Electronic Supplementary Material (ESI) for New Journal of Chemistry.

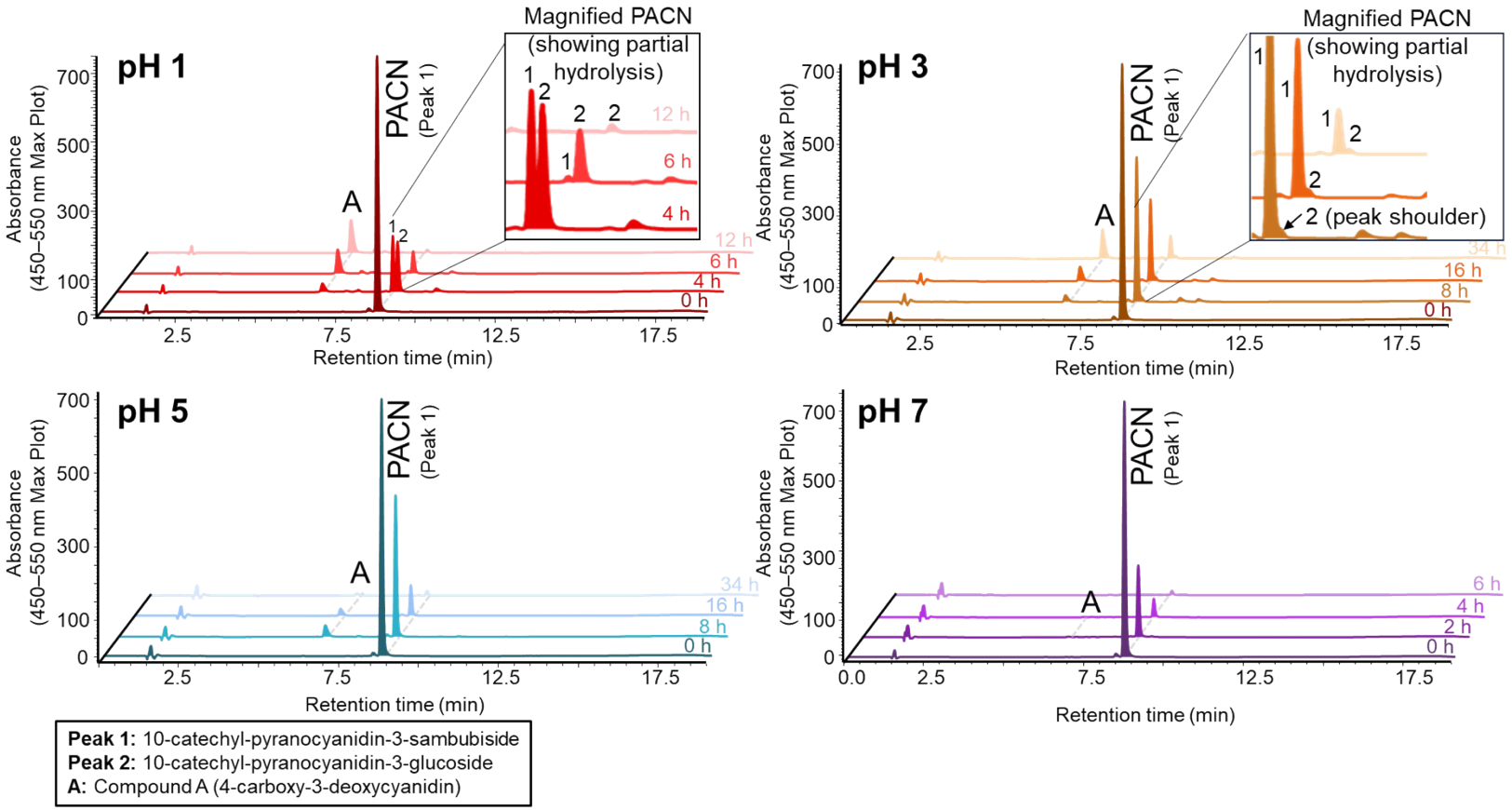


Figure S1. HPLC-PDA chromatograms of 10-catechyl-pyranocyanidin-3-sambubiside (peak 1) at four pH values heated at 90 °C. Compound **A** (peak A) formed at all pH values, however the peak was very small at pH 7.

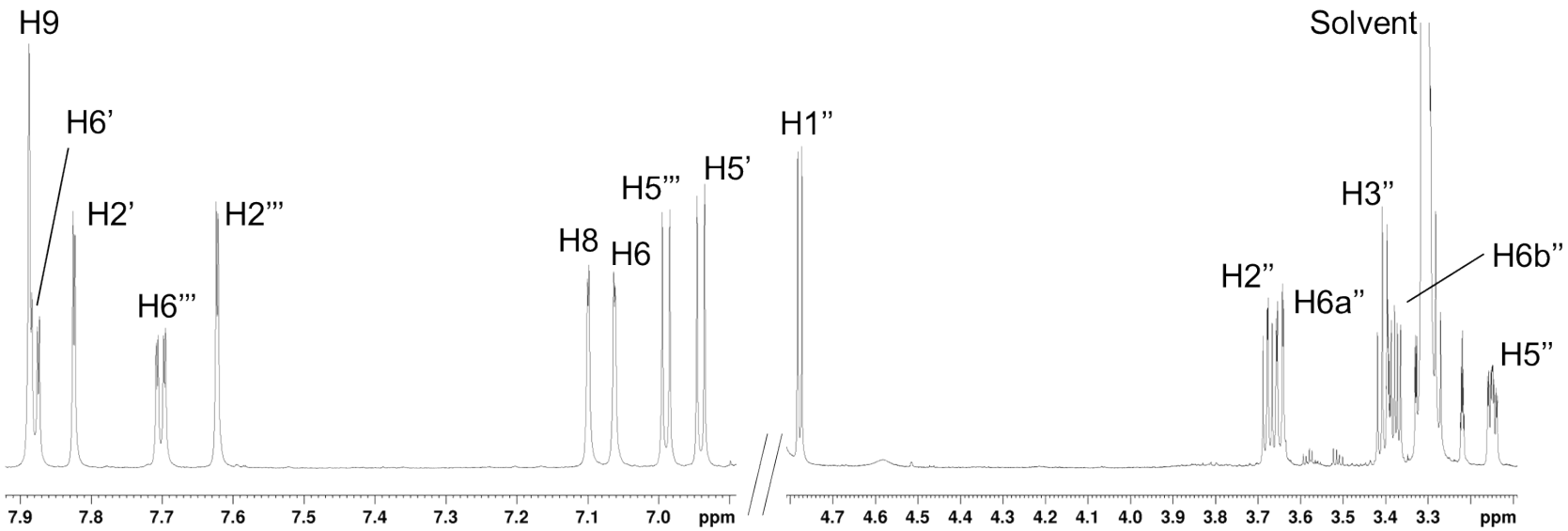


Figure S2. ^{1}H NMR spectrum for 10-catechyl-pyranocyanidin-3-O-β-glucoside.

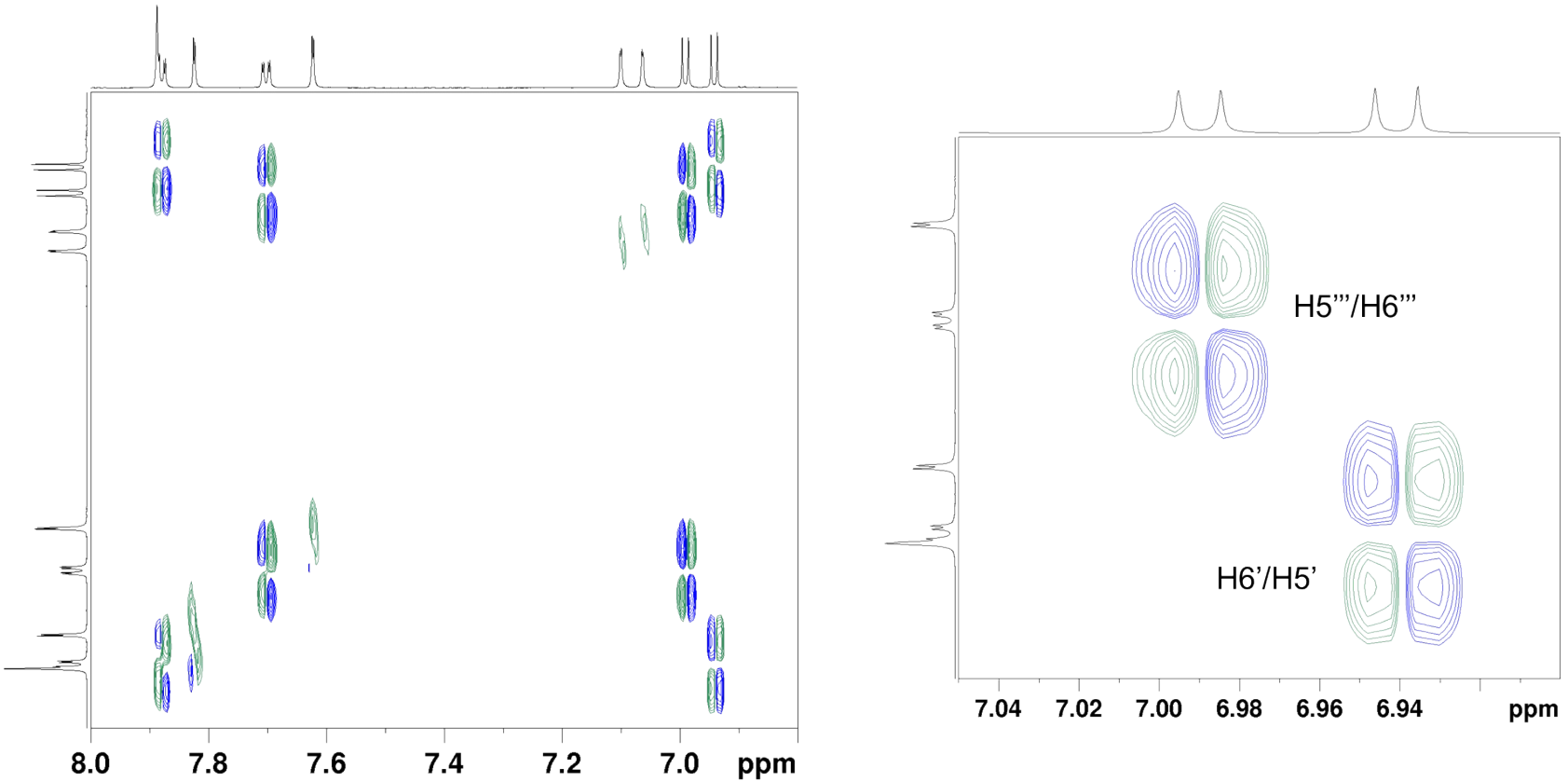


Figure S3. COSY spectrum for 10-catechyl-pyranocyanidin-3-O-β-glucoside.

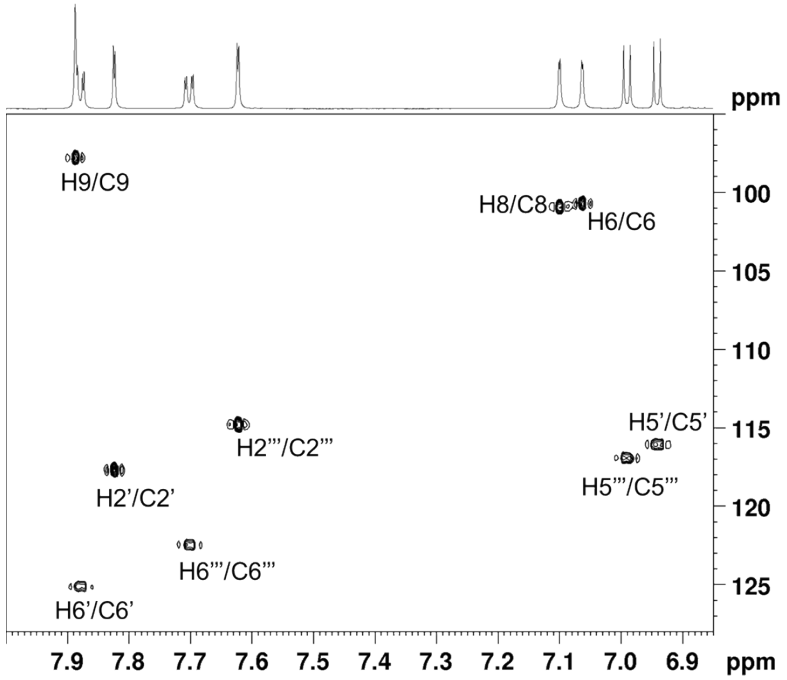


Figure S4. HSQC-DEPT spectrum for 10-catechyl-pyranocyanidin-3-O-β-glucoside.

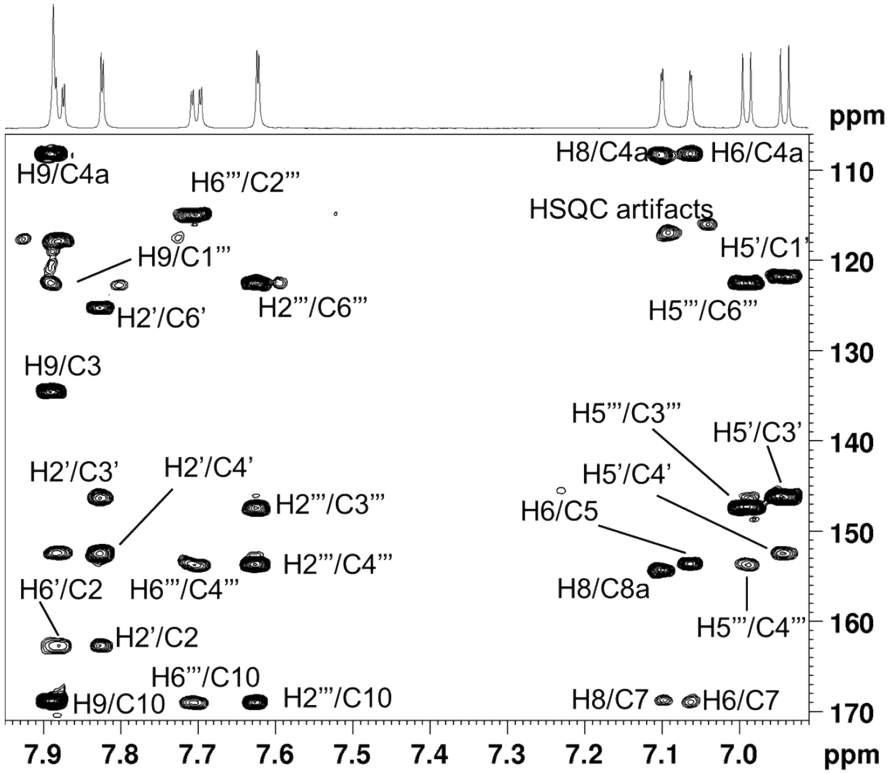


Figure S5. HMBC spectrum for 10-catechyl-pyranocyanidin-3-O-β-glucoside.

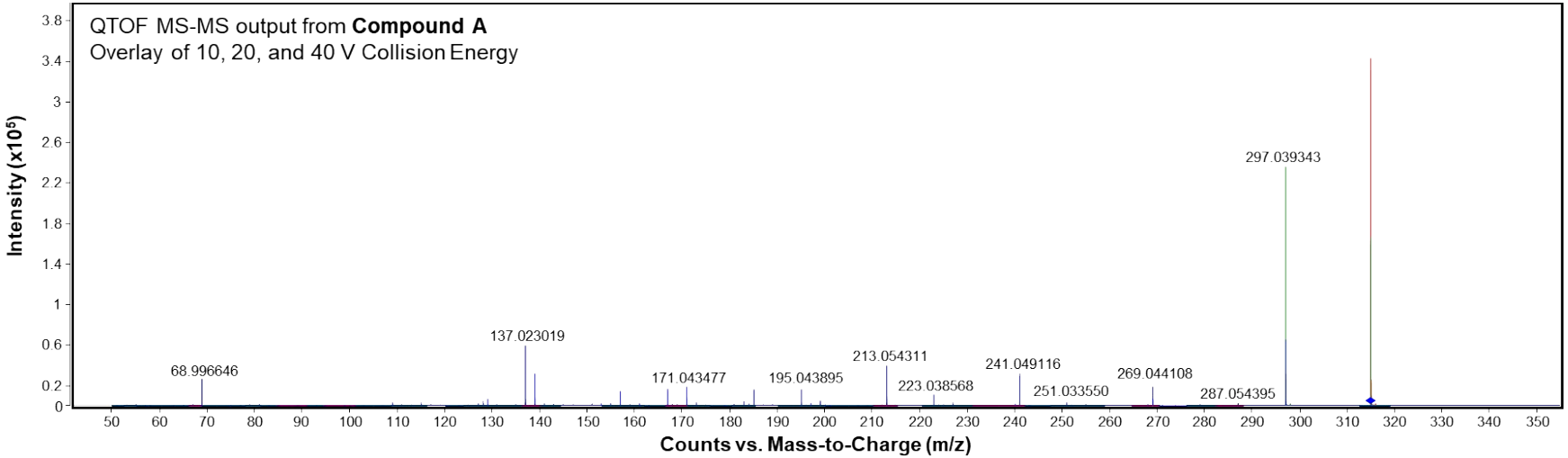


Figure S6. High resolution MS/MS fragmentation of 4-carboxy-3-deoxycyanidin (compound **A**) in positive ion mode using collision energies of 10 (red), 20 (green), and 40 eV (blue), where eV is electron volts.

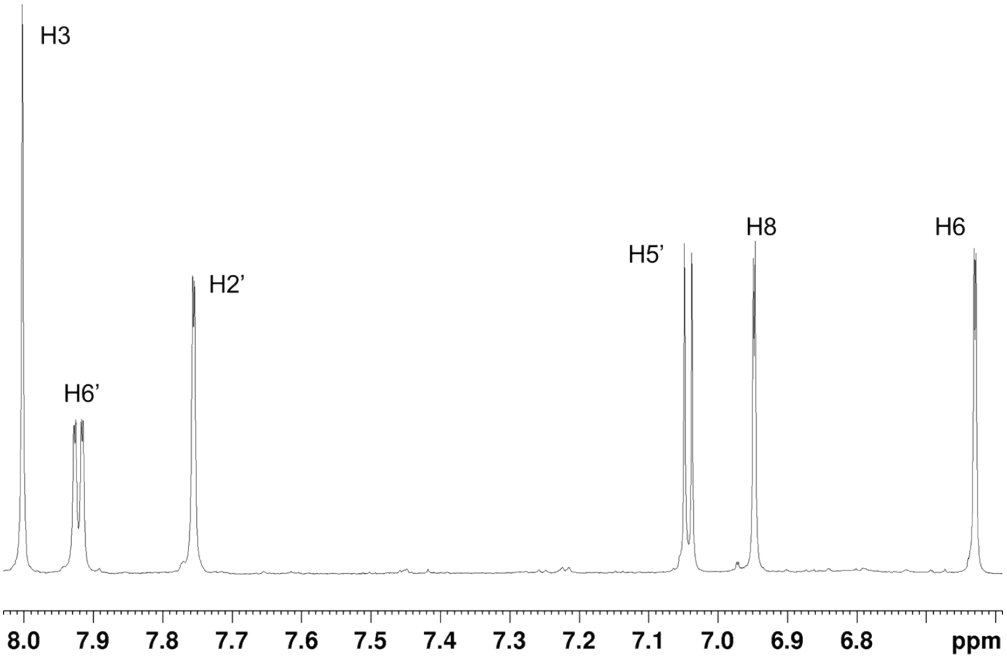


Figure S7. ^{1}H NMR spectrum for 4-carboxy-3-deoxycyanidin (compound **A**).

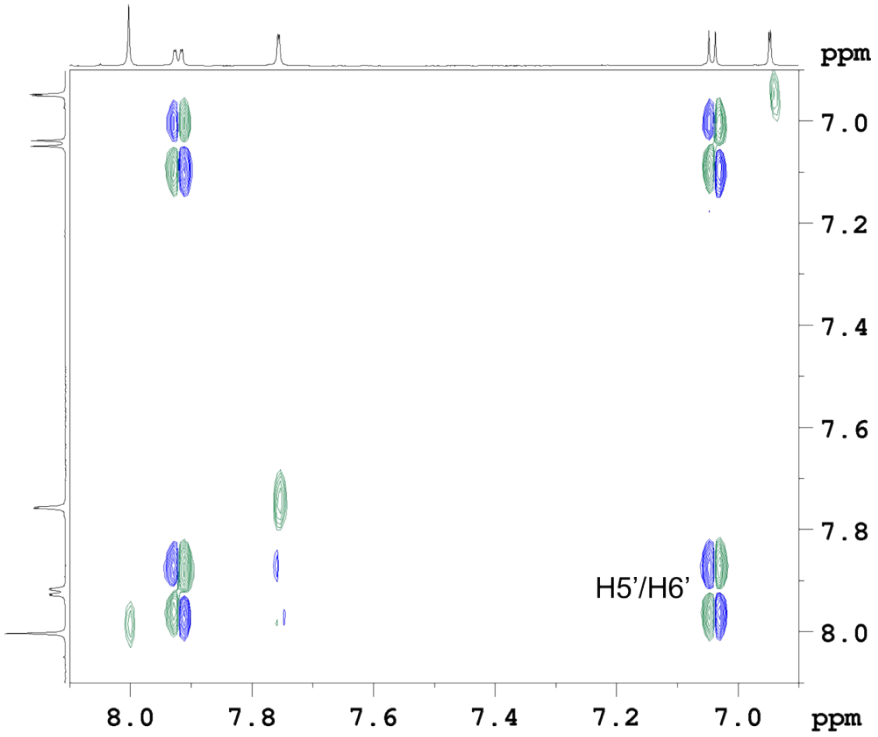


Figure S8. COSY spectrum for 4-carboxy-3-deoxycyanidin (compound **A**).

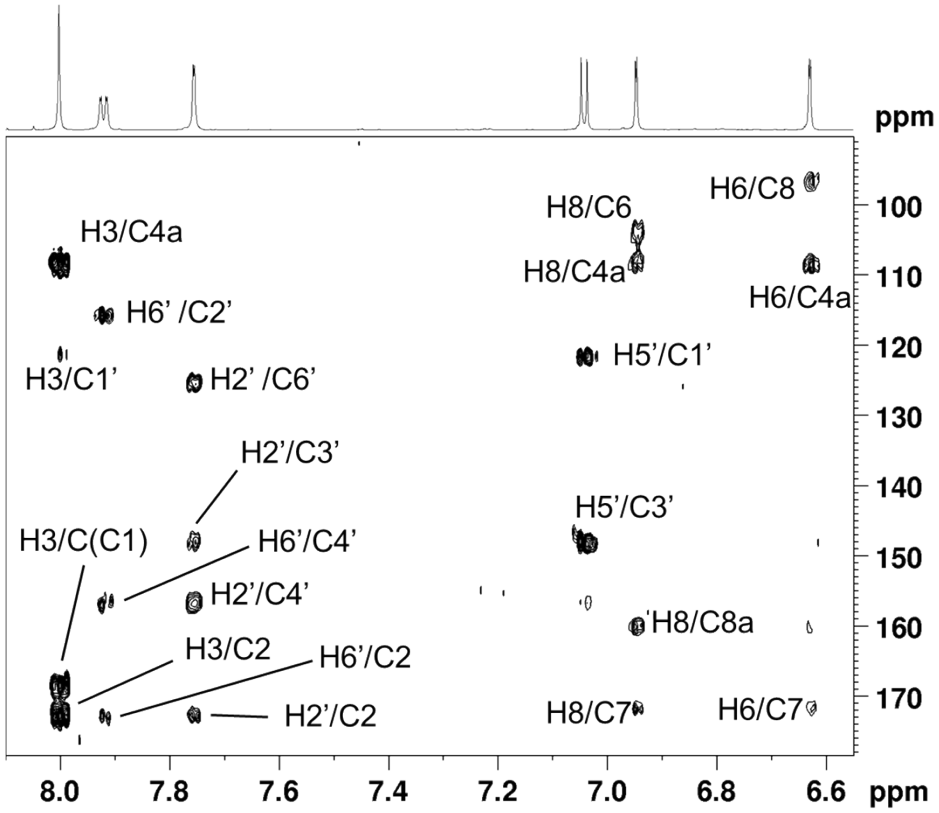


Figure S9. HMBC spectrum for 4-carboxy-3-deoxycyanidin (compound **A**).

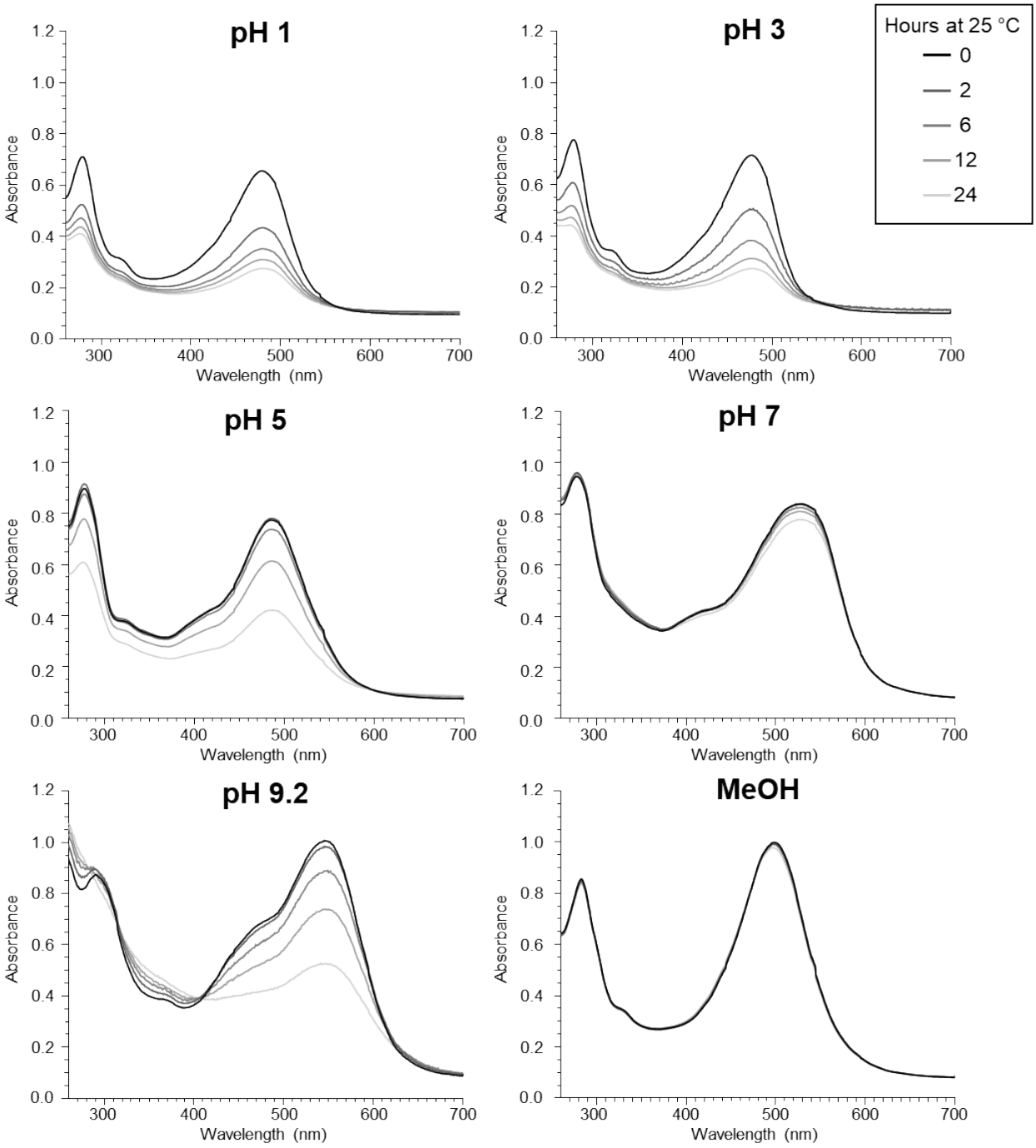
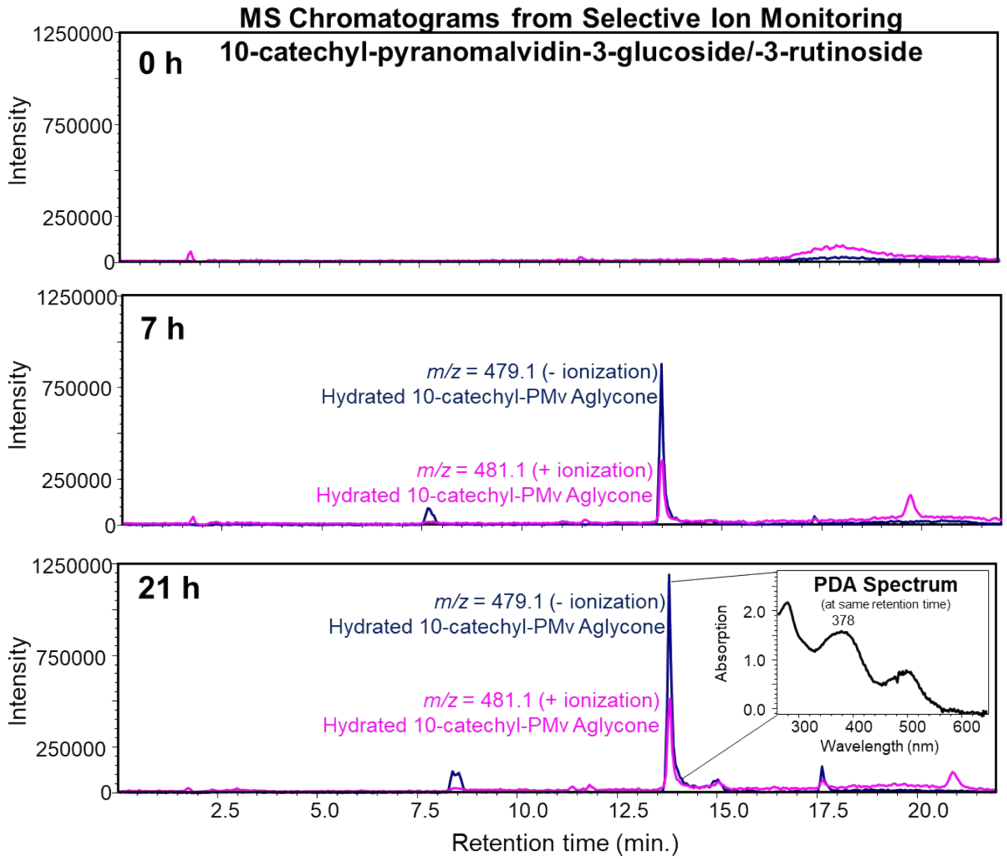


Figure S10. Full spectrum absorbance for 4-carboxy-3-deoxycyanidin (compound **A**) in pH 1–9.2 buffers and MeOH. Spectra show the mean absorption over 24 hours at 25 °C.



HPLC Parameters
Solvent A: Water, Solvent B: Acetonitrile
Flow: 0.35 mL/min, Column Oven: 45 °C
Column: Raptor ARC-18 (150 x 3.0 mm, 2.7 uM) Restek

MS Parameters
Selective Ion Monitoring for predicted compounds
Nebulizing Gas: 1.5 L/min
Drying Gas Flow: 13 L/min
DL Temp. : 230 °C
Heat Block Temp.: 200 °C

Figure S11: MS chromatogram of 10-catechyl-pyranomalvidin-3-glucoside/3-rutinoside in pH 2.8 H_2O (with HCl) heated at 90 °C for 21 hours. A peak consistent with a hydrated aglycone appeared with heating both in positive and negative ionization mode (481.1 and 479.1, respectively) which corresponded to a peak in PDA with absorption in 370 to 385 nm region. Conditions for HPLC-PDA-MS analysis are shown in the figure using the equipment described in Section 2.2.