

## Supporting Information

### Comparative Profiling of *Chlorella vulgaris* Cells, Extracts, and Intact Chloroplasts Using Electron Transfer Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry (ET-MALDI-MS)

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**Table S1** Compounds detected in *C. vulgaris* intact cells by ET MALDI-MS.

Compound	Abbreviation	Ion type	<i>m/z Theo</i>	MALDI MS		
				<i>m/z Exp</i>	Mass Accuracy (ppm)	S/N
<b>Chlorophyll derivatives</b>						
Chlorophyll <i>b</i>	Chld <i>b</i>	[C <sub>35</sub> H <sub>32</sub> MgN <sub>4</sub> O <sub>6</sub> ] <sup>++</sup>	628.217	628.218	1.3	38.1
	Chl <i>b</i>	[C <sub>55</sub> H <sub>70</sub> MgN <sub>4</sub> O <sub>6</sub> ] <sup>++</sup>	906.515	906.512	2.9	15.6
	Chl <i>b</i> -NH <sub>4</sub>	[C <sub>55</sub> H <sub>70</sub> MgN <sub>4</sub> O <sub>6</sub> + NH <sub>4</sub> ] <sup>+</sup>	924.549	924.539	10.8	8.7
Pheophorbide <i>a</i>	Phd <i>a</i>	[C <sub>35</sub> H <sub>36</sub> N <sub>4</sub> O <sub>5</sub> ] <sup>++</sup>	592.269	592.267	3.4	100.3
	Chld <i>a</i> (II)	[C <sub>30</sub> H <sub>25</sub> MgN <sub>4</sub> O] <sup>+</sup>	481.152	481.150	3.1	59.7
Chlorophyllide <i>a</i>	Chld <i>a</i> (I)	[C <sub>33</sub> H <sub>31</sub> MgN <sub>4</sub> O <sub>3</sub> ] <sup>+</sup>	555.225	555.229	7.7	7.2
	Chld <i>a</i>	[C <sub>35</sub> H <sub>34</sub> MgN <sub>4</sub> O <sub>5</sub> ] <sup>++</sup>	614.238	614.239	1.6	245.0
Pheophytin <i>a</i>	Phtn <i>a</i>	[C <sub>55</sub> H <sub>74</sub> N <sub>4</sub> O <sub>5</sub> ] <sup>++</sup>	870.566	870.568	2.2	16.6
	Phtn <i>a</i> -Cu	[C <sub>55</sub> H <sub>72</sub> N <sub>4</sub> O <sub>5</sub> Cu] <sup>++</sup>	931.480	931.485	5.6	25.1
Chlorophyll <i>a</i>	Chl <i>a</i>	[C <sub>55</sub> H <sub>72</sub> MgN <sub>4</sub> O <sub>5</sub> ] <sup>++</sup>	892.535	892.534	1.5	90.1
	[7-hydroxymethyl]-Chl <i>a</i>	[7-hyd]-Chl <i>a</i>	[C <sub>55</sub> H <sub>72</sub> MgN <sub>4</sub> O <sub>6</sub> ] <sup>++</sup>	908.530	908.530	0.2
<b>Carotenoids</b>						
Lutein	Lut	[C <sub>40</sub> H <sub>56</sub> O <sub>2</sub> ] <sup>++</sup>	568.428	568.431	5.3	33.3
<b>Lipids</b>						
Phosphatidylcholine	PC(14:0/18:1)	[C <sub>40</sub> H <sub>80</sub> NO <sub>7</sub> P + K] <sup>+</sup>	756.531	756.536	6.7	16.0
Glycosylceramide	GlcCer(15:2/22:0)	[C <sub>43</sub> H <sub>81</sub> NO <sub>8</sub> + K] <sup>+</sup>	778.560	778.559	0.6	12.7

**Table S2** Compounds detected in *C. vulgaris* intact chloroplasts by ET MALDI-MS.

Compound	Abbreviation	Proposed Formula	<i>m/z Theo</i>	MALDI MS		
				<i>m/z Exp</i>	Mass accuracy (ppm)	S/N
<b>Chlorophyll derivatives</b>						
Chlorophyllide <i>b</i>	Chld <i>b</i>	[C <sub>35</sub> H <sub>32</sub> MgN <sub>4</sub> O <sub>6</sub> ] <sup>++</sup>	628.217	628.221	6.1	10.3
Chlorophyll <i>b</i>	Chl <i>b</i>	[C <sub>55</sub> H <sub>70</sub> MgN <sub>4</sub> O <sub>6</sub> ] <sup>++</sup>	906.515	906.512	2.9	6.9
Pheophorbide <i>a</i>	Phd <i>a</i>	[C <sub>35</sub> H <sub>36</sub> N <sub>4</sub> O <sub>5</sub> ] <sup>++</sup>	592.269	592.273	7.4	44.8
Chlorophyllide <i>a</i>	Chld <i>a</i> (I)	[C <sub>30</sub> H <sub>25</sub> MgN <sub>4</sub> O] <sup>+</sup>	481.152	481.155	7.3	10.1
	Chld <i>a</i>	[C <sub>35</sub> H <sub>34</sub> MgN <sub>4</sub> O <sub>5</sub> ] <sup>++</sup>	614.238	614.233	8.1	41.0
Pheophytin <i>a</i>	Phtn <i>a</i>	[C <sub>55</sub> H <sub>74</sub> N <sub>4</sub> O <sub>5</sub> ] <sup>++</sup>	870.566	870.562	4.5	65.3
Chlorophyll <i>a</i>	Chl <i>a</i>	[C <sub>55</sub> H <sub>72</sub> MgN <sub>4</sub> O <sub>5</sub> ] <sup>++</sup>	892.535	892.533	2.6	27.4
	[7-hydroxymethyl]-Chl <i>a</i>	[7-hyd]Chl <i>a</i>	[C <sub>55</sub> H <sub>72</sub> MgN <sub>4</sub> O <sub>6</sub> ] <sup>++</sup>	908.530	908.526	4.6
<b>Carotenoids</b>						
Lutein	Lut	[C <sub>40</sub> H <sub>56</sub> O <sub>2</sub> ] <sup>++</sup>	568.428	568.427	1.8	4.7
Loroxanthin	Lor	[C <sub>40</sub> H <sub>56</sub> O <sub>3</sub> ] <sup>++</sup>	584.423	584.420	5.0	3.3
<b>Lipids</b>						
Ceramide	Cer(18:0/16:0)	[C <sub>34</sub> H <sub>69</sub> NO <sub>4</sub> + H] <sup>+</sup>	556.531	556.536	9.9	4.5

**Table S3** Compounds detected in *C. vulgaris* UAE extract by MALDI MS.

Compound	Abbreviation	Proposed formula	<i>m/z Theo</i>	MALDI MS		
				<i>m/z Exp</i>	Mass accuracy (ppm)	S/N
<b>Chlorophyll pigments</b>						
Pheophorbide <i>a</i>	Phd <i>a</i>	[C <sub>35</sub> H <sub>36</sub> N <sub>4</sub> O <sub>5</sub> ] <sup>+</sup> **	592.268	592.266	3.4	54.7
Chlorophyllide <i>a</i>	Chld <i>a</i>	[C <sub>35</sub> H <sub>34</sub> N <sub>4</sub> O <sub>5</sub> Mg] <sup>+</sup> **	614.237	614.232	8.1	7.7
Pheophytin <i>a</i>	Phtn <i>a</i>	[C <sub>55</sub> H <sub>74</sub> N <sub>4</sub> O <sub>5</sub> ] <sup>+</sup> **	870.565	870.566	1.1	169.9
[7-hydroxymethyl]-Chl <i>a</i>	[7-Hyd]Chl <i>a</i>	[C <sub>55</sub> H <sub>72</sub> N <sub>4</sub> O <sub>6</sub> Mg] <sup>+</sup> **	908.530	908.525	5.5	19.2
		[C <sub>55</sub> H <sub>72</sub> N <sub>4</sub> O <sub>6</sub> Mg + H] <sup>+</sup>	909.538	909.528	11.0	19.4
		[C <sub>55</sub> H <sub>70</sub> N <sub>4</sub> O <sub>6</sub> Mg] <sup>+</sup> **	906.514	906.499	16.5	12.7
Chlorophyll <i>b</i>	Chl <i>b</i>	[C <sub>55</sub> H <sub>70</sub> N <sub>4</sub> O <sub>6</sub> Mg + NH <sub>4</sub> ] <sup>+</sup>	924.548	924.533	16.2	10.6
		[C <sub>55</sub> H <sub>72</sub> N <sub>4</sub> O <sub>5</sub> Mg] <sup>+</sup> **	892.535	892.535	0.1	42.0
Chlorophyll <i>a</i>	Chl <i>a</i>	[C <sub>55</sub> H <sub>72</sub> N <sub>4</sub> O <sub>5</sub> Mg + K] <sup>+</sup>	931.499	931.497	2.1	7.0
<b>Carotenoids</b>						
Carotene	Car	[C <sub>40</sub> H <sub>56</sub> - C <sub>7</sub> H <sub>8</sub> ] <sup>+</sup>	444.438	444.431	15.8	52.7
Lutein	Lut	[C <sub>40</sub> H <sub>56</sub> O <sub>2</sub> ] <sup>+</sup> **	568.428	568.432	7.0	23.3
Loroxanthin	Lor	[C <sub>40</sub> H <sub>56</sub> O <sub>3</sub> ] <sup>+</sup> **	584.422	584.427	8.6	10.0
Violaxanthin	Vio (I)	[C <sub>40</sub> H <sub>53</sub> ] <sup>+</sup>	583.617	583.621	6.9	12.6
		[C <sub>40</sub> H <sub>56</sub> O <sub>4</sub> ] <sup>+</sup> **	600.417	600.421	6.7	5.0
<b>Lipids</b>						
Ceramides	Cer(44:1;O4)	[C <sub>44</sub> H <sub>87</sub> NO <sub>5</sub> + Na] <sup>+</sup>	732.648	732.629	25.9	7.2
Diacylglycerols	DG(22:2/22:2/0:0)	[C <sub>47</sub> H <sub>84</sub> O <sub>5</sub> + Na] <sup>+</sup>	751.621	751.632	14.6	6.9
	PS(13:0/20:2)	[C <sub>39</sub> H <sub>72</sub> NO <sub>10</sub> P + Na] <sup>+</sup>	768.479	768.491	15.6	9.5
	Phosphatidylserines	PS(19:0/20:1)	[C <sub>45</sub> H <sub>86</sub> NO <sub>10</sub> P + H] <sup>+</sup>	832.606	832.618	14.4
Triacylglycerols	TG(18:3/18:3/20:2)	[C <sub>48</sub> H <sub>82</sub> NO <sub>10</sub> P + Na] <sup>+</sup>	886.557	886.552	5.6	11.8
		[C <sub>59</sub> H <sub>98</sub> O <sub>6</sub> + Na] <sup>+</sup>	925.726	925.719	7.6	7.1
	TG(16:0/20:0/20:0)	[C <sub>59</sub> H <sub>114</sub> O <sub>6</sub> + Na] <sup>+</sup>	941.851	941.864	13.8	7.0

**Table S4** Compounds detected in *C. vulgaris* SFE extract by MALDI MS.

Compound	Abbreviation	Proposed formula	<i>m/z Theo</i>	MALDI MS			
				<i>m/z Exp</i>	Mass accuracy (ppm)	S/N	
<b>Chlorophyll pigments</b>							
Pheophytin <i>a</i>	Phtn <i>a</i>	[C <sub>55</sub> H <sub>74</sub> N <sub>4</sub> O <sub>5</sub> ] <sup>+</sup> **	870.565	870.565	0.1	129.6	
<b>Carotenoids</b>							
Lutein	Lut (II)	[C <sub>40</sub> H <sub>53</sub> ] <sup>+</sup>	533.428	533.431	5.6	7.8	
		[C <sub>40</sub> H <sub>55</sub> O] <sup>+</sup>	551.428	551.440	21.8	55.5	
Antheraxanthin	Ante	[C <sub>40</sub> H <sub>55</sub> O <sub>2</sub> ] <sup>+</sup>	567.422	567.431	15.9	12.2	
<b>Lipids</b>							
Vitamin D3 and derivatives	Vitamin D3 derivat	[C <sub>29</sub> H <sub>44</sub> O <sub>3</sub> + Na] <sup>+</sup>	463.318	463.311	16.8	39.6	
	Vitamin D3 diacetate	[C <sub>31</sub> H <sub>48</sub> O <sub>4</sub> + Na] <sup>+</sup>	507.345	507.339	11.8	49.3	
	DipropylVitamin D3	[C <sub>33</sub> H <sub>56</sub> O <sub>3</sub> + Na] <sup>+</sup>	523.412	523.417	8.2	57.7	
Diacylglycerophosphoglycerols	PG(10:0/10:0)	[C <sub>26</sub> H <sub>51</sub> O <sub>10</sub> P + Na] <sup>+</sup>	577.311	577.316	7.4	7.3	
		DG(12:0/20:0)	[C <sub>35</sub> H <sub>68</sub> O <sub>5</sub> + Na] <sup>+</sup>	591.496	591.500	6.8	8.2
		DG(13:0/20:5)	[C <sub>36</sub> H <sub>60</sub> O <sub>5</sub> + Na] <sup>+</sup>	595.433	595.431	3.4	42.8
Diacylglycerols	DG(dO-36:4)	[C <sub>39</sub> H <sub>72</sub> O <sub>3</sub> + Na] <sup>+</sup>	611.537	611.530	11.4	9.0	
		DG(15:0/19:0)	[C <sub>37</sub> H <sub>72</sub> O <sub>5</sub> + Na] <sup>+</sup>	619.527	619.535	12.9	16.7
		DG(13:0/22:6)	[C <sub>38</sub> H <sub>62</sub> O <sub>5</sub> + Na] <sup>+</sup>	621.449	621.442	11.3	107.0
		PA(13:0/17:2)	[C <sub>33</sub> H <sub>61</sub> O <sub>8</sub> P + Na] <sup>+</sup>	639.400	639.400	0.2	29.7
Diacylglycerophosphates	PA(14:0/18:3)	[C <sub>35</sub> H <sub>63</sub> O <sub>8</sub> P + Na] <sup>+</sup>	665.415	665.411	6.0	8.1	
		PA(13:0/20:1)	[C <sub>36</sub> H <sub>69</sub> O <sub>8</sub> P + Na] <sup>+</sup>	683.462	683.450	17.6	14.2
Phosphatidylserines	PS(20:1/22:6)	[C <sub>48</sub> H <sub>80</sub> NO <sub>10</sub> P + Na] <sup>+</sup>	812.541	812.550	11.1	8.9	
Triacylglycerols	TG(16:0/16:0/18:1)	[C <sub>53</sub> H <sub>100</sub> O <sub>6</sub> + Na] <sup>+</sup>	855.741	855.744	3.5	23.9	

TG(15:0/15:0/22:2)	[C <sub>55</sub> H <sub>102</sub> O <sub>6</sub> + Na] <sup>+</sup>	881.757	881.748	10.2	12.3
TG(14:1/19:0/19:0)	[C <sub>55</sub> H <sub>104</sub> O <sub>6</sub> + Na] <sup>+</sup>	883.773	883.766	7.9	27.4
TG(17:2/17:2/20:5)	[C <sub>57</sub> H <sub>92</sub> O <sub>6</sub> + Na] <sup>+</sup>	895.679	895.683	4.5	10.5
TG(17:2/17:2/20:4)	[C <sub>57</sub> H <sub>94</sub> O <sub>6</sub> + Na] <sup>+</sup>	897.694	897.705	12.3	15.3
TG(16:1/16:1/22:0)	[C <sub>57</sub> H <sub>106</sub> O <sub>6</sub> + Na] <sup>+</sup>	909.788	909.783	5.5	7.3
TG(16:0/17:1/21:0)	[C <sub>57</sub> H <sub>108</sub> O <sub>6</sub> + Na] <sup>+</sup>	911.804	911.799	5.5	10.9
TG(17:0/18:2/20:0)	[C <sub>58</sub> H <sub>108</sub> O <sub>6</sub> + Na] <sup>+</sup>	923.804	923.794	10.8	6.0
TG(18:3/18:3/20:2)	[C <sub>59</sub> H <sub>98</sub> O <sub>6</sub> + Na] <sup>+</sup>	925.761	925.763	2.2	6.2