The heart of oxygenic photosynthesis illuminated

Janssen, G.J.

APPENDIX A

Determination of the level of isotope labeling in Synechocystis sp. PCC 6803 and duckweed by LC-MS.

Table A-1. LCMS peak intensities and calculated $^{L}I_t$ **and** P_n values for unlabeled and labeled Chl *a* isolated from *Synechocystis* sp. PCC 6803

m/z	^{U}I	$^{U}I_{\%}$	^{L}I	$^{L}I_t$	P_n
893.5	429304.0	1	190318.8	190318.8	0.545
894.5	288949.2	0.67	245637.4	117540.6	0.336
895.5	73242.9	0.17	147672.0	36089.6	0.103
896.5	26567.0	0.06	56997.8	876.1	0.003
897.5	7339.1	0.02	16776.9	2756.2	0.008
898.5	1579.5	0.00	5400.6	1162.7	0.003
899.5	0.0	0.00	4324.3	782.6	0.002
900.5	0.0	0.00	0.0	0.0	0.000
901.5	0.0	0.00	0.0	0.0	0.000

Table A-2. LCMS peak intensities and calculated $^{L}I_t$ **and** P_n values for unlabeled and labeled Chl *a* isolated from duckweed

m/z	^{U}I	$^{U}I_{\%}$	^{L}I	$^{L}I_t$	P_n
893.5	161481.0	1	118245.9	118245.9	0.289
894.5	120301.9	0.74	193086.8	104994.7	0.257
895.5	68342.5	0.42	173475.7	45211.2	0.111
896.5	9208.8	0.17	121856.1	36994.8	0.090
897.5	3323.8	0.02	75276.7	22594.0	0.055
898.5	1277.0	0.00	41455.4	6387.8	0.016
899.5	633.7	0.00	26502.6	10071.8	0.025
900.5	0.0	0.00	28208.2	16712.9	0.041
901.5	0.0	0.00	64674.5	47596.7	0.116

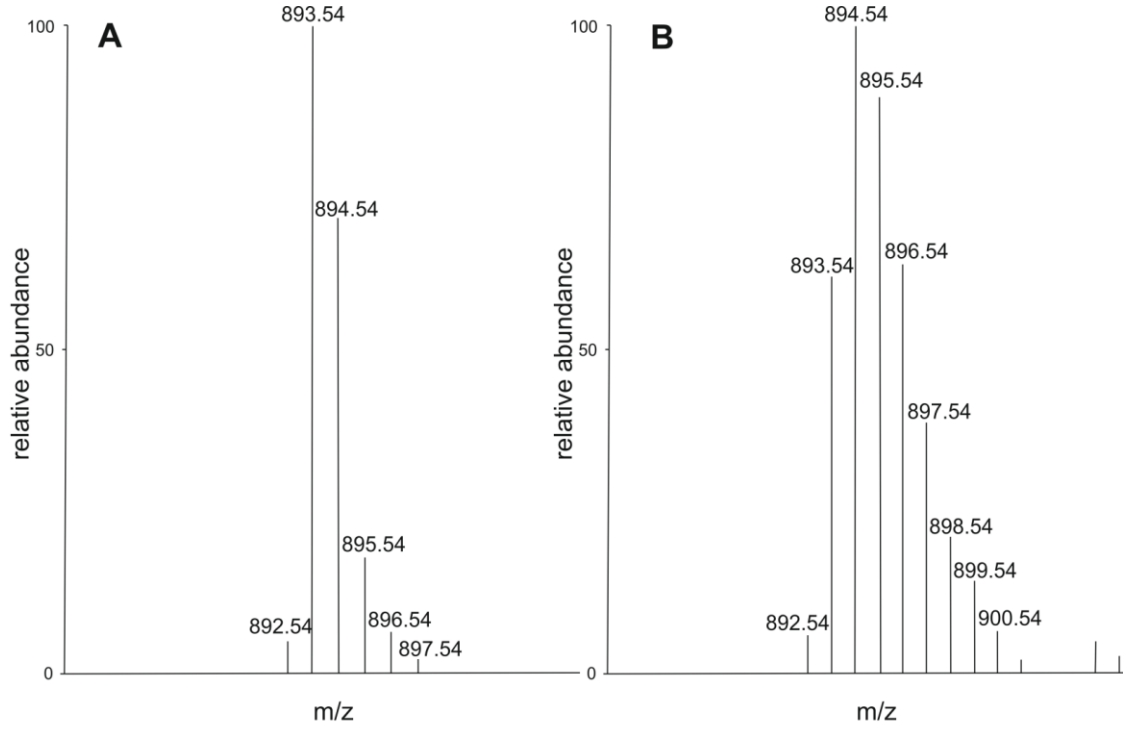
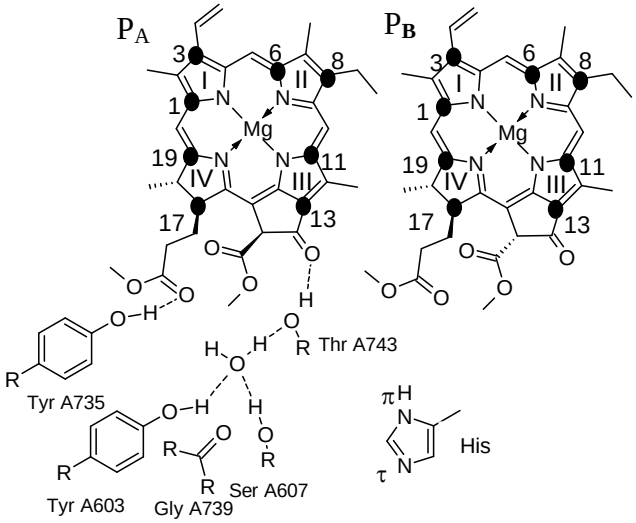


Figure-A 1: ^{13}C isotope incorporation determined by LCMS for Chl *a* isolated from duckweed leaves grown on unlabeled substrate (A) and with the ^{13}C 4-ALA precursor in the medium (B).

APPENDIX B

Quantum Chemistry Calculations on PSI



Appendix-B 1: The theoretical model used for the calculations on the PSI RC. Depicted are the two central Chls, P_A and P_B of the Chl *a*/Chl *a*' dimer P700, and the hydrogen bonds of P_A to the aminogroups of the surrounding protein matrix. The Mg atoms of the P_A and P_B cofactors are coordinated to respectively the His residues 680 and 660 of the protein backbone. A His residue is depicted and the π and τ nitrogen are indicated. The carbon atoms which are labeled in the ^{13}C 4-ALA treated plants are indicated by the black dots and numbered according to the IUPAC nomenclature.

Table Appendix-B 1: **Theoretically calculated ^{13}C and ^{15}N chemical shifts for photo-CIDNP signals expected from selected atoms within the PSI RC**

Carbon	**P_B**	**P_A**	**A_{0B}**	**A_{0A}**
C-1	153.7	155.0	154.3	154.7
C-3	143.7	142.1	143.3	143.1
C-6	154.3	154.1	153.9	153.8
C-8	147.3	147.0	149.4	149.4
C-11	152.9	152.5	153.1	152.8
C-13	134.6	135.0	135.8	134.8
C-17	59.0	58.9	60.3	60.5
C-19	166.6	167.4	168.7	168.4
Nitrogen	**P_B**	**P_A**	**A_{0B}**	**A_{0A}**
N-I	195.6	193.3	196.3	192.7
N-II	210.0	212.1	208.3	207.3
N-III	196.9	198.9	193.2	194.0
N-IV	263.2	255.5	252.1	248.3
His_Nπ	164.2	160.3		
His_Nτ	231.3	239.5		

Calculated chemical shifts in ppm for the 15N and 13C isotope labeled atoms in PSI. The system was truncated and all H-bonded amino-acid side chains were simplified to phenol, methanol or formaldehyde. The coordinates of heavy atoms were kept fixed. Histidines were truncated to methyl-imidazole and the methyl carbons were kept at fixed positions. The phytyl chain was truncated to methyl which was also fixed in the calculations. Optimization was done in Turbomole with the BP86 functional and the TZVP basis using the resolution of identity approximation. The structure published by Jordan et. al. 2011, PDB 2WSC was used as a starting point. The minimized structure was used for single point calculations in ADF. NMR shift calculations were performed using a triple-zeta basis and the SAOP model potential. The P_B Chl *a* and P_A Chl *a*' of P700 were treated as a dimer and the hydrogen bonds were taken into account.

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