212	2.796374	0.383399
1	11.58764	3.025966	0.571511
6	10.74897	1.292463	2.21361
8	9.916438	1.167262	3.078239
8	12.07343	1.47048	2.504749
1	12.12939	1.489912	3.479178

Table S7. A comparison of structural parameters in COM unit before and after binding with apigenin.

Structural parameters	COM unit bond lengths in Å	COM-Apigenin complex bond lengths in Å
Ca1-O2	2.31	2.37
Ca1-O3	2.28	2.35
Ca1-O4	2.34	2.41
Ca1-O8	2.35	2.47
H2-O9	1.92	1.84
Ca1-Ca2	5.77	5.85
Ca2-Ca3	5.73	5.83
Ca3-Ca4	5.66	4.44
Ca4-Ca1	5.62	5.95



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