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Electrochemical oxidation of curcuminoids: an experimental and computational investigation

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Abstract: Curcuminoids, reported to have important biological properties, such as antioxidant, anti-Alzheimer, and antidiabetic properties, comprise curcumin (CRM; 1,7-bis [4-hydroxy-3-methoxyphenyl]-1,6-heptadiene-3,5-dione) and its derivatives demethoxycurcumin (DMC; (E,6E)-1-(3,4-dimethoxy-cyclohexyl)-7-(3,4-dimethoxyphenyl)hepta-1,6-diene-3,5-dione) and bisdemethoxycurcumin (BDMC; 1,7-bis[4-hydroxyphenyl]-1,6-heptadiene-3,5-dione). Their electrochemical oxidations are thoroughly explored by applying cyclic and differential pulse voltammetric techniques. The dependence of current intensities and potentials on pH, concentration, scan rate, and nature of the buffer was investigated. The outcome is supported by density functional theory computations indicating the transfer of 4-e^-/H^+, 6-e^-/H^+, and 8-e^-/H^+ couples involved in the oxidation mechanisms of CRM, DMC, and BDMC, respectively, leading to the formation of the same oxidized product.

Key words: Cyclic voltammetry, curcuminoids, density functional theory, differential pulse voltammetry

1. Introduction

In ancient times, natural products were the basis of traditional medicine.[1] They still play an important role in the drug discovery field due to their close linkage to promising medicinal applications. Turmeric (*Curcuma longa*) is a plant that has a deep-rooted history of medicinal use as well as culinary purposes. After recognition of its importance, comprehensive scientific investigations were devoted to turmeric, focusing on the elaboration of its main bioactive component, curcumin (CRM). Additionally, turmeric contains two more important curcumin derivatives, namely demethoxycurcumin (DMC), with only one MeO unit, and bisdemethoxycurcumin (BDMC), lacking MeO subgroups (Chart). These three compounds known as curcuminoids have been of great interest.

Curcuminoids have been reported as antioxidant, anti-Alzheimer, antidiabetic, antimicrobial, antiinflammatory, and anticancer agents.[2–5] All these properties endow curcuminoids with important clinical applications and distinctive attributes in the search for new drugs. However, it is necessary to reveal the respective quantities of each curcuminoid in turmeric samples as the activities of curcuminoids may differ. Simultaneous determination of the three curcuminoids in turmeric samples was successfully achieved by chromatographic, capillary electrophoretic, and spectroscopic techniques.[6–10]

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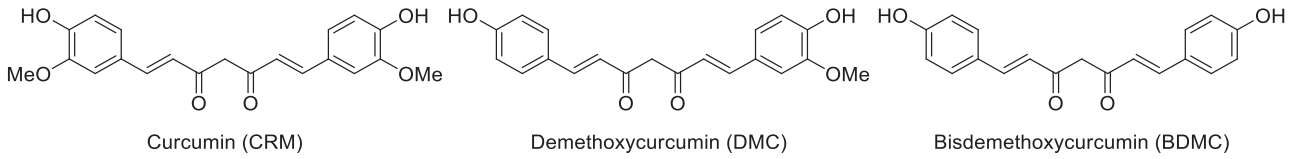


Chart. Curcuminoids: curcumin and its two derivatives.

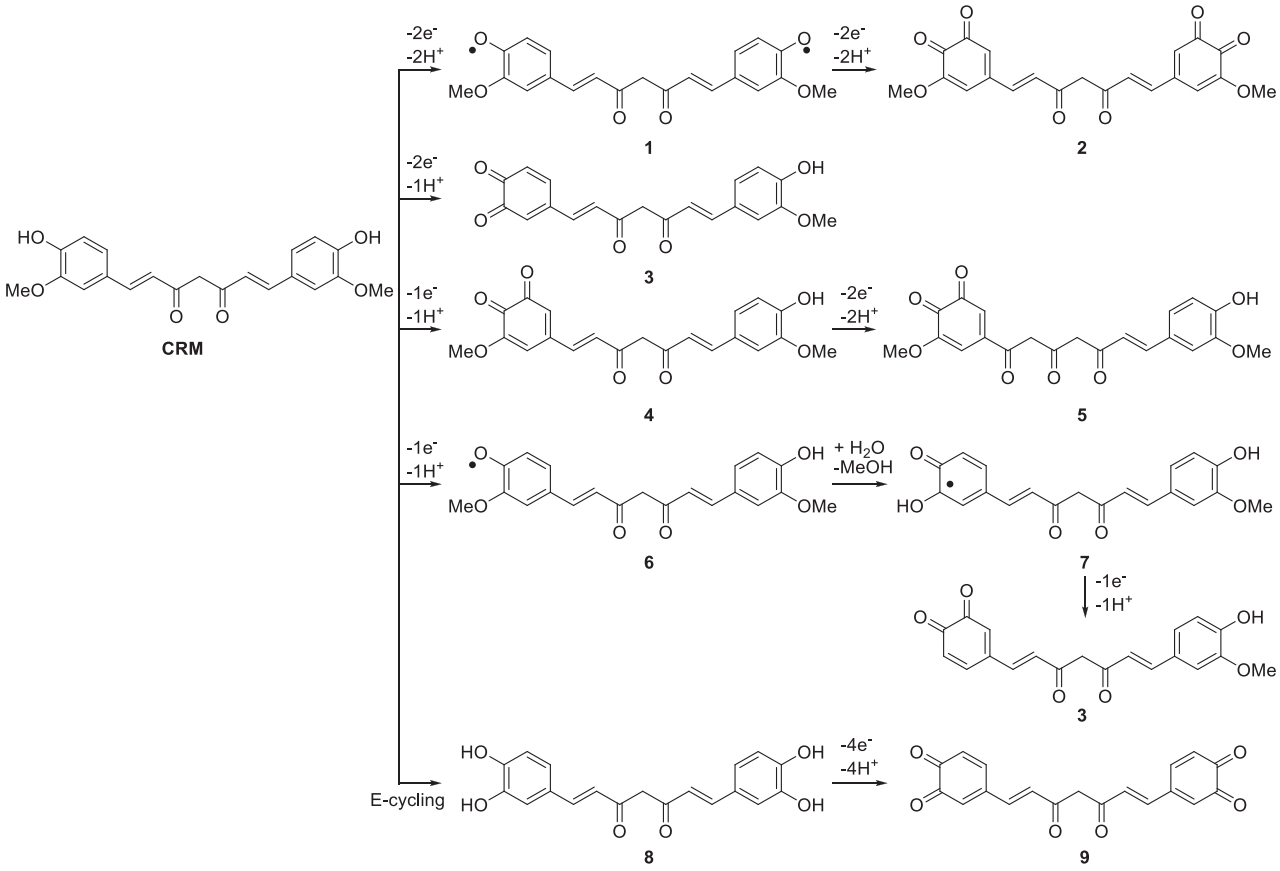
Mechanism-based screening is, however, still needed in order to supplement enzymatic and sensory studies. Electrochemical methods provide an alternative analytical approach presenting both high sensitivity and compatibility with diagnostic techniques in the discovery of biological activities of electroactive species. CRM, DMC, and BDMC contain phenol and methoxyphenol groups, linked through conjugated double bonds, which enable electrochemical responses (Chart). CRM has been extensively investigated for both its quantification in turmeric samples and its characterization by several electrochemical methods, such as voltammetry and polarography.[11–18]

The antioxidant activity of CRM was also probed by both free-radical scavenger and charge transfer properties.[2] In our recent study, we compared the antioxidant activities of curcumin, DMC, and BDMC considering 2,2-diphenyl-1-picrylhydrazyl free radical scavenger activity and ferric reducing antioxidant potential methods, which have different operating mechanisms.[2] Chemical carcinogens, such as reactive oxygen species and reactive nitrogen species, could be blocked by curcuminoids, attributed to their antitumor activities. Beyond the evaluation of antioxidant activities alone, the electrochemical behavior of natural antioxidant compounds should also be taken into the consideration to reveal their thermodynamic properties such as oxidation potential, number of electrons transferred, and rate constants of electrode reactions as mechanisms that can contribute to clinical studies on biological objects, such as DNA, signal transducers, and activators.

Electrochemical techniques conducted under different conditions provide an understanding of the redox behavior of electroactive compounds. The comparison of unique electrochemical properties of isomers is an appealing topic. However, studies on CRM and its two natural derivatives, DMC and BDMC, are still scarce. Zhang et al.[17] investigated the electrochemical reaction mechanisms of CRM, DMC, and BDMC at electrochemically reduced graphene oxide modified glass carbon electrode (GCE). DMC was evaluated for its oxidation process and kinetics, rate constant, electron transfer, and diffusion coefficients for electrochemical oxidation. The obtained results were corroborated by density functional theory (DFT) calculations.[19] CRM and BDMC were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at GCE.[20] DFT computations were conducted as well for the systematic examination of the electronic and geometrical structure of CRM and its 7 analogues including BDMC, rendering the reactivity order of these molecules.[21]

Manaia et al.[11] and Maseket al.[12] proposed the mechanism for the electrochemical oxidation of CRM involving the transfer of 4 electrons and 4 protons (4-e^-/H^+ couple) to furnish a hexaoxo product (**2**), which contains two intact MeO units (Scheme 1). Another suggested mechanism indicates the oxidation of one phenyl unit via transfer of $2e^-/1H^+$ at the expense of the MeO subgroup.[13] It was also suggested that transfer of only $1e^-/1H^+$ surprisingly leads to the oxidation of one phenyl unit to the *o*-quinone group in compound **4**, which, however, contradicts the formation of **2** in the 4-e^-/H^+ couple process. The subsequent two-electron/proton couple results in the oxidation of the β-carbon of enone to the carbonyl unit (**5**).[22] Incorporation of water or OH^- followed by elimination of MeOH was also considered as the key step. In the first step, transfer of

the 1-e$^-$/H$^+$ couple renders a phenoxy radical **6** followed by addition of H_2O and subsequent elimination of MeOH furnishing an α-radical **7**, which is stabilized by the OH substituent and conjugate double bonds. In the last step, removal of the 1-e$^-$/H$^+$ couple gives rise to an *o*-quinone substituent in compound **3**.[20,23] Dinesh et al.[18] reported the replacement of both methoxy units with OH in the first step, E-cycling, followed by the 4-e$^-$/H$^+$ couple transfer rendering the other hexaoxo product (**9**) lacking MeO subunits.



Scheme 1. Proposed electrochemical oxidations of curcumin (CRM) [11, 12, 18, 20, 22, 23].

In this paper, determination of the electrochemical behavior of CRM, DMC, and BDMC is realized using CV and DPV techniques systematically. The obtained products in electrolysis are analyzed by mass spectroscopic measurements and their oxidative formation mechanisms are assessed computationally. To the best of our knowledge, detailed oxidation mechanisms of curcuminoids have not been reported in the literature so far by combining experimental and computational investigations.

2. Results and discussion

2.1. Electrochemical investigations

Electrochemical behavior of CRM, DMC, and BDMC was investigated in different buffer solutions in the pH range of 0.3–0.3 by using CV and DPV techniques rendering the maximum responses with pH 1.5 (0.1 M) PB solution for all three curcuminoids. The electrochemical behavior of three compounds in acidic (pH 1.5), neutral (pH 7.0), and basic (pH 9.0) media is illustrated in Figure 1. Among the three media, curcuminoids provided

the best peak shape and currents under acidic conditions upon applied potentials. DPV results gave similar responses for the three compounds (Supplementary data).

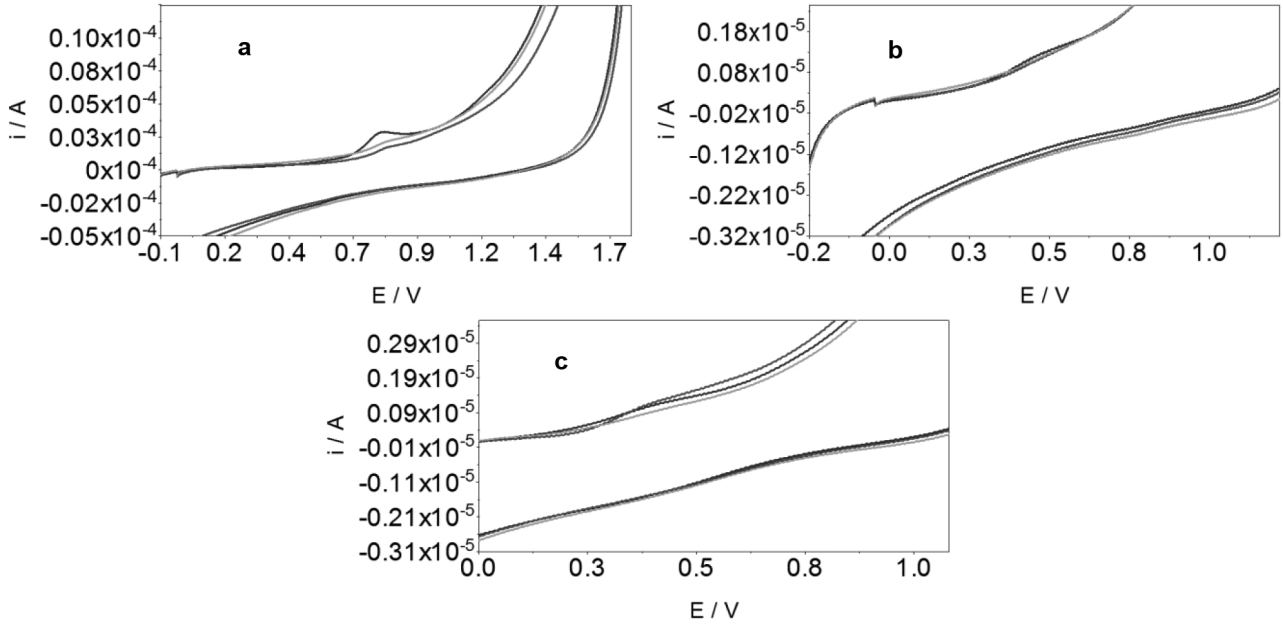


Figure 1. pH effect on the peak currents of 1×10^{-4} M CRM (blue line), DMC (red line), and BDMC (green line) in a) pH 1.5 (0.1 M) PB, b) pH 7.0 (0.1 M) PB, and c) pH 9.0 (0.1 M) borate buffer solutions by CV technique between –0.2 and 1.8 V at 0.1 V s^{-1} with GCE.

Electrochemical investigations on CRM indicated an anodic peak I with EpaI = +0.62 V, a well-defined anodic peak at EpaII = +0.8 V, and an anodic wave III with EpcIII = +1.05 V. In the second cycle scan, a new cathodic peak (IV) appeared with a low potential of EpaIV = +0.51 V, which designates the formation of a product with a high-lying HOMO, while current intensities of anodic peaks I and II decreased. Anodic peak I and cathodic peak IV show up as reversible peaks, which might interconvert upon applying voltages. The compound formed during the process in the main anodic peak I is strongly adsorbed on the electrode surface and hence brings about an irreversible peak. These results are in good alignment with the literature studies.[13–23] The main anodic peak II, which is nearly at the same potential for CRM, DMC, and BDMC, can be attributed to the oxidation of the phenol unit, but anodic peak III is more apparent in CRM and DMC in Figure 2 by DPV technique emerging from the methoxy groups attached to phenyl rings in CRM and DMC.

In neutral media, peak potentials shifted to less positive values and well-defined peak shapes disappeared; the main peaks were converted to anodic waves in pH 7.0 (0.1 M) PB. In basic media, similar behavior was witnessed for the curcuminoids. The peak potentials shifted to lower values that indicate the deprotonation of phenolic OH units with low pKa values and consequently the increase in the energy of HOMO levels. The decrease in current values was also recorded in pH 9.0 (0.1 M) borate buffer solution. Hydronium ions increase with increasing pH values. Hence, the oxidation of protonated molecules becomes more difficult compared to the unprotonated molecules.

Electrochemical oxidation mechanisms of CRM, DMC, and BDMC are influenced by methoxy and hydroxyl substituents. Three voltammograms gave oxidation peaks at about 0.8 V attributed to the oxidation of phenolic parts (Figure 2). CRM and DMC also gave a third anodic peak (EpaIII) after the main peaks (EpaII).

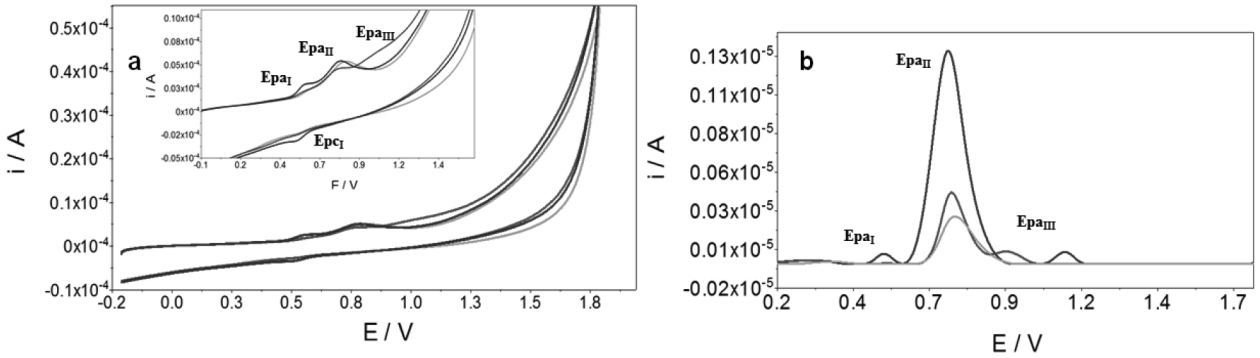


Figure 2. Electrochemical behavior of 5×10^{-4} M CRM (blue line), DMC (red line), and BDMC (green line) in 0.1 M PB (pH 1.5) solution by a) CV and b) DPV at GCE.

However, BDMC has only one main anodic peak (EpaI = +0.8 V) and a reversible couple (EpcII = +0.51 V, EpaIII = +0.62 V) stemming from the phenolic part in the structure. The reversible couple in the BDMC response is less intense than CRM and DMC's reversible couple responses that can be related to the absence of methoxy groups in the BDMC structure. The follow-up reduction process of CRM, DMC, and BDMC brings about the corresponding catechol formation from *ortho*-dioxobenzene groups.[24,25]

In order to observe the influence of pH on the main anodic peak (EpaII) potentials, Ep vs. pH relations were investigated by analyzing the CV and DPV for each compound, giving the CV equations below.

Equations from CV analysis:

CRM Epa (mV) = –49.71 pH + 874.25 (r = 0.983)

DMC Epa (mV) = –51.18 pH + 930.04 (r = 0.975)

BDM CEpa (mV) = –57.10 pH + 895.35 (r = 0.996)

Equations from DPV analysis:

CRM Epa (mV) = –52.09 pH + 829.2 (r = 0.998)

DMC Epa (mV) = –52.17 pH + 835.25 (r = 0.994)

BDMC Epa (mV) = –48.79 pH + 837.2 (r = 0.997)

The increase in the pH of the solutions caused a shift to the less positive value in the peak potentials, pointing out the increased electron densities and thereby diminished ionization potentials (Figure 1). The slopes obtained from the data for the main oxidation peak (EpaII) of CRM are 49.71 mV pH^{-1} with CV and 52.09 mV pH^{-1} with DPV, which match well with the theoretical value of 59 mV. The slopes calculated using a well-defined peak of DMC are 51.18 mV pH^{-1} with CV and 52.17 mV pH^{-1} with DPV techniques. Similar results were obtained in the case of BDMC and they are 57.10 mV pH^{-1} with CV and 48.79 mV pH^{-1} with DPV. All the electrochemical results revealed an equal number of electrons and protons involved in the electrochemical oxidation reactions.

The other significant parameter is the scan rate (ν), the effect of which on the main peak current (Ipa2) of three compounds was elaborated for 0.1 M PB (pH 1.5) solution in the presence of 5.0×10^{-4} M CRM, DMC, and BDMC using the GCE in the range of 5–500 mV s^{-1} (Figure 3).

Well-defined peak currents as a function of scan rate obtained for CRM, DMC, and BDMC are given below with linearity behavior:

CRM Ip (µA) = 0.0227 v (mV s^{-1}) – 0.1428 (r = 0.997)

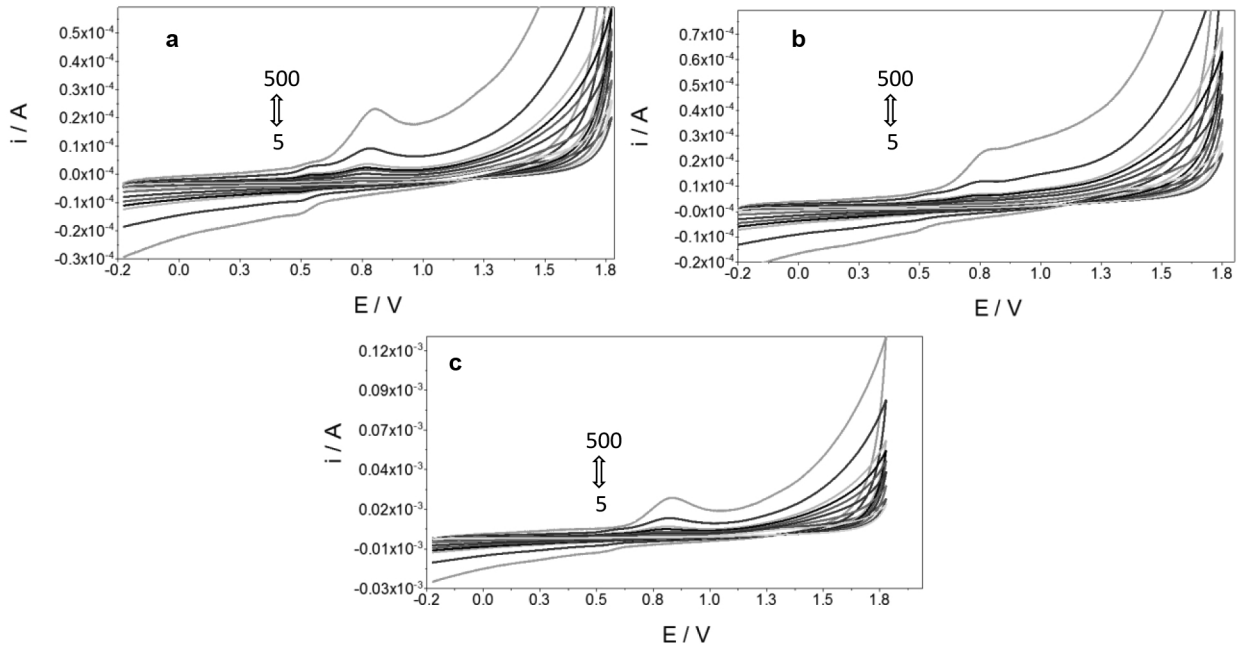


Figure 3. The effect of scan rate (ν) on electrochemical responses of curcuminoids in 0.1 M PB (pH 1.5) solution in the presence of 5.0×10^{-4} M a) CRM, b) DMC, and c) BDMC using GCE within the range of 5–500 mV s^{-1}.

DMC Ip (µA) = 0.009 v (mV s^{-1}) – 0.124 (r = 0.999)

BDMC Ip (µA) = 0.0279 v (mV s^{-1}) – 0.5771 (r = 0.996)

The plot of the logarithm of the peak currents (log Ip) against logarithm of scanning rate (log ν) exhibited a linear relationship between 5.00 mV s^{-1} and 500 mV s^{-1} scan rates, resulting in the following equations:

CRM log Ip (µA) = 0.951 log v (mV s^{-1}) – 1.601 (r = 0.997)

DMC log Ip (µA) = 1.11 log v (mV s^{-1}) – 2.441 (r = 0.997)

BDMC log Ip (µA) = 1.06 log v (mV s^{-1}) – 1.818 (r = 0.991)

The slopes of 0.951, 1.11, and 1.06 confirm an adsorption controlled process on the electrode surfaces. When the scan rates were increased, the peak potentials slightly shifted to more positive values due to the irreversible behavior of the main peaks of CRM, DMC, and BDMC (Figure 3).[26] For the theory of stationary electrode polarography, single scan and cyclic methods were applied to reversible, irreversible, and kinetic systems (Figure 3).[27] The linear relationship between the peak potential and the logarithm of the scan rate was obtained as follows:

CRM Ep (V) = 0.0269 log v (V s^{-1}) – 19.257 (r = 0.992)

DMC Ep (V) = 0.0198 log v (V s^{-1}) – 13.236 (r = 0.917)

BDMC Ep (V) = 0.0148 log v (V s^{-1}) – 9.981 (r = 0.964)

According to Laviron, for the irreversible electrode process (Ipa2), the following equation is given:

$$Ep = E^{\circ'} + \left(\frac{2.303RT}{\alpha nF}\right)\log\left(\frac{RTk^{\circ}}{\alpha nF}\right) + \left(\frac{2.303RT}{\alpha nF}\right) log\vartheta$$

Here, α is the electron transfer coefficient (accepted as approximately 0.5), k° is the standard heterogeneous rate constant of the reaction, n is the number of electrons transferred, v is the scan rate, E° is the formal redox

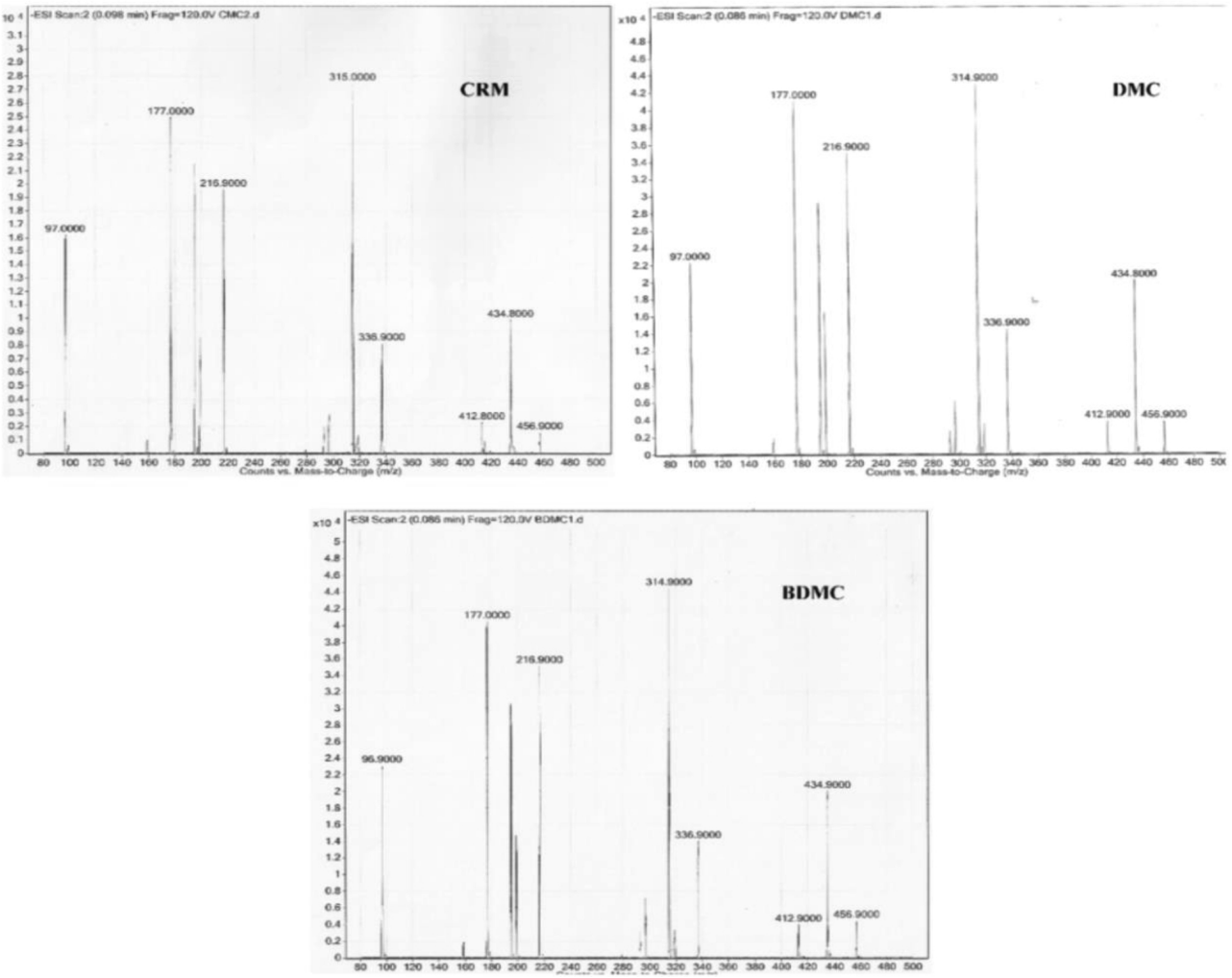


Figure 4. ESI spectra of curcuminoids demonstrating the formation of the same compound (**9**) possessing two *ortho*-dioxophenyl units.

potential, T = 298 K, R = 8.314 J K^{-1} mol^{-1}, and F = 96485 C mol^{-1}. Considering the slope as 0.0269, the value of αn was calculated to be 2.2, resulting in the number of electrons transferred (n) as 4.4 $\approx$ 4. Hence, CRM undergoes four-proton and four-electron transfer in the electrooxidation reaction. For DMC with only one MeO unit, the αn value was found as 2.985 using the slope of 0.0198, rendering a transferred electron number n of 5.97 $\approx$ 6. Six-proton/electron couple is involved in the anodic redox reaction of DMC. The slope of 0.0148 calculated for BDMC lacking the MeO group provided an αn value and transferred electron number of 3.995 and 7.99 $\approx$ 8, respectively, unveiling the oxidation mechanism of BDMC with the transfer of eight proton/electron couples in aqueous media.

2.2. Mass analysis

Mass analysis of CRM, DMC, and BDMC was performed by injecting the curcuminoids, which were subjected to bulk electrolysis, to disclose the oxidation products (Figure 4). The spectra depicted below clearly indicate the replacement of MeO units with oxo groups, thereby furnishing the same oxidized compound (9) (m/z: 337) with two *ortho*-dioxophenyl substituents.

2.3. Computation

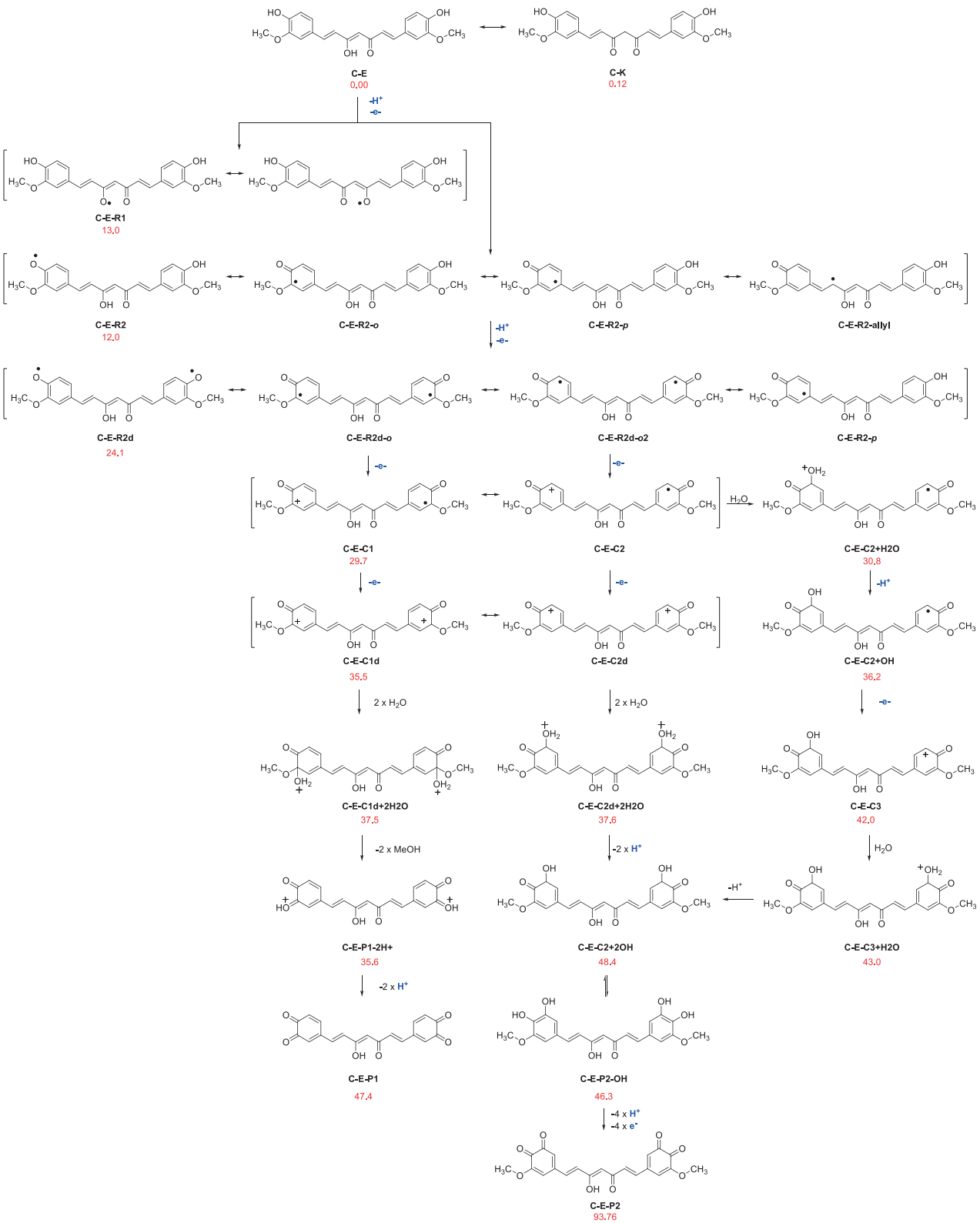
Since all the mechanisms provided in the literature are based on assumptions, DFT computations were conducted using the Gaussian 09 program[28] to shed light on the electrochemical reaction mechanisms of CRM, DMC, and BDMC in depth. The mPW3PBE[29–31] method with conventional all-electron basis set 6-31 + G(d) was applied on closed shell molecules. Unrestricted mPW3PBE/6-31 + G(d) was considered for the radicals and singlet diradicals. A self-consistent reaction field was used to incorporate solvent effect with united atom Hartree–Fock parametrization[32] of the conductor-like polarizable continuum model (CPCM).[33,34] Water with a dielectric constant of $\varepsilon = 78.3553$ was chosen as a solvent to mimic the experimental investigations. The minima were verified by analyzing the harmonic vibrational frequencies using analytical second derivatives, which lacking imaginary points (NImag = 0).

Curcumin has two tautomers, namely enol (C-E) and ketone (C-K). The enol tautomer of curcumin was calculated to be more stable than its keto form by a relative Gibbs free energy of 0.12 eV. Therefore, computational studies were started with the concurrent removal of a one-proton/electron couple from phenolic and enolic OH units of enol tautomer C-E, giving rise to radicals C-E-R1 and C-E-R2 with relative energies of 13.0 and 12.0 eV, respectively (Scheme 2). While the other resonance structure of radical C-E-R1 was found to be identical, the three major resonance structures of C-E-R2 were predicted to be C-E-R2-*o* (*ortho*, the other *ortho* radical is excluded), C-E-R2-*p* (*para*), and C-E-R2-allyl in a 1.0:1.1:1.5:1.1 ratio, respectively, based on spin densities.

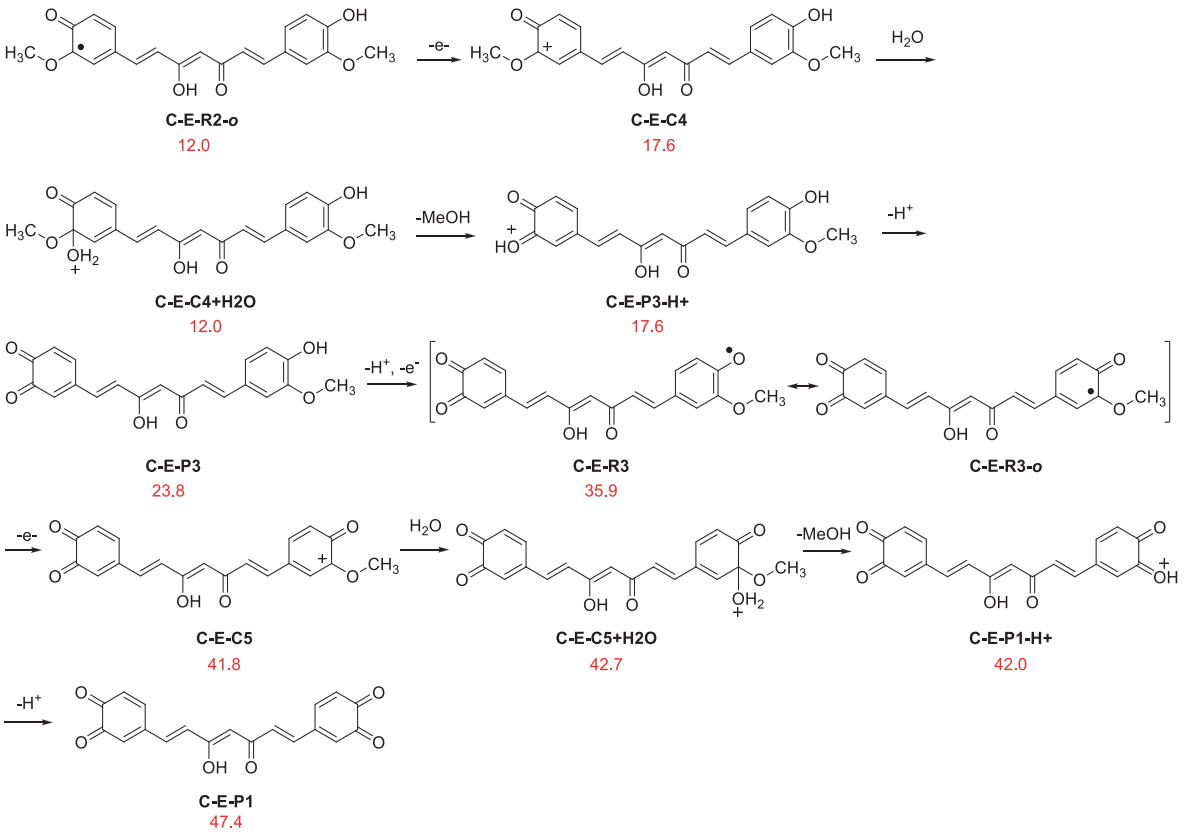
Removal of the second proton/electron couple from phenolic OH of C-E-R2 rendered a diradical C-E-R2d higher in energy by 12.1 eV. Four resonance structures of C-E-R2d were estimated to be C-E-R2d-*o* (proximate to MeO), C-E-R2d-*o*2, C-E-R2d-p (*para*), and C-E-R2d-allyl (not depicted) in a 1.3:1.4:2.0:1.5 ratio, respectively. Sequential removal of two electrons from C-E-R2d-*o* provided the formation of carbocations C-E-C1 and C-E-C1d, respectively (Scheme 2).[35] Electron-donating MeO units stabilize them and render the more stable resonance structures with respect to C-E-C2 and C-E-C2d. Reaction of C-E-C1d with two equivalents of water released 2 mol of protons and MeOH, ending up with the product C-E-P1 with a relative energy of 47.4 eV. In the case of C-E-C2d, reaction with two equivalents of water and liberation of 2 mol of protons resulted in the formation of a diol C-E-C2 + 2OH with a relative energy of 48.4 eV, which is in equilibrium with its less energetic catechol derivative C-E-P2-OH by 2.1 eV. Subsequent transfer of four-proton/electron couples oxidized catechol units to the high energy *ortho*-quinone product C-E-P2. Alternatively, two consecutive processes involving an electron transfer, addition of water, and liberation of a proton provided a diol C-E-C2 + 2OH from C-E-R2d-*o*2 via C-E-C2 + OH over six steps (Scheme 2).

The mechanism of the formation of product P1 was also elaborated by considering a stepwise process including the intermediate product C-E-P3 with relative energy of 23.8 eV (Scheme 3). Removal of one electron from C-E-R2-*o* resulted in the carbocation C-E-C4, which was treated with water, followed by elimination of a proton and MeOH furnishing C-E-P3. Removal of the one-proton/electron couple provided the radical C-E-R3, which is 12.1 eV higher in energy compared to C-E-P3. The same consecutive process was applied to obtain the product C-E-P1 via monocarbocation C-E-C5.

These computations suggested, contrary to the literature reports,[11,12,22] that formation of product C-E-P1 is preferred over C-E-P2, as mentioned in the recent paper of Kumar,[18] owing to the high-lying C-E-C2d + $2H_2O$ compared to C-E-C1d + $2H_2O$ by a relative energy of 0.1 eV (Table S1 in Supplementary data). Formation of C-E-P1 is also witnessed by electrospray ionization mode (ESI)-mass analysis providing



Scheme 2. (CPCM: water) -mPW3PBE/6-31 + G(d) level computations (relative Gibbs free energies with unscaled zpe are given in eV).



Scheme 3. (CPCM: water) -mPW3PBE/6-31 + G(d) level computations (relative Gibbs free energies with unscaled zpe are given in eV).

an m/z peak of 337 belonging to P1. Electrochemical investigations additionally demonstrated the reversible oxidation and reduction processes observed with anodic peak III and cathodic peak IV that unambiguously depict the formation of the *ortho*-dioxophenyl-containing product (**9**) and its reduction to the corresponding catechol (**8**). While transfer of four proton/electron couples steered the reaction toward the formation of C-E-P1, the generation of C-E-P2, having intact MeO units, required eight proton/electron couples released from the system. Based on the computational results, the electrochemical oxidation of CRM with two MeO units, DMC having only one MeO group and BDMC lacking the MeO substituent, involves four-, six-, and eight-proton/electron couples to finalize the reaction with the formation of C-E-P1 in all three electrochemical studies.

2.4. Conclusions

Electrochemical oxidation of curcumin and its two natural derivatives was elaborated thoroughly for the first time by CV and DPV investigations. The products formed in the oxidation of all three curcuminoids were ascertained by ESI-mass analyses, indicating the formation of the same oxidized product with m/z of 337 attributed to a compound with two *ortho*-dioxophenyl substituents. Comprehensive DFT computations shed light on the intriguing mechanisms providing the dioxophenyl-possessing product via transfer of 4-, 6-, and 8-electron/proton couples for CRM, DMC, and BDMC, respectively.

3. Experimental

An AUTOLAB-PGSTAT302 (Eco Chemie, Utrecht, the Netherlands) instrument was used as an electrochemical analyzer with General Purpose Electrochemical Software 4.9. CV and DPV techniques were applied. The electrochemical cell consists of three electrodes: working, auxiliary, and reference. Bare GCE (BASi; ø: 3 mm) is used as the working electrode, platinum wire (BASi) as the auxiliary electrode, and Ag/AgCl (BASi; 3 M KCl) as the reference electrode. All pH measurements were performed using a pH-meter, Model 538 (WTW, Austria), with a combined electrode (glass electrode and reference electrode) with an accuracy of pH ±0.05. The CV technique was applied between –0.2 and 1.8 V with different scan rates (5–500 mV s^{-1}). The DPV method was realized under the following conditions: modulation amplitude of 50.5 mV; interval time of 0.500 s; step potential of 7.95 mV; modulation time of 0.050 s. Baseline correction was made using a moving average "peak width" of 0.010 V. Bulk electrolysis was conducted according to the CV response at room temperature for approximately 20 min. CRM, DMC, and BDMC were dissolved in methanol and a 10% methanol ratio was fixed in all measurement solutions. The applied potential of 1.7 V was adjusted for 5×10^{-4} M CRM, DMC, and BDMC electrooxidation processes in pH 1.5 (0.1 M) phosphate buffer (PB) solution. The glassy carbon electrode provided a large surface area at which the electroactive CRM, DMC, and BDMC were quantitatively oxidized. The progress of the electrolysis was monitored by measuring the total charge current over time. After electrolysis, the solution was subjected to LC-MS/MS analysis for identification of the oxidation products. The mass spectrometric experiments were performed using triple quadrupole mass spectrometry (Agilent 6420). ESI was used in negative ion mode with nitrogen as the spray and collision gas and capillary voltage of 4000 V. Methanol and formic acid (MeOH/1% formic acid, 98:2, v/v) were used as the mobile phase. The mass spectrometer was operated at scan mode 80–500 m/z values. Fragmentor voltage was optimized to 120 V.

Curcuminoids were isolated from turmeric according to the literature procedure.[10]

Acknowledgments

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Supplementary data

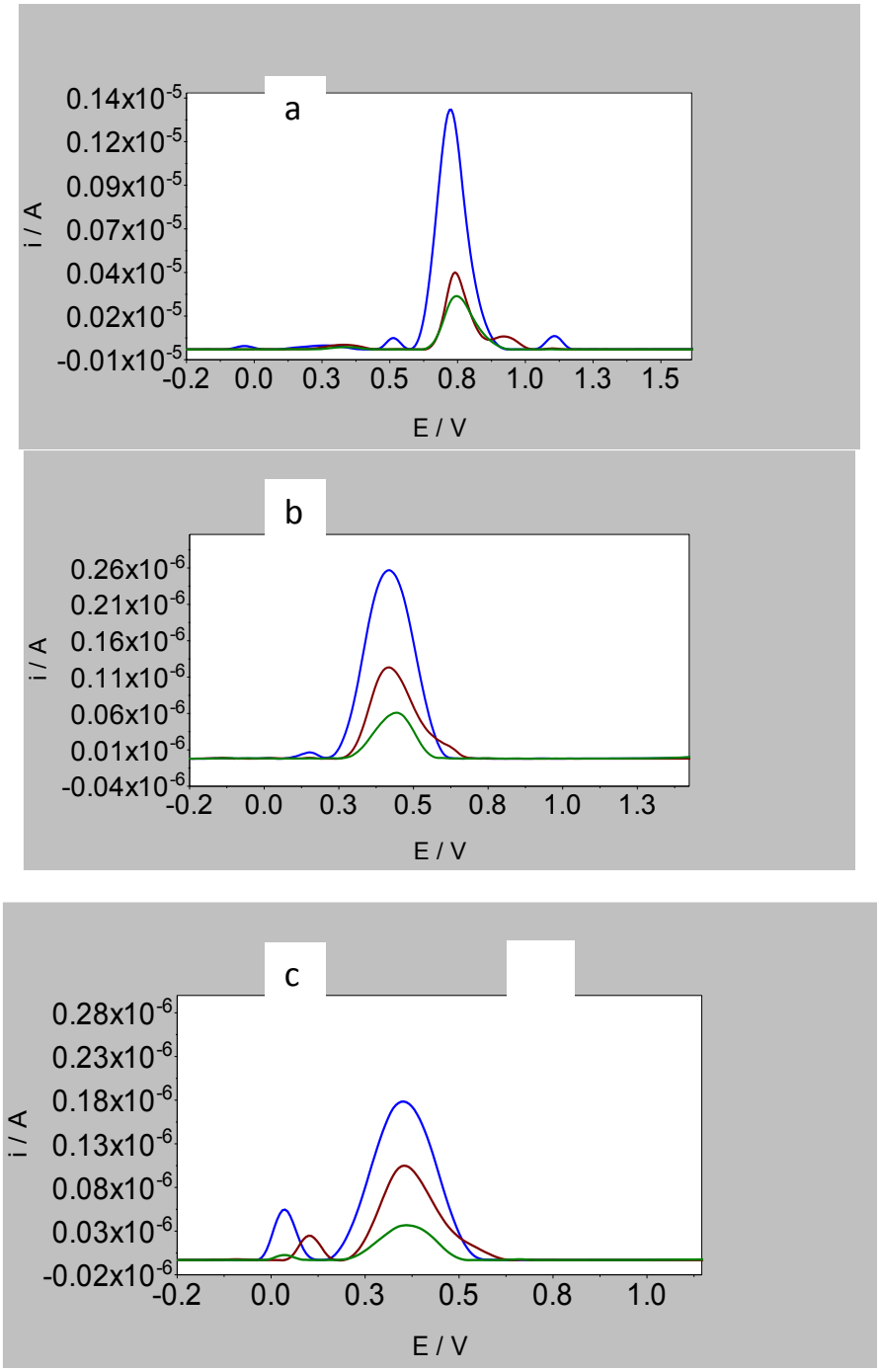

Figure S1. pH effect on the peak currents of 1 × 10^{-4} M CRM (blue line), DMC (red line), and BDMC (green line) in a) pH 1.5 (0.1 M) PB, b) pH 7.0 (0.1 M) PB, and c) pH 9.0 (0.1 M) borate buffer solutions by DPV technique between –0.2 and 1.8 V under the following conditions: modulation amplitude of 0.0505 V; interval time of 0.500 s; step potential of 0.00795 V; modulation time of 0.050 switch GCE.

Table S1. Cartesian coordinates.

C-E

C	0.0302390	−2.4830940	−0.0572280
H	0.0310670	−2.4109880	−1.1426310
C	−0.0330980	2.4730000	−0.1886980
H	−0.0336990	2.3693880	−1.2709010
C	−0.0451040	3.6885960	0.4109010
H	−0.0417640	3.7051190	1.5006330
C	0.0430790	−3.6783070	0.5775470
H	0.0394900	−3.6481200	1.6679180
C	−0.0608860	4.9916870	−0.2334040
C	−0.0605850	6.1393750	0.5911090
C	−0.0760220	5.1668350	−1.6281390
C	−0.0738720	7.4105170	0.0359650
H	−0.0492640	6.0140430	1.6700060
C	−0.0897460	6.4402570	−2.1867940
H	−0.0779580	4.3065380	−2.2911000
C	−0.0886480	7.5647580	−1.3653800
H	−0.1017470	6.5777240	−3.2648300
C	0.0600630	−5.0053270	−0.0166200
C	0.0612430	−6.1215210	0.8497510
C	0.0750560	−5.2315390	−1.4038910
C	0.0759300	−7.4123610	0.3418730
H	0.0500200	−5.9560730	1.9232460
C	0.0900870	−6.5245820	−1.9154000
H	0.0757680	−4.3952310	−2.0969850
C	0.0905130	−7.6179290	−1.0528170
H	0.1019380	−6.7020340	−2.9875950
O	0.1051900	−8.8768630	−1.5522340
H	0.1032130	−9.4997590	−0.8023720
O	−0.1019950	8.8045070	−1.9108020
H	−0.0991050	9.4544440	−1.1842800
O	0.0781900	−8.5648040	1.0659190
O	−0.0744570	8.5886870	0.7171730
C	−0.0600720	8.5474260	2.1395340
H	−0.0633040	9.5874570	2.4675470
H	−0.9509650	8.0365520	2.5230480
H	0.8445850	8.0477600	2.5052100
C	0.0648790	−8.4712380	2.4858110
H	0.0698220	−9.4985120	2.8518240
H	0.9553490	−7.9453740	2.8495260
H	−0.8401550	−7.9596910	2.8336720
C	−0.0174930	1.2332150	0.5532990
C	−0.0022560	−0.0019800	−0.0757480
H	−0.0023050	−0.0401470	−1.1600530
C	0.0136820	−1.2192350	0.6812540
O	0.0134230	−1.1983140	1.9529220
O	−0.0178430	1.3152050	1.8828080
H	−0.0057380	0.3481040	2.2047090

C-E-K

O	1.9409490	0.9960630	−2.4394910
C	0.1163090	−2.0024120	−1.8461540
H	1.1870600	−1.9264880	−2.0206690
C	−0.1345080	2.0009160	−1.8474500
H	−1.2068170	1.9252880	−2.0122650
C	0.4019150	2.9505370	−1.0428930
H	1.4884230	2.9407200	−0.9425920
C	−0.4124390	−2.9514560	−1.0358600
H	−1.4980200	−2.9421320	−0.9259530
C	−0.2887860	3.9832570	−0.2934580
C	0.4863110	4.8556140	0.5042350
C	−1.6840020	4.1553420	−0.3224340
C	−0.1182120	5.8599030	1.2447470
H	1.5646560	4.7282140	0.5310640
C	−2.2920690	5.1619100	0.4180790
H	−2.3055150	3.5020270	−0.9276930
C	−1.5196070	6.0160720	1.2022380
H	−3.3698780	5.2991980	0.3978440
C	0.2854750	−3.9829920	−0.2914940
C	−0.4821000	−4.8555800	0.5131900
C	1.6805810	−4.1536650	−0.3318860
C	0.1295600	−5.8587690	1.2493210
H	−1.5603260	−4.7292960	0.5488340
C	2.2957940	−5.1590470	0.4043240
H	2.2963960	−3.5001150	−0.9426940
C	1.5307310	−6.0134470	1.1954450
H	3.3735470	−5.2952000	0.3753060
O	2.1307300	−6.9916520	1.9111520
H	1.4399990	−7.4812500	2.3947750
O	−2.1126520	6.9954610	1.9221030
H	−1.4174340	7.4847000	2.3996200
O	−0.4894640	−6.7594210	2.0590300
O	0.5083990	6.7603640	2.0488130
C	1.9256250	6.6942720	2.1629620
H	2.2068100	7.4976830	2.8445880
H	2.2376380	5.7297860	2.5802200
H	2.4018470	6.8529720	1.1884790
C	−1.9058330	−6.6951990	2.1843020
H	−2.1805250	−7.4985500	2.8686410
H	−2.2158890	−5.7308780	2.6033880
H	−2.3894990	−6.8551950	1.2137040
C	0.7136860	1.0256210	−2.5381340
C	−0.0165270	−0.0017230	−3.4009410
H	−0.7644790	0.4963810	−4.0258160
H	0.7254480	−0.5004990	−4.0323790
C	−0.7384880	−1.0282530	−2.5302600
O	−1.9648200	−0.9990860	−2.4206040

C-E-R1

C	2.4871730	0.4146340	0.0233170
H	2.4715420	1.5014650	0.0332120
C	−2.4871790	0.4146160	−0.0236160
H	−2.4715610	1.5014490	−0.0333770
C	−3.6440050	−0.2889650	−0.0194050
H	−3.5635570	−1.3761520	−0.0016650
C	3.6440020	−0.2889440	0.0191430
H	3.5635440	−1.3761290	0.0012940
C	−5.0000610	0.2353940	−0.0313210
C	−6.0679240	−0.6885220	0.0190120
C	−5.2995210	1.6073990	−0.0890820
C	−7.3838880	−0.2498970	0.0152250
H	−5.8458830	−1.7509860	0.0626240
C	−6.6180290	2.0491340	−0.0947590
H	−4.5022330	2.3436470	−0.1330200
C	−7.6636570	1.1307850	−0.0425980
H	−6.8523540	3.1093790	−0.1406620
C	5.0000580	0.2354030	0.0312350
C	6.0679240	−0.6885190	−0.0189280
C	5.2995150	1.6074110	0.0889840
C	7.3838880	−0.2498980	−0.0149760
H	5.8458850	−1.7509830	−0.0625370
C	6.6180230	2.0491420	0.0948260
H	4.5022210	2.3436610	0.1327720
C	7.6636550	1.1307860	0.0428430
H	6.8523460	3.1093880	0.1407180
O	8.9471350	1.5624990	0.0488060
H	9.5295020	0.7817290	0.0087940
O	−8.9471380	1.5625040	−0.0484030
H	−9.5295020	0.7817380	−0.0082750
O	8.4955610	−1.0331080	−0.0622370
O	−8.4955570	−1.0331040	0.0626490
C	−8.3259880	−2.4447490	0.1243060
H	−9.3321470	−2.8642140	0.1548990
H	−7.7994100	−2.8124760	−0.7640450
H	−7.7785030	−2.7316810	1.0297010
C	8.3259990	−2.4447590	−0.1237630
H	9.3321620	−2.8642300	−0.1541440
H	7.7992740	−2.8123850	0.7645420
H	7.7786620	−2.7317900	−1.0292170
C	−1.1765830	−0.2310930	−0.0114170
C	−0.0000040	0.5373040	−0.0001560
H	−0.0000020	1.6208740	−0.0000130
C	1.1765860	−0.2310820	0.0109140
O	1.0868330	−1.5078790	0.0106150
O	−1.0868210	−1.5078860	−0.0114690

C-E-R2

C	2.4146600	0.1822900	0.0000400
H	2.3133990	1.2650980	−0.0001170
C	−2.5337370	0.1983740	0.0000960
H	−2.4477950	1.2812500	−0.0000670
C	−3.7481380	−0.4267250	0.0002020
H	−3.7484650	−1.5157610	0.0003200
C	3.6275100	−0.4221500	0.0001330
H	3.6248300	−1.5129390	0.0002500
C	−5.0358800	0.2046040	0.0001320
C	−6.1872460	−0.6202640	0.0000070
C	−5.2016680	1.6288350	0.0001780
C	−7.4571470	−0.0767100	−0.0001340
H	−6.0482990	−1.6971670	0.0000010
C	−6.4432750	2.1900630	0.0000430
H	−4.3271150	2.2725510	0.0003440
C	−7.6506900	1.3859250	−0.0001420
H	−6.5766890	3.2687980	0.0000860
C	4.9366470	0.2049180	0.0000770
C	6.0749760	−0.6331450	−0.0000790
C	5.1261060	1.5984400	0.0001730
C	7.3515570	−0.0918990	−0.0001610
H	5.9369740	−1.7104930	−0.0001470
C	6.4047120	2.1432990	0.0000980
H	4.2718450	2.2690890	0.0003270
C	7.5201110	1.3085730	−0.0000700
H	6.5548170	3.2196320	0.0001830
O	8.7642560	1.8401090	−0.0001390
H	9.4071790	1.1071150	−0.0002280
O	−8.7904930	1.8924010	−0.0002910
O	8.5226630	−0.7839750	−0.0003310
O	−8.5965020	−0.7742070	−0.0002730
C	−8.5263400	−2.1991690	−0.0002480
H	−9.5605250	−2.5438710	−0.0003650
H	−8.0137860	−2.5615620	−0.8982680
H	−8.0139950	−2.5615380	0.8979020
C	8.4677890	−2.2062290	−0.0002450
H	9.5046740	−2.5439090	−0.0002930
H	7.9590040	−2.5756130	0.8977250
H	7.9588920	−2.5757190	−0.8981090
C	−1.2841770	−0.5227820	0.0001770
C	−0.0681830	0.1374920	0.0000560
H	−0.0584850	1.2222760	−0.0001020
C	1.1754570	−0.5905120	0.0001500
O	1.1790500	−1.8585380	0.0003210
O	−1.3460270	−1.8539390	0.0003720
H	−0.3783110	−2.1614090	0.0003920

C-E-R2d

C	−2.4741480	0.1690050	0.0000230
H	−2.3735430	1.2511100	0.0000760
C	2.4677120	0.1909180	−0.0000100
H	2.3790870	1.2733630	−0.0000100
C	3.6848400	−0.4328980	−0.0000220
H	3.6867170	−1.5218830	−0.0000080
C	−3.6920440	−0.4423550	−0.0000250
H	−3.6911090	−1.5321930	−0.0000640
C	4.9692570	0.2001800	−0.0000420
C	6.1223870	−0.6227980	0.0000180
C	5.1309830	1.6261550	−0.0001200
C	7.3905390	−0.0762930	0.0000160
H	5.9856400	−1.6999280	0.0000710
C	6.3701450	2.1904720	−0.0001240
H	4.2545420	2.2671440	−0.0001810
C	7.5801080	1.3882970	−0.0000540
H	6.5013830	3.2693940	−0.0001860
C	−4.9787740	0.1943000	−0.0000200
C	−6.1314270	−0.6256950	0.0000100
C	−5.1356680	1.6206360	−0.0000420
C	−7.3998030	−0.0756540	0.0000310
H	−5.9971560	−1.7031420	0.0000240

C −6.3732140 2.1890110 −0.0000220
H −4.2561590 2.2574400 −0.0000800
C −7.5849600 1.3896710 0.0000180
H −6.5020620 3.2682420 −0.0000410
O −8.7211240 1.9008310 0.0000370
O 8.7174160 1.8967960 −0.0000530
O −8.5409070 −0.7655790 0.0000660
O 8.5314290 −0.7691410 0.0000730
C 8.4670370 −2.1948010 0.0001320
H 9.5026310 −2.5350140 0.0001650
H 7.9560100 −2.5586320 0.8983390
H 7.9560420 −2.5587080 −0.8980620
C −8.4817110 −2.1918620 0.0000420
H −9.5185460 −2.5280550 0.0000380
H −7.9720290 −2.5570580 −0.8982360
H −7.9720280 −2.5570870 0.8983080
C 1.2234380 −0.5331530 0.0000090
C 0.0022560 0.1265970 0.0000310
H −0.0108560 1.2110840 0.0000500
C −1.2315690 −0.6059270 0.0000100
O −1.2447310 −1.8728400 −0.0000690
O 1.2831300 −1.8619450 0.0000150
H 0.3174330 −2.1738880 0.0000700

C-E-C1

C 2.4566150 0.1282920 0.0000280
H 2.3427130 1.2083620 −0.0000040
C −2.4643770 0.1219580 −0.0000270
H −2.3661450 1.2024830 −0.0000620
C −3.6876490 −0.4994380 −0.0000160
H −3.7012100 −1.5870630 0.0000190
C 3.6837480 −0.4732860 0.0000730
H 3.6950120 −1.5626090 0.0001360
C −4.9483370 0.1579580 −0.0000380
C −6.1088170 −0.6419940 0.0000090
C −5.0584350 1.6116940 −0.0000890
C −7.3598120 −0.0563530 −0.0000230
H −5.9995800 −1.7213790 0.0000260
C −6.2600720 2.2225720 −0.0001370
H −4.1559690 2.2126930 −0.0001150
C −7.5038830 1.4467450 −0.0000960
H −6.3586900 3.3038990 −0.0001710
C 4.9551110 0.1799160 0.0000850
C 6.1159200 −0.6250220 0.0000020
C 5.0839490 1.6173400 0.0001550
C 7.3740310 −0.0528250 −0.0000080
H 5.9983210 −1.7040190 −0.0000400
C 6.3039840 2.2098480 0.0001410
H 4.1911170 2.2342710 0.0002140
C 7.5333010 1.4271450 0.0000550
H 6.4143860 3.2905990 0.0001940
O 8.6541950 1.9497190 0.0000520
O −8.6108260 1.9663170 −0.0001220
O 8.5222600 −0.7106920 −0.0001250
O −8.5065560 −0.6815470 0.0000300
C −8.5408730 −2.1198380 0.0001820
H −9.5980470 −2.3789980 0.0002800
H −8.0539280 −2.5034110 −0.9006510
H −8.0537980 −2.5032090 0.9010280
C 8.5066330 −2.1422020 −0.0002820
H 9.5535580 −2.4433340 −0.0004350
H 8.0080000 −2.5176500 0.8990040
H 8.0077980 −2.5174720 −0.8995300
C −1.2299750 −0.6132550 0.0000130
C −0.0198960 0.0629230 0.0000290
H −0.0203450 1.1472680 0.0000140
C 1.2323980 −0.6624870 0.0000470
O 1.2448520 −1.9232670 0.0000660
O −1.2970460 −1.9377660 0.0000250
H −0.3396000 −2.2607040 0.0000610

C-E-C1d

C 2.4806200 0.1164190 −0.0001130
H 2.3771720 1.1970580 −0.0002360
C −2.4708140 0.1147490 −0.0000460
H −2.3740250 1.1951840 −0.0002790
C −3.6823230 −0.5117100 0.0001760
H −3.6976090 −1.5989610 0.0004280
C 3.6855600 −0.5063160 −0.0000180
H 3.6910750 −1.5945690 0.0001510
C −4.9516540 0.1505260 0.0000720
C −6.1000690 −0.6507270 0.0001850
C −5.0530230 1.6101280 −0.0000890
C −7.3553310 −0.0580730 0.0000480
H −5.9938920 −1.7302380 0.0004220
C −6.2465520 2.2311820 −0.0001190
H −4.1456120 2.2028610 −0.0001790
C −7.4949710 1.4584490 −0.0000920
H −6.3389210 3.3128030 −0.0002270
C 4.9650330 0.1522320 0.0000020
C 6.1040300 −0.6542450 −0.0000850
C 5.0692880 1.6122460 0.0001270
C 7.3647670 −0.0637420 0.0000010
H 5.9944810 −1.7333990 −0.0002510
C 6.2629220 2.2326720 0.0001600
H 4.1613210 2.2040390 0.0001580
C 7.5092230 1.4565540 0.0001390
H 6.3571910 3.3140660 0.0002130
O 8.6149270 1.9613410 0.0002110
O −8.5986960 1.9707540 −0.0002070
O 8.4975960 −0.6767710 −0.0001860
O −8.4941560 −0.6699460 0.0000210
C −8.5603610 −2.1133980 −0.0000230
H −9.6234560 −2.3441220 −0.0009100
H −8.0801830 −2.5005300 −0.9018620
H −8.0817410 −2.5004440 0.9026860
C 8.5690150 −2.1223900 −0.0002920
H 9.6331290 −2.3473570 −0.0000220
H 8.0904230 −2.5087730 0.9023210
H 8.0909090 −2.5085770 −0.9032500
C −1.2228390 −0.6208520 −0.0000050
C −0.0164680 0.0561340 −0.0000960
H −0.0151110 1.1399630 −0.0002400
C 1.2265040 −0.6728490 −0.0000090
O 1.2589340 −1.9232710 0.0001330
O −1.3013800 −1.9390900 0.0001910
H −0.3582890 −2.2850710 0.0002230

C-E-C1d+2H2O

C −2.4778560 0.0463280 0.0349190
H −2.3878590 1.0669250 0.3945730
C 2.4841180 0.0269660 0.0395010
H 2.3827480 1.0451710 0.4049760
C 3.6811280 −0.5439210 −0.2010440
H 3.6838880 −1.5662010 −0.5768690
C −3.6727380 −0.5373470 −0.2028420
H −3.6803320 −1.5604510 −0.5735000
C 4.9894800 0.0734260 −0.0268120
C 6.0985850 −0.6257220 −0.3719140
C 5.1126290 1.4404950 0.5131850
H 6.0402530 −1.6394940 −0.7584450
C 6.2756590 2.1268630 0.5548520
H 4.2099910 1.9343020 0.8585040
C 7.4661070 1.5115570 0.0126500
H 6.3291750 3.1607350 0.8808660
C −4.9804630 0.0782200 −0.0284530
C −6.0903900 −0.6237270 −0.3685770
C −5.1051810 1.4463510 0.5087990
H −6.0315380 −1.6388860 −0.7512740
C −6.2695450 2.1300830 0.5520620
H −4.2039990 1.9440180 0.8521690
C −7.4605410 1.5114500 0.0144700
H −6.3244740 3.1642660 0.8768650
O −8.4851720 2.0778870 −0.3435960
O 8.4889580 2.0796220 −0.3480480
O −8.1600400 −0.5197800 0.9014360
O 8.1661570 −0.5186140 0.9004830
C 7.9201880 −1.8595390 1.3899320
H 8.6734990 −2.0070370 2.1623270
H 6.9190480 −1.9223280 1.8211680
H 8.0502620 −2.6008030 0.5970330
C −7.9128710 −1.8602580 1.3911020
H −8.6660420 −2.0084770 2.1635020
H −8.0421480 −2.6017080 0.5982220
H −6.9115820 −1.9220310 1.8221710
C 1.2284740 −0.7106850 −0.2008750
C −0.0058430 −0.0180440 0.0372450
H 0.0049540 1.0077190 0.3883920
C −1.2181040 −0.6430230 −0.1855280
O −1.2854170 −1.8957320 −0.6143840
O 1.2475280 −1.9040600 −0.6070590
H −0.3255230 −2.2024530 −0.7129130
C 7.4322910 −0.0304050 −0.1203030
C −7.4237440 −0.0302960 −0.1166860
H 8.8995140 0.6135210 −1.3964460
H 8.8377360 −0.9930680 −1.4501190
O 8.2882070 −0.1803030 −1.4512160
H −8.8280290 −0.9956500 −1.4501300
H −8.8944710 0.6096270 −1.3952540
O −8.2806410 −0.1815610 −1.4513560

C-E-P1-2H+

C −2.4813200 −0.0977890 −0.0037180
H −2.3788980 0.9826820 −0.0249330
C 2.4699430 −0.1008260 0.0035990
H 2.3731770 0.9793620 0.0226410
C 3.6820450 −0.7296930 −0.0172780
H 3.6944590 −1.8166570 −0.0411970
C −3.6855620 −0.7242340 0.0190870
H −3.6873360 −1.8121440 0.0441670
C 4.9514310 −0.0734120 −0.0101310
C 6.0979830 −0.8765650 −0.0468510
C 5.0544370 1.3914990 0.0381310
C 7.3370540 −0.2672630 −0.0324200
H 6.0226910 −1.9587080 −0.0859660
C 6.2425580 2.0251370 0.0604160
H 4.1440550 1.9790430 0.0597080
C 7.4743650 1.2421330 0.0327510
H 6.3282250 3.1062450 0.1000800
C −4.9659130 −0.0725440 0.0119310
C −6.1020560 −0.8816580 0.0514410
C −5.0731220 1.3930610 −0.0393490
C −7.3470420 −0.2750800 0.0364860
H −6.0230180 −1.9633400 0.0929180
C −6.2615030 2.0255220 −0.0630920
H −4.1625020 1.9800850 −0.0623340
C −7.4907570 1.2386200 −0.0339480
H −6.3496650 3.1062490 −0.1054170
O −8.6267130 1.6807820 −0.0623130
O 8.6084850 1.6938280 0.0583970
O −8.4499740 −0.9469750 0.0765770
O 8.4478320 −0.9363240 −0.0691570
C 1.2232130 −0.8370470 −0.0003200
C 0.0170670 −0.1584430 0.0043160
H 0.0166860 0.9253560 0.0110210
C −1.2268500 −0.8871540 −0.0003560
O −1.2600250 −2.1367050 −0.0028390
O 1.3022550 −2.1546480 −0.0096580
H 0.3607250 −2.5028770 −0.0094810
H 9.2005040 −0.2964510 −0.0469210
H −9.2098210 −0.3140700 0.0535060

C-E-P1

C −2.4837100 −0.1186440 0.0000370
H −2.3826510 0.9630570 0.0000900
C 2.4762330 −0.1010300 0.0000530
H 2.3861980 0.9809340 0.0001760
C 3.6758310 −0.7290800 −0.0000830
H 3.6834420 −1.8173970 −0.0002190
C −3.6850490 −0.7358100 −0.0000120
H −3.6883040 −1.8250630 −0.0000600
C 4.9789570 −0.0919400 −0.0000930
C 6.0975410 −0.8772870 0.0000570
C 5.1049390 1.3749690 −0.0001820
C 7.4315080 −0.3023840 0.0000720

H 6.0252340 −1.9623130 0.0001540
C 6.2948620 2.0071730 −0.0001450
H 4.1972720 1.9702760 −0.0002120
C 7.5447440 1.2462650 −0.0000260
H 6.3670270 3.0914540 −0.0001610
C −4.9895540 −0.0967710 −0.0000070
C −6.1074300 −0.8809080 −0.0001000
C −5.1132800 1.3702820 0.0000880
C −7.4419890 −0.3029490 −0.0001220
H −6.0367720 −1.9660290 −0.0001680
C −6.3019670 2.0050410 0.0001040
H −4.2034880 1.9624510 0.0001540
C −7.5529980 1.2464440 0.0000170
H −6.3720890 3.0894480 0.0001810
O −8.6553500 1.7713130 0.0000940
O 8.6475160 1.7705710 −0.0000110
O −8.4645860 −0.9764000 −0.0001190
O 8.4543380 −0.9770150 0.0001620
C 1.2187710 −0.8253880 0.0000220
C 0.0056270 −0.1617600 0.0000530
H −0.0051410 0.9224690 0.0000900
C −1.2292740 −0.8942670 0.0000440
O −1.2474050 −2.1550510 0.0000330
O 1.2855980 −2.1495970 0.0000020
H 0.3258070 −2.4716010 0.0000240

C-E-C2d+2H2O
C 2.4891170 −0.0583240 −0.1747690
H 2.4074740 0.9354870 0.2605730
C −2.4741300 −0.0457110 −0.1037580
H −2.3921930 0.9317200 0.3652760
C −3.6736200 −0.6148230 −0.3396610
H −3.6987640 −1.6205270 −0.7562200
C 3.6863310 −0.6353710 −0.3846460
H 3.7028140 −1.6589830 −0.7589180
C −4.9716190 0.0004070 −0.0516380
C −6.0960180 −0.9194760 0.1450310
C −5.1460210 1.3437350 0.0193910
C −7.3826890 −0.5161010 0.3518480
H −5.8764570 −1.9801090 0.0657100
H −4.3415460 2.0580010 −0.1245390
C −7.6486450 0.9133330 0.3055640
C 4.9858920 −0.0119980 −0.1167810
C 6.0846180 −0.9162240 0.2332170
C 5.1769380 1.3277260 −0.1986970
C 7.3669780 −0.5052670 0.4520590
H 5.8510950 −1.9762270 0.2679880
H 4.3860400 2.0244070 −0.4578950
C 7.6581340 0.9048090 0.2474290
O 8.7569020 1.4054290 0.0122150
O −8.7291240 1.4576570 0.0851370
O 8.4442370 −1.2585060 0.6903540
O −8.4784910 −1.2742480 0.4489650
C −8.3206420 −2.6900870 0.3382790
H −9.3228080 −3.1045380 0.4432770
H −7.9067790 −2.9540870 −0.6414290
H −7.6748480 −3.0685480 1.1382120
C 8.2653640 −2.6749600 0.7488800
H 9.2539590 −3.0860060 0.9509440
H 7.5774370 −2.9419620 1.5587250
H 7.8905560 −3.0537670 −0.2085340
C −1.2169500 −0.6971660 −0.4268970
C −0.0006790 −0.0948470 −0.1653880
H 0.0157730 0.8891370 0.2899130
C 1.2296960 −0.7594880 −0.4864520
O 1.2409630 −1.9074980 −1.0110540
O −1.2883370 −1.8996300 −0.9827160
H −0.3274050 −2.1898720 −1.1243600
C 6.4702080 1.8564910 0.2804150
H 6.3667570 2.1910570 1.3259160
C −6.4515210 1.8311630 0.5088670
H −6.3904240 2.0287060 1.5915630
O −6.9272580 3.0785830 −0.1284750
H −7.9446710 2.9087850 −0.1716680
H −6.7399620 3.8866370 0.3945090
O 6.9998710 3.0065430 −0.4856350
H 6.8142040 3.8758170 −0.0715980
H 8.0151850 2.8113140 −0.4615420

C-E-C2+2OH
C 2.4828310 −0.0568210 −0.0181240
H 2.3934600 0.9602840 0.3581930
C −2.4791000 −0.0354300 −0.0135200
H −2.4037470 0.9834420 0.3591620
C −3.6785080 −0.6229140 −0.2138990
H −3.6904440 −1.6636430 −0.5361320
C 3.6870440 −0.6296070 −0.2168370
H 3.6966120 −1.6693050 −0.5455780
C −4.9848920 0.0060920 −0.0155300
C −6.1269040 −0.8880710 0.1674470
C −5.1710930 1.3498490 −0.0319730
C −7.4119030 −0.4469000 0.2583180
H −5.9187260 −1.9541330 0.1919550
H −4.3606830 2.0507870 −0.2135510
C −7.6863600 0.9916740 0.1232360
C 4.9926580 0.0007330 −0.0143260
C 6.1376440 −0.8909570 0.1608760
C 5.1743240 1.3450080 −0.0214270
C 7.4214550 −0.4463400 0.2530750
H 5.9327460 −1.9578020 0.1778700
H 4.3604890 2.0438610 −0.1956150
C 7.6910770 0.9938490 0.1267140
O 8.8011330 1.4752620 −0.0709100
O −8.7984220 1.4679400 −0.0752830
O 8.5323190 −1.1995820 0.3353310
O −8.5202250 −1.2029810 0.3473600
C −8.3580370 −2.6178340 0.3493650
H −9.3643440 −3.0315960 0.4197270
H −7.8813080 −2.9549670 −0.5788900
H −7.7640060 −2.9406990 1.2126690
C 8.3743740 −2.6148880 0.3284790
H 9.3819880 −3.0260750 0.3951840
H 7.7821780 −2.9450330 1.1902900
H 7.8976970 −2.9475760 −0.6014110
C −1.2200220 −0.7116250 −0.2557000
C −0.0030770 −0.0929260 −0.0292540
H 0.0100990 0.9271240 0.3390860
C 1.2304410 −0.7811090 −0.2779070
O 1.2420200 −1.9737280 −0.7042280
O −1.2796310 −1.9606850 −0.7056830
H −0.3115410 −2.2541730 −0.8051900
C 6.5004410 1.9169270 0.3235570
H 6.4795300 2.0094630 1.4377990
C −6.4983950 1.9199710 0.3116900
H −6.4766120 2.0216680 1.4250440
O −6.7279020 3.1736680 −0.2748690
H −7.6978660 3.2828970 −0.3016470
O 6.7251650 3.1758620 −0.2532370
H 7.6948340 3.2873360 −0.2823800

C-E-P2-OH
C 2.4808560 −0.0645140 −0.0489820
H 2.3860600 1.0191380 −0.0544240
C −2.4768400 −0.0378240 0.0454730
H −2.3958560 1.0462600 0.0485880
C −3.6791310 −0.6623580 0.0612630
H −3.6755360 −1.7519300 0.0519660
C 3.6883900 −0.6742620 −0.0621300
H 3.6831840 −1.7647480 −0.0508370
C −4.9954750 −0.0436170 0.0866210
C −6.1204210 −0.8952030 0.0700770
C −5.1818570 1.3488960 0.1255560
C −7.4028590 −0.3572470 0.0894610
H −5.9738110 −1.9702770 0.0406820
H −4.3411270 2.0357680 0.1426020
C −7.5771460 1.0327950 0.1277640
C 5.0032330 −0.0515490 −0.0868340
C 6.1313160 −0.8986530 −0.0702630
C 5.1836300 1.3416560 −0.1251030
C 7.4116330 −0.3554440 −0.0892650
H 5.9886310 −1.9742780 −0.0412890
H 4.3389290 2.0236950 −0.1415590
C 7.5799750 1.0353300 −0.1271010
O 8.5839370 −1.0448200 −0.0753550
O −8.5721020 −1.0516200 0.0755460
C −8.5112880 −2.4735000 0.0374200
H −9.5470360 −2.8147490 0.0322520
H −8.0047210 −2.8170770 −0.8718740
H −7.9979080 −2.8649560 0.9232180
C 8.5289880 −2.4669320 −0.0378410
H 9.5661250 −2.8039450 −0.0325890
H 8.0236180 −2.8129960 0.8711800
H 8.0173940 −2.8601350 −0.9239040
C −1.2214780 −0.7537410 0.0215500
C −0.0004030 −0.0984050 −0.0015450
H 0.0147320 0.9864190 −0.0021290
C 1.2324400 −0.8296400 −0.0242470
O 1.2388080 −2.1009710 −0.0227440
O −1.2759140 −2.0843880 0.0224650
H −0.3028260 −2.3865180 0.0047290
C 6.4644090 1.8784660 −0.1451980
C −6.4649410 1.8802300 0.1460830
O −6.6385740 3.2295010 0.1850080
H −7.5914820 3.4244160 0.1973010
O 6.6328320 3.2284850 −0.1833490
H 7.5849750 3.4270940 −0.1951720
O 8.8093660 1.6133620 −0.1479900
H 9.4841090 0.9111180 −0.1344310
O −8.8089020 1.6058270 0.1491170
H −9.4808080 0.9008780 0.1354840

C-E-P2
C 2.4864420 0.0197620 −0.2066850
H 2.4003400 1.0672500 0.0729750
C −2.4758750 0.0446850 −0.1945410
H −2.3958350 1.0938400 0.0777460
C −3.6748940 −0.5670650 −0.3200290
H −3.6847450 −1.6320620 −0.5450450
C 3.6854800 −0.5819300 −0.3418530
H 3.6898700 −1.6467730 −0.5729380
C −4.9766940 0.0674240 −0.1396810
C −6.0949320 −0.8504410 0.0614220
C −5.1452850 1.4274480 −0.1700460
C −7.3640980 −0.4122290 0.2576790
H −5.8697140 −1.9122280 0.0588940
H −4.3201360 2.1073190 −0.3590830
C −7.6455460 1.0495740 0.2606130
C 4.9890920 0.0547040 −0.1640850
C 6.1034280 −0.8561010 0.0833190
C 5.1565800 1.4117750 −0.2402990
C 7.3701610 −0.4115800 0.2822980
H 5.8773790 −1.9172710 0.1131420
H 4.3327830 2.0823310 −0.4652970
C 7.6522820 1.0495570 0.2387370
O 8.7636790 1.5055380 0.4174430
O −8.7600550 1.4986520 0.4386070
O 8.4557160 −1.1486050 0.5236810
O −8.4530850 −1.1564810 0.4589310
C −8.2982210 −2.5754410 0.4752620
H −9.2955560 −2.9786640 0.6496890
H −7.9139090 −2.9307940 −0.4874470
H −7.6249080 −2.8785060 1.2849840
C 8.2993120 −2.5662220 0.5860720
H 9.2937210 −2.9637510 0.7880160
H 7.6143790 −2.8410460 1.3961250
H 7.9280260 −2.9537690 −0.3692730
C −1.2184930 −0.6547500 −0.3832320
C −0.0042200 −0.0139110 −0.2179020
H 0.0086250 1.0345540 0.0580730
C 1.2290930 −0.7253260 −0.4039370
O 1.2435640 −1.9454170 −0.7227270
O −1.2864540 −1.9358000 −0.7183850
H −0.3261190 −2.2476360 −0.7996860
C 6.4558700 2.0034190 −0.0493810
C −6.4459440 2.0120300 0.0234080

O −6.6739140 3.2190780 0.0119800
O 6.6836220 3.2086490 −0.0999930

C-E-C2+H2O
C 2.8208750 0.1185300 0.0867650
H 2.6964480 1.1654080 0.3511760
C −2.1376590 0.0066440 0.0161230
H −2.0963560 1.0587600 0.2875030
C −3.3143450 −0.6308720 −0.1509070
H −3.3016070 −1.6994120 −0.3603450
C 4.0487230 −0.4480580 −0.0660450
H 4.0682310 −1.5042300 −0.3342360
C −4.6355830 −0.0069730 −0.0489740
C −5.7503750 −0.8989210 0.2836120
C −4.8390880 1.3168140 −0.2638980
C −7.0530090 −0.4989750 0.3475320
H −5.5065680 −1.9464000 0.4341070
H −4.0411470 2.0082350 −0.5151500
C −7.3443590 0.8807050 −0.0091090
C 5.3265630 0.1940040 0.0838340
C 6.4900780 −0.5788980 −0.1318360
C 5.4612330 1.5768430 0.4391860
C 7.7505400 −0.0225110 −0.0076270
H 6.3724000 −1.6244790 −0.3999620
H 4.5721950 2.1770280 0.6079700
C 7.9136420 1.3993950 0.3558180
O 9.0424800 1.9153770 0.4700610
O −8.4235930 1.3341540 −0.3864320
O 8.9011500 −0.6701310 −0.1917940
O −8.1370750 −1.2521430 0.5543220
C −7.9456040 −2.6544870 0.7503170
H −8.9428440 −3.0672740 0.8995390
H −7.4821060 −3.1051230 −0.1344030
H −7.3292290 −2.8383310 1.6372020
C 8.8637550 −2.0518170 −0.5496460
H 9.9056780 −2.3579410 −0.6430450
H 8.3717360 −2.6400150 0.2325490
H 8.3484650 −2.1885440 −1.5065650
C −0.8551410 −0.6591440 −0.1289220
C 0.3371710 0.0146350 0.0542910
H 0.3164500 1.0668600 0.3161330
C 1.5945780 −0.6624900 −0.1060800
O 1.6432130 −1.8905530 −0.4070110
O −0.8793270 −1.9471270 −0.4497190
H 0.0950850 −2.2280100 −0.5045720
C 6.6901160 2.1501290 0.5690940
H 6.8013790 3.1972930 0.8380720
C −6.1776460 1.8569260 0.0476090
H −6.1809130 2.2878950 1.0621170
O −6.6437850 2.9213720 −0.8703060
H −7.6539220 2.7131980 −0.9233770
H −6.5046500 3.8286150 −0.5245120

C-E-C2+OH
C 2.7880410 0.1345010 0.0448550
H 2.6687040 1.1925200 0.2637060
C −2.1702200 0.0384440 0.0053590
H −2.1234790 1.1011990 0.2308300
C −3.3528980 −0.6027230 −0.1190470
H −3.3348920 −1.6785140 −0.2904780
C 4.0135500 −0.4446630 −0.0741790
H 4.0288470 −1.5117860 −0.2952270
C −4.6766650 0.0123170 −0.0224830
C −5.7991450 −0.8785540 0.2665960
C −4.8953450 1.3361990 −0.2242330
C −7.0957720 −0.4629960 0.2811470
H −5.5653840 −1.9256580 0.4377460
H −4.0998880 2.0268350 −0.4910560
C −7.4030820 0.9365820 −0.0506380
C 5.2939590 0.1964170 0.0588870
C 6.4555900 −0.5922030 −0.1061150
C 5.4338310 1.5933930 0.3498970
C 7.7178620 −0.0381890 0.0081070
H 6.3345830 −1.6485990 −0.3261770
H 4.5469110 2.2066120 0.4783530
C 7.8859840 1.3974460 0.3073870
O 9.0171740 1.9111600 0.4137870
O −8.5231680 1.3526700 −0.3244290
O 8.8669850 −0.7009160 −0.1310920
O −8.1865350 −1.2288440 0.4580060
C −7.9902400 −2.6263890 0.6490580
H −8.9871230 −3.0532410 0.7622040
H −7.4919460 −3.0703140 −0.2211060
H −7.4011390 −2.8170500 1.5540040
C 8.8245280 −2.0978750 −0.4217280
H 9.8653770 −2.4145120 −0.4888450
H 8.3205630 −2.6447130 0.3826570
H 8.3184940 −2.2785030 −1.3763160
C −0.8938760 −0.6334140 −0.1292450
C 0.3072620 0.0413050 0.0181850
H 0.2934840 1.1030990 0.2388500
C 1.5565620 −0.6467380 −0.1190460
O 1.6025050 −1.8877750 −0.3733880
O −0.9170620 −1.9334080 −0.3996840
H 0.0591470 −2.2144860 −0.4491890
C 6.6651180 2.1646930 0.4682980
H 6.7798530 3.2228000 0.6887790
C −6.2409420 1.9127780 0.0230340
H −6.2378880 2.1656260 1.1122860
O −6.4918030 3.0682740 −0.7320090
H −7.4635940 3.1474090 −0.7851310

C-E-C3
C −2.7967020 0.0950610 0.0121850
H −2.6843060 1.1636720 −0.1446770
C 2.1462380 0.0358460 −0.0268600
H 2.0830520 1.1062490 −0.2024210
C 3.3382080 −0.6056770 0.0522550
H 3.3207450 −1.6868720 0.1838220
C −4.0159670 −0.5072230 0.1008040
H −4.0281840 −1.5848790 0.2523210
C 4.6571640 0.0063780 −0.0393710
C 5.7938960 −0.8903030 −0.2351390
C 4.8605690 1.3450660 0.0919730
C 7.0872130 −0.4646200 −0.2174740
H 5.5741170 −1.9468800 −0.3584680
H 4.0545400 2.0452160 0.2930460
C 7.3730720 0.9555010 0.0462800
C −5.2801870 0.1521840 0.0008790
C −6.4372650 −0.6368500 0.0809500
C −5.3747020 1.6004430 −0.1805480
C −7.6865960 −0.0461810 −0.0223470
H −6.3365600 −1.7080850 0.2191480
H −4.4636650 2.1859070 −0.2286920
C −7.8172380 1.4552840 −0.2223310
O −8.9177360 1.9682820 −0.3198380
O 8.4763700 1.3958340 0.3418850
O −8.8319560 −0.6506980 0.0342500
O 8.1879310 −1.2272760 −0.3066570
C 8.0117340 −2.6361460 −0.4284490
H 9.0163250 −3.0569820 −0.4748720
H 7.4801300 −3.0358320 0.4432140
H 7.4642580 −2.8815380 −1.3460400
C −8.8996080 −2.0794530 0.2269480
H −9.9627210 −2.3101760 0.2444190
H −8.4096090 −2.5853970 −0.6085940
H −8.4323020 −2.3435310 1.1788910
C 0.8890460 −0.6557010 0.0969060
C −0.3321320 0.0216490 0.0017180
H −0.3336290 1.0927150 −0.1645490
C −1.5551740 −0.6923430 0.1223790
O −1.6054210 −1.9422880 0.3139120
O 0.9109620 −1.9587640 0.3016720
H −0.0634870 −2.2545260 0.3524540
C −6.5653680 2.2188350 −0.2861550
H −6.6524010 3.2924080 −0.4219470
C 6.2090820 1.9154990 −0.1395470
H 6.2418260 2.0836550 −1.2453400
O 6.4190300 3.1248240 0.5345310
H 7.3867370 3.2220590 0.6199170

C-E-C3+H2O
C −2.4555220 −0.0495990 0.1256640
H −2.3802920 0.9553070 −0.2848970
C 2.5080740 −0.0171600 0.0437210
H 2.4244540 0.9823530 −0.3761570
C 3.7108480 −0.5965410 0.2504620
H 3.7260170 −1.6197230 0.6244220
C −3.6489470 −0.6338330 0.3369350
H −3.6564190 −1.6656460 0.6881290
C 5.0153190 0.0155650 −0.0016100
C 6.1544060 −0.8911310 −0.1344180
C 5.2035410 1.3573220 −0.0756090
C 7.4394580 −0.4593000 −0.2613620
H 5.9443440 −1.9560900 −0.0885220
H 4.3962100 2.0710310 0.0652080
C 7.7169780 0.9846250 −0.2203300
C −4.9548940 −0.0109250 0.1015780
C −6.0597050 −0.9173240 −0.2236190
C −5.1484790 1.3282410 0.1894600
C −7.3480690 −0.5101320 −0.4120990
H −5.8241870 −1.9767520 −0.2635560
H −4.3538340 2.0274290 0.4297300
C −7.6382390 0.8989310 −0.2006900
O −8.7330260 1.3964010 0.0593300
O 8.8302380 1.4709010 −0.0570680
O −8.4289150 −1.2665450 −0.6238940
O 8.5456660 −1.2217070 −0.3082580
C 8.3813500 −2.6333160 −0.2149460
H 9.3865320 −3.0527700 −0.2642240
H 7.9103510 −2.9066980 0.7369180
H 7.7810400 −3.0115820 −1.0509180
C −8.2489260 −2.6828530 −0.6803580
H −9.2414240 −3.0965510 −0.8562790
H −7.5806070 −2.9527990 −1.5054790
H −7.8502390 −3.0566010 0.2693910
C 1.2558880 −0.6816670 0.3415680
C 0.0317130 −0.0749270 0.1079810
H 0.0091370 0.9267110 −0.3070210
C −1.1906750 −0.7559830 0.4050380
O −1.1993640 −1.9260890 0.8854390
O 1.3244700 −1.9067440 0.8477560
H 0.3610540 −2.1999260 0.9780750
C −6.4539030 1.8538510 −0.2586730
H −6.3768690 2.1926400 −1.3051040
C 6.5295270 1.9004770 −0.4645480
H 6.5009160 1.9254690 −1.5822200
O 6.7640050 3.1905420 0.0338250
H 7.7344440 3.2977050 0.0527090
O −6.9693970 3.0002670 0.5235580
H −6.7939740 3.8713200 0.1089250
H −7.9845340 2.8030400 0.5204910

C-E-C4
C 2.3875760 0.1330670 −0.0002300
H 2.2671260 1.2130030 −0.0003080
C −2.5272820 0.1140720 −0.0002810
H −2.4285810 1.1945520 −0.0004030
C −3.7521590 −0.5063550 −0.0000850
H −3.7670250 −1.5938260 0.0000670
C 3.6171930 −0.4552120 −0.0001120
H 3.6297730 −1.5456750 −0.0001410
C −5.0088730 0.1543730 −0.0000480
C −6.1727980 −0.6413050 0.0001550
C −5.1122780 1.6110090 −0.0002290
C −7.4202490 −0.0503000 0.0001680
H −6.0674780 −1.7210470 0.0003110
C −6.3095200 2.2277940 −0.0002040
H −4.2066920 2.2070810 −0.0003680
C −7.5576870 1.4565110 −0.0000090
H −6.4034600 3.3094940 −0.0003280
C 4.9049200 0.1902430 0.0000040
C 6.0604450 −0.6287620 0.0000150
C 5.0643810 1.5926570 0.0001250
C 7.3225360 −0.0624180 0.0001030

H 5.9421170 −1.7081550 −0.0000580
C 6.3271370 2.1626560 0.0002430
H 4.1956910 2.2436890 0.0001690
C 7.4598940 1.3462810 0.0002320
H 6.4581850 3.2410350 0.0003440
O 8.6851370 1.8999920 0.0003520
H 9.3476070 1.1832060 0.0003420
O −8.6610760 1.9792770 −0.0000090
O 8.5075620 −0.7213890 0.0001120
O −8.5694640 −0.6670870 0.0003780
C −8.6148190 −2.1058070 0.0005400
H −9.6739850 −2.3563410 0.0004330
H −8.1303820 −2.4921240 −0.9003440
H −8.1306210 −2.4918900 0.9016560
C 8.4915650 −2.1462640 −0.0000170
H 9.5373090 −2.4543380 0.0000010
H 7.9927310 −2.5271660 0.8983250
H 7.9927980 −2.5270230 −0.8984590
C −1.2926890 −0.6213510 −0.0002960
C −0.0890810 0.0581510 −0.0004020
H −0.0951240 1.1427500 −0.0004980
C 1.1762880 −0.6620380 −0.0003210
O 1.1749920 −1.9245750 −0.0003050
O −1.3606940 −1.9482310 −0.0001110
H −0.3986340 −2.2631320 −0.0001890

C-E-C4+H2O
C −2.7682460 0.1684410 −0.0527500
H −2.6498800 1.2406570 0.0846380
C 2.1856730 0.1078850 −0.1292210
H 2.1155520 1.1826970 0.0098070
C 3.3700960 −0.5375940 −0.2105250
H 3.3564860 −1.6166820 −0.3507850
C −3.9899570 −0.4170800 −0.0986020
H −4.0028700 −1.4989010 −0.2375390
C 4.6903060 0.0680570 −0.1249340
C 5.7894260 −0.7246840 −0.2044180
C 4.8403580 1.5246270 0.0536030
H 5.7087700 −1.8020610 −0.3198740
C 6.0279390 2.1670140 0.0046740
H 3.9415310 2.1175910 0.1880950
C 7.2225280 1.4007310 −0.2698440
H 6.1065490 3.2483710 0.0556690
C −5.2890430 0.2187370 0.0158280
C −6.4384990 −0.6013040 −0.0540450
C −5.4586010 1.6037880 0.1917000
C −7.7067280 −0.0507040 0.0488500
H −6.3154690 −1.6719310 −0.1895040
C −6.7287960 2.1580650 0.2941870
H −4.5953320 2.2602320 0.2490870
C −7.8553400 1.3412520 0.2238640
H −6.8639010 3.2278560 0.4293410
O −9.0910280 1.8820040 0.3230060
H −9.7442230 1.1616620 0.2511890
O 8.2922600 1.8316050 −0.6820550
O −8.8870090 −0.7246750 −0.0015360
O 7.7716790 −0.3497460 1.1533290
C 7.4244220 −1.5010910 1.9597440
H 8.0909710 −1.4396000 2.8187080
H 6.3836540 −1.4322550 2.2826070
H 7.6040800 −2.4319660 1.4156000
C −8.8525130 −2.1367270 −0.1773240
H −9.8937050 −2.4606810 −0.1876450
H −8.3746740 −2.3983700 −1.1285660
H −8.3238530 −2.6189860 0.6530780
C 0.9116120 −0.5859700 −0.2142590
C −0.2841300 0.0900650 −0.1092680
H −0.2736130 1.1650710 0.0354730
C −1.5432800 −0.6138830 −0.1824300
O −1.5654050 −1.8690590 −0.3514100
O 0.9557240 −1.9036710 −0.3920010
H −0.0173700 −2.1959870 −0.4192090
C 7.1267380 −0.1217350 −0.0093480
H 8.7092770 0.1411840 −1.2875120
H 8.5929510 −1.4226680 −0.9405120
O 8.0739380 −0.6292800 −1.1924620

C-E-P3-H+
C 2.0125570 0.0810500 −0.0191950
H 1.8614340 1.1569600 −0.0201810
C −2.8952220 −0.0758880 −0.0070540
H −2.8243220 1.0066760 0.0020920
C −4.1054330 −0.7300160 −0.0118380
H −4.0891090 −1.8174670 −0.0237490
C 3.2596920 −0.4722190 −0.0139070
H 3.3037140 −1.5617520 −0.0081620
C −5.3783550 −0.1074810 −0.0024420
C −6.5216980 −0.9333840 −0.0135550
C −5.5191290 1.3503480 0.0198580
C −7.7673930 −0.3558760 −0.0017860
H −6.4208360 −2.0143180 −0.0313550
C −6.7269220 1.9504150 0.0343760
H −4.6254160 1.9636960 0.0261850
C −7.9382400 1.1385290 0.0267100
H −6.8403070 3.0297960 0.0525100
C 4.5261610 0.2100940 −0.0129590
C 5.7056250 −0.5744210 0.0121190
C 4.6431200 1.6178300 −0.0363780
C 6.9494450 0.0296900 0.0154420
H 5.6188300 −1.6566770 0.0301650
C 5.8869760 2.2256440 −0.0346300
H 3.7551440 2.2417670 −0.0578030
C 7.0439000 1.4430450 −0.0087710
H 5.9860710 3.3071730 −0.0535160
O 8.2501290 2.0326840 −0.0069500
H 8.9349080 1.3371070 0.0124790
O −9.0847000 1.5748000 0.0421390
O 8.1536520 −0.5905010 0.0400740
C 8.1840520 −2.0153000 0.0646020
H 9.2392250 −2.2885320 0.0820020
H 7.6871020 −2.3963770 0.9638040
H 7.7087520 −2.4268940 −0.8328690
C −1.6442750 −0.7782660 −0.0144840
C −0.4587040 −0.0639930 −0.0143210
H −0.4958010 1.0200510 −0.0091140
C 0.8259650 −0.7489130 −0.0204830
O 0.8598550 −2.0110060 −0.0256770
O −1.6732990 −2.1058750 −0.0213180
H −0.7023680 −2.3932730 −0.0249300
O −8.8755550 −1.0542800 −0.0127120
H −9.6304190 −0.4198390 0.0001770

C-E-P3
C 1.9811910 0.1232610 −0.0002920
H 1.8410260 1.2016040 −0.0005440
C −2.9688300 −0.0486860 −0.0001430
H −2.9213230 1.0362040 −0.0002710
C −4.1447660 −0.7215500 0.0000350
H −4.1097460 −1.8094140 0.0001600
C 3.2150240 −0.4388180 −0.0000470
H 3.2497650 −1.5290230 0.0001590
C −5.4699050 −0.1350880 0.0001010
C −6.5616350 −0.9592690 0.0000380
C −5.6493090 1.3264150 0.0001890
C −7.9133430 −0.4345500 0.0000770
H −6.4497400 −2.0409510 −0.0000180
C −6.8615050 1.9149250 0.0002370
H −4.7635570 1.9538960 0.0002050
C −8.0827940 1.1086170 0.0001630
H −6.9733960 2.9958990 0.0003000
C 4.5012430 0.2315650 −0.0000730
C 5.6669160 −0.5684750 0.0000430
C 4.6435220 1.6308930 −0.0001840
C 6.9243620 0.0151710 0.0000450
H 5.5646860 −1.6498300 0.0000960
C 5.9028730 2.2181710 −0.0001550
H 3.7671430 2.2722750 −0.0002710
C 7.0455700 1.4208510 −0.0000180
H 6.0171110 3.2988630 −0.0002490
O 8.2706170 1.9935050 0.0000070
H 8.9379860 1.2826200 0.0001320
O −9.2038740 1.5936480 0.0001340
O 8.1180500 −0.6366090 0.0001870
C 8.1112410 −2.0599780 0.0005830
H 9.1589110 −2.3624620 0.0008720
H 7.6149870 −2.4460000 0.8985620
H 7.6152930 −2.4464830 −0.8973560
C −1.6835410 −0.7224050 −0.0001770
C −0.5013070 −0.0134380 −0.0000960
H −0.5348150 1.0708580 0.0000330
C 0.7730820 −0.6945470 −0.0002410
O 0.8208780 −1.9600990 −0.0002680
O −1.7001440 −2.0528700 −0.0003500
H −0.7219510 −2.3265300 −0.0003090
O −8.9131450 −1.1450640 0.0000410

C-E-R3
C 2.0467900 0.1274890 −0.0000120
H 1.9107630 1.2056450 −0.0001790
C −2.9064020 −0.0444560 −0.0000250
H −2.8604500 1.0403430 −0.0000460
C −4.0803590 −0.7202360 −0.0000150
H −4.0432260 −1.8080100 −0.0000120
C 3.2816360 −0.4453930 0.0001020
H 3.3146290 −1.5347100 0.0002670
C −5.4074970 −0.1366610 −0.0000190
C −6.4950620 −0.9652980 −0.0000730
C −5.5919740 1.3240850 0.0000730
C −7.8498100 −0.4446100 −0.0000640
H −6.3796940 −2.0465660 −0.0001120
C −6.8062290 1.9083800 0.0000790
H −4.7084030 1.9546290 0.0001660
C −8.0248470 1.0980930 −0.0001020
H −6.9216740 2.9889430 0.0001860
C 4.5507020 0.2294680 0.0000220
C 5.7240980 −0.5583130 0.0001200
C 4.6669360 1.6592530 −0.0001640
C 6.9773130 0.0273510 0.0000300
H 5.6200720 −1.6390880 0.0002620
C 5.8881230 2.2622970 −0.0002600
H 3.7698290 2.2710980 −0.0002290
C 7.1217290 1.4973450 −0.0001720
H 5.9861490 3.3447120 −0.0004030
O 8.2434800 2.0396620 −0.0002590
O −9.1477400 1.5783880 0.0000300
O 8.1362460 −0.6308970 0.0001060
C 8.1169170 −2.0586690 0.0003520
H 9.1628530 −2.3652190 0.0004370
H 7.6178090 −2.4375240 0.8988160
H 7.6178640 −2.4378310 −0.8980140
C −1.6209660 −0.7172680 −0.0000150
C −0.4362500 −0.0069440 −0.0000120
H −0.4683490 1.0771290 −0.0000610
C 0.8306960 −0.6903120 0.0000980
O 0.8901260 −1.9530750 0.0001400
O −1.6353470 −2.0450430 −0.0000260
H −0.6604390 −2.3239580 −0.0000720
O −8.8456380 −1.1594350 −0.0000720

C-E-C5
C −2.0638980 0.0946210 0.0000240
H −1.9367700 1.1728590 −0.0000060
C 2.8896730 −0.0466230 0.0000170
H 2.8382590 1.0375000 0.0000070
C 4.0655510 −0.7197180 0.0000080
H 4.0326370 −1.8076050 0.0000250
C −3.2870340 −0.4991040 0.0000360
H −3.3148290 −1.5869900 0.0000750
C 5.3915530 −0.1310550 −0.0000160
C 6.4757970 −0.9618180 0.0000030
C 5.5759970 1.3293460 −0.0000580
C 7.8341730 −0.4389780 −0.0000140
H 6.3612990 −2.0430470 0.0000350
C 6.7903720 1.9133710 −0.0000740
H 4.6926150 1.9600840 −0.0000730

C 8.0095000 1.1039150 −0.0000530
H 6.9052770 2.9938910 −0.0001020
C −4.5463300 0.1853240 0.0000130
C −5.7081360 −0.5953310 −0.0000510
C −4.6210360 1.6468690 0.0000660
C −6.9527470 0.0196390 −0.0000690
H −5.6196580 −1.6765290 −0.0000800
C −5.8029690 2.2896300 0.0000750
H −3.7017500 2.2212870 0.0000990
C −7.0650550 1.5392650 0.0000240
H −5.8762430 3.3727160 0.0001110
O −8.1594140 2.0708700 0.0000630
O 9.1326070 1.5821410 −0.0000660
O −8.1024340 −0.5706940 −0.0001060
C −8.1958900 −2.0127590 −0.0001670
H −9.2631450 −2.2232710 −0.0002160
H −7.7238180 −2.4085520 −0.9024950
H −7.7238910 −2.4086160 0.9021720
C 1.6117490 −0.7280850 0.0000470
C 0.4126770 −0.0208780 0.0000330
H 0.4336080 1.0628110 0.0000080
C −0.8300800 −0.7211240 0.0000530
O −0.9026860 −1.9794630 0.0001200
O 1.6238660 −2.0470390 0.0001000
H 0.6527760 −2.3410050 0.0001160
O 8.8256140 −1.1563860 0.0000060

C-E-C5+H2O

C −1.7076630 0.0411540 −0.1611280
H −1.5883280 1.1109920 −0.0137710
C 3.2541340 −0.0513250 −0.0898150
H 3.1878890 1.0220510 0.0596060
C 4.4387940 −0.7048530 −0.1438640
H 4.4212150 −1.7827530 −0.2933450
C −2.9140390 −0.5552010 −0.2366160
H −2.9304840 −1.6342770 −0.3837820
C 5.7558250 −0.1099680 −0.0171630
C 6.8547560 −0.9198230 −0.0821900
C 5.9169340 1.3403210 0.1789460
C 8.2010550 −0.3881120 0.0410990
H 6.7572700 −1.9930730 −0.2273270
C 7.1206280 1.9331550 0.3031710
H 5.0243850 1.9564630 0.2234110
C 8.3511700 1.1432580 0.2493580
H 7.2181900 3.0058990 0.4466610
C −4.2163950 0.0902390 −0.1358090
C −5.3336890 −0.6751580 −0.2015600
C −4.3257030 1.5505710 0.0394160
H −5.2813240 −1.7541280 −0.3191310
C −5.4970320 2.2230860 0.0016410
H −3.4090430 2.1191620 0.1591580
C −6.7136550 1.4863410 −0.2560800
H −5.5471410 3.3062880 0.0482780
O −7.7775060 1.9399100 −0.6585900
O 9.4653780 1.6306320 0.3592120
O −7.2748550 −0.2376230 1.1935870
C −6.9400570 −1.3927640 2.0006510
H −7.5971060 −1.3164110 2.8656890
H −7.1412840 −2.3223820 1.4618840
H −5.8953780 −1.3408780 2.3138290
C 1.9818310 −0.7371500 −0.2216180
C 0.7827920 −0.0524310 −0.1481470
H 0.7939220 1.0205420 0.0078850
C −0.4661840 −0.7500960 −0.2681690
O −0.5093680 −1.9964180 −0.4525560
O 2.0220770 −2.0488690 −0.4113700
H 1.0564740 −2.3454930 −0.4753970
O 9.2064790 −1.0862700 −0.0114420
C −6.6549690 −0.0373190 0.0115370
O −7.6306960 −0.5279270 −1.1381820
H −8.1668210 −1.3036880 −0.8667930
H −8.2457190 0.2606630 −1.2340810

C-E-P1-H+

C −2.4383550 −0.0930820 −0.0001350
H −2.3366020 0.9878290 −0.0002280
C 2.5121540 −0.0900050 −0.0000430
H 2.4259800 0.9919270 0.0000080
C 3.7092560 −0.7249540 −0.0000620
H 3.7119270 −1.8133030 −0.0001100
C −3.6492060 −0.7148120 −0.0000220
H −3.6539010 −1.8029880 0.0000700
C 5.0153410 −0.0934540 −0.0000150
C 6.1256300 −0.8891780 −0.0000710
C 5.1525770 1.3720960 0.0000970
C 7.4668120 −0.3225230 −0.0000320
H 6.0459400 −1.9735650 −0.0001480
C 6.3474980 1.9948360 0.0001280
H 4.2496800 1.9745270 0.0001570
C 7.5920420 1.2251890 0.0000350
H 6.4275130 3.0784890 0.0002150
C −4.9186220 −0.0542670 −0.0000060
C −6.0701150 −0.8548470 0.0001050
C −5.0211230 1.4056100 −0.0001250
C −7.3187290 −0.2620080 0.0001150
H −5.9762330 −1.9379190 0.0001850
C −6.2149330 2.0262610 −0.0001540
H −4.1128940 1.9969030 −0.0001940
C −7.4619010 1.2507880 −0.0000720
H −6.3088870 3.1076810 −0.0002390
O −8.5688460 1.7560490 0.0000020
O 8.6989950 1.7394890 0.0001960
O −8.4593640 −0.8889800 0.0002910
C 1.2568610 −0.8111930 −0.0000840
C 0.0361800 −0.1399640 −0.0001580
H 0.0247860 0.9437310 −0.0002110
C −1.1846050 −0.8767720 −0.0001360
O −1.2224550 −2.1365060 0.0001200
O 1.3072680 −2.1285010 −0.0000930
H 0.3455440 −2.4518610 −0.0002140
O 8.4807840 −1.0075010 −0.0000020
H −8.3544890 −1.8601700 0.0004170

Table S2. Calculated energy values for compounds.

Compound	Energy [Hartree]	Compound	Energy [Hartree]	Compound	Energy [Hartree]
C-E	–1262.474013	C-K	–1262.469446	C-E-R1	–1261.819909
C-E-R2	–1261.856397	C-E-R2d	–1261.236680	C-E-C1	–1261.649600
C-E-C2+H2O	–1337.366310	C-E-C1d	–1260.808649	C-E-C2+OH	–1336.992820
C-E-C1d+2H2O	–1413.488712	C-E-C2d+2H2O	–1413.493815	C-E-C3	–1336.781309
C-E-P1-2H+	–1182.312739	C-E-C2+2OH	–1412.748078	C-E-C3+H2O	–1413.121638
C-E-P1	–1181.530545	C-E-P2-OH	–1412.825514	C-E-P2	–1410.379045