Table 1

Structural arrangements of type-I and type-II phyllobilins

Name	R_1	R_2	R_3	R_4	R_5	References
Type-I phyllobilins (NCCs)						
Hv-NCC1[a]/*So*-NCC2/*Mc*-NCC42/*Ej*-NCC1[b]/*Pd*-NCC40[b]	$CH(OH)–CH_2OH$	CH_3	OH	CH_3	OH	Kräutler et al. (1991), Oberhuber et al. (2001), Berghold et al. (2002), Moser et al. (2012), Ríos et al. (2014b) and Erhart et al. (2016)
Sw-NCC58[a]/*Cj*-NCC1/*So*-NCC4/*Pc*-NCC2/*Md*-NCC2/*Mc*-NCC61/*Ej*-NCC4[b]/*Pd*-NCC60/*Ps*-NCC3[b]	$CH=CH_2$	CH_3	OH	CH_3	OH	Curty and Engel (1996), Berghold et al. (2002), Oberhuber et al. (2003), Müller et al. (2007), Kräutler et al. (2010), Ríos et al. (2014b), Erhart et al. (2016) and Roca et al. (2017)
Cj-NCC2/*So*-NCC5/*Pd*-NCC71	$CH=CH_2$	CH_3	H	CH_3	OH	Berghold et al. (2002), Oberhuber et al. (2003) and Erhart et al. (2016)
At-NCC4[b]/*Nr*-NCC2/*Zm*-NCC2/*Pc*-NCC1/*Md*-NCC1/*Tc*-NCC2/*Mc*-NCC59/*Pd*-NCC56[b]/*Ug*-NCC43/*Ps*-NCC2[b]	$CH=CH_2$	CH_3	O-β-Glc	CH_3	OH	Berghold et al. (2004), Pružinska et al. (2005), Berghold et al. 2006; Müller et al. (2007), Moser et al. (2012), Scherl et al. (2012), Erhart et al. (2016), Scherl et al. (2016) and Roca et al. (2017)
Zm-NCC1/*Tc*-NCC1/*Co*-NCC1[b]/*Pd*-NCC35[b]	$CH(OH)–CH_2OH$	CH_3	O-β-Glc	CH_3	OH	Berghold et al. (2006), Scherl et al. (2012), Ríos et al. (2014a) and Erhart et al. (2016)
Nr-NCC1	$CH=CH_2$	CH_3	*O*-β-(6′-*O*-Mal)Glc	CH_3	OH	Berghold et al. (2004)
Ej-NCC2[b]	$CH=CH_2$	CH_3	O-Mal	CH_3	OH	Ríos et al. (2014b)
Bn-NCC4[a]/*At*-NCC5[a]/*Bo*-NCC2[a]	$CH=CH_2$	CH_3	H	H	OH	Mühlecker and Kräutler (1996), Pružinska et al. (2005) and Roiser et al. (2015)
At-NCC3[a]	$CH=CH_2$	$CH_2–$	OH	H	OH	Pružinska et al. (2005)

Name	R_1	R_2	R_3	R_4	R_5	References
		OH				
Bn-NCC3[a]/*At*-NCC2[a]/*So*-NCC3/*Mc*-NCC49/*Ej*-NCC3[b]/*Ps*-NCC1[b]	$CH=CH_2$	CH_3	OH	H	OH	Mühlecker and Kräutler (1996), Berghold et al. (2002), Pružinska et al. (2005), Moser et al. (2012), Ríos et al. (2014b) and Roca et al. (2017)
So-NCC1/*Mc*-NCC26	$CH(OH)–CH_2OH$	CH_3	OH	H	OH	Berghold et al. (2002) and Moser et al. (2012)
Bn-NCC1[a]	$CH=CH_2$	CH_3	O-Mal	H	OH	Mühlecker and Kräutler (1996)
Bn-NCC2[a]/*At*-NCC1[a]/*Bo*-NCC1[a]	$CH=CH_2$	CH_3	O-β-Glc	H	OH	Mühlecker and Kräutler (1996), Pružinska et al. (2005) and Roiser et al. (2015)
Co-NCC2[b]	$CH(OH)–CH_2OH$	CH_3	O-β-Glc	H	OH	Ríos et al. (2014a)
Cl-NCC3[b]	$CH(OH)–CH_2OH$	CH_3	CH_3	H	OH	Ríos et al. (2015)
Pd-NCC32	$CH(OH)–CH_2O$-Glc	CH_3	O-β-Glc	CH_3	OH	Erhart et al. (2016)
Mc-NCC55[b]/*Mc*-NCC8[b]	$CH=CH_2$	CH_3	OH	CH_3	Daucic acid	Moser et al. (2012)
Ug-NCC53[c]	$CH=CH_2$	CH_3	O-β-Glc	CH_3	O-β-Glc	Erhart et al. (2016)
Type-II phyllobilins (DNCCs)						
UCC[a]/*Co*-DNCC2[b]/*Ap*-DNCC	$CH(OH)–CH_2OH$	CH_3	OH	CH_3	OH	Losey and Engel (2001), Müller et al. (2011a,, b) and Ríos et al. (2014a)
UNCC-*Pp*/UNCC-*Hvir*/*Ej*-CNCC1[b]	$CH=CH_2$	CH_3	OH	CH_3	OH	Djapic and Pavlovic (2008, 2009) and Ríos et al. (2014b)
Co-DNCC1[b]	$CH(OH)–CH_2OH$	CH_3	O-β-Glc	CH_3	OH	Ríos et al. (2014a)
Bo-DNCC[a]	$CH=CH_2$	CH_3	H	H	OH	Christ et al. (2013) and Roiser et al. (2015)
At-DNCC1[a](*At*-DNCC33)/*Bo*-NCC[a]	$CH=CH_2$	CH_3	OH	H	OH	Roiser et al. (2015)
At-DNCC45[a]/*At*-DNCC48[a]	$CH=CH_2$	CH_3	CH_3	H	OH	Süssenbacher et al. (2015a, b)

Hv, *Hordeum vulgare*; So, *Spinacia oleracea*; Mc, *Musa cavendish*; Ej, *Eriobotrya japonica*; Pd, *Prunus domestica*; Sw, *Spathiphyllum wallisii*; Cj, *Cercidiphyllum japonicum*; Pc, *Pyrus communis*; Md, *Malus domestica*; At, *Arabidopsis thaliana*; Nr, *Nicotiana rustica*; Zm, *Zea mays*; Tc, *Tilia cordata*; Ug, *Ulmus glabra*; Co, *Cydonia oblonga*; Cl, *Citrus lemon*; Bn, *Brassica napus*; Bo, *Brassica oleracea*; Ap, *Acer platanoides*, Pp, *Parrotia Persica*; *Hvir*, *Hamamelis Virginiana*; Ps, *Prunus salicina*. For R_1, R_2, R_3, R_4, and R_5 positions see Fig. 1
[a]Catabolite derived from type-I RCC reductase activity
[b]Structure assigned by UV–visible and mass spectrometry data
[c]The β-glucopyranosyl group bound to $C3^2$ also esterifies the propionate function

Table 2

Diagnostic losses for structural elucidation of NCCs and DNCCs from MS^2 data

Loss from $[M + H]^+$ (Da)	Neutral loss assignment	Structural hint of the NCC/DNCC product
18	H_2O	The structure contains OH group(s)[a]
32	CH_3OH	The structure is methylated at O8[4a]
46	CHOOH or H_2O + CO	The structure presents a free propionic residue, or it is demethylated at O8[4a]
60	$COOCH_3$	The structure is methylated at the O8[4a]
88	$C_3H_4O_3$	The structure presents a malonyl group and it is hydroxylated at C3[2b]
104	$C_3H_4O_4$	The structure presents a malonyl group and it is hydroxylated at C3[2b]
123	C_7H_9NO	Ring D presents the 18^1,18^2-vinyl arrangement[a]
125	$C_7H_{11}NO$	Ring A is not hydroxylated at C3[2a]
137	$C_8H_{11}NO$	Ring D presents the 18^1,18^2-vinyl arrangement[a] or ring A is not hydroxylated at C3[2a]
141	$C_7H_{11}NO_2$	Ring A is hydroxylated at C3[2a]
151	$C_9H_{13}NO$	Ring A is not hydroxylated at C3[2b]
153	$C_8H_{11}NO_2$	Ring A is hydroxylated at C3[2a]
155	$C_8H_{13}NO_2$	Ring A is hydroxylated at C3[2c]
157	$C_7H_{11}NO_3$	Ring D presents the 18^1,18^2-dihydroxyethyl arrangement[a]
162	$C_6H_{10}O_5$	The structure contains a glucopyranosyl group and it is hydroxylated at C3[2d]
164	$C_6H_{12}O_5$	The structure contains a glucopyranosyl group and it is hydroxylated at C3[2d]
167	$C_9H_{13}NO_2$	Ring A is hydroxylated at C3[2b]
171	$C_8H_{13}NO_3$	Ring D presents the 18^1,18^2-dihydroxyethyl arrangement[a]
180	$C_6H_{12}O_6$	The structure contains a glucopyranosyl group and it is hydroxylated at C3[2d]
248	$C_9H_{12}O_8$	The structure contains a glucopyranosyl–yl group and it is hydroxylated at C3[2e]
266	$C_9H_{14}O_9$	The structure contains a glucopyranosyl–malonyl group and it is hydroxylated at C3[2e]

[a]Loss from $[M + H]^+$ is also possible for type-II phyllobilins

[b]Loss from $[M + H]^+$ is only possible for type-I phyllobilins

[c]Loss from $[M + H]^+$ is only possible for type-II phyllobilins

[d]This is unequivocally true if the ring D presents the $18^1,18^2$-vinyl arrangement. Esterification with glucopyranosyl function has been described at ring D with the $18^1,18^2$-dihydroxyethyl arrangement (*Pd*-NCC32)

[e]Only described for *Nr*-NCC1

Figure 1

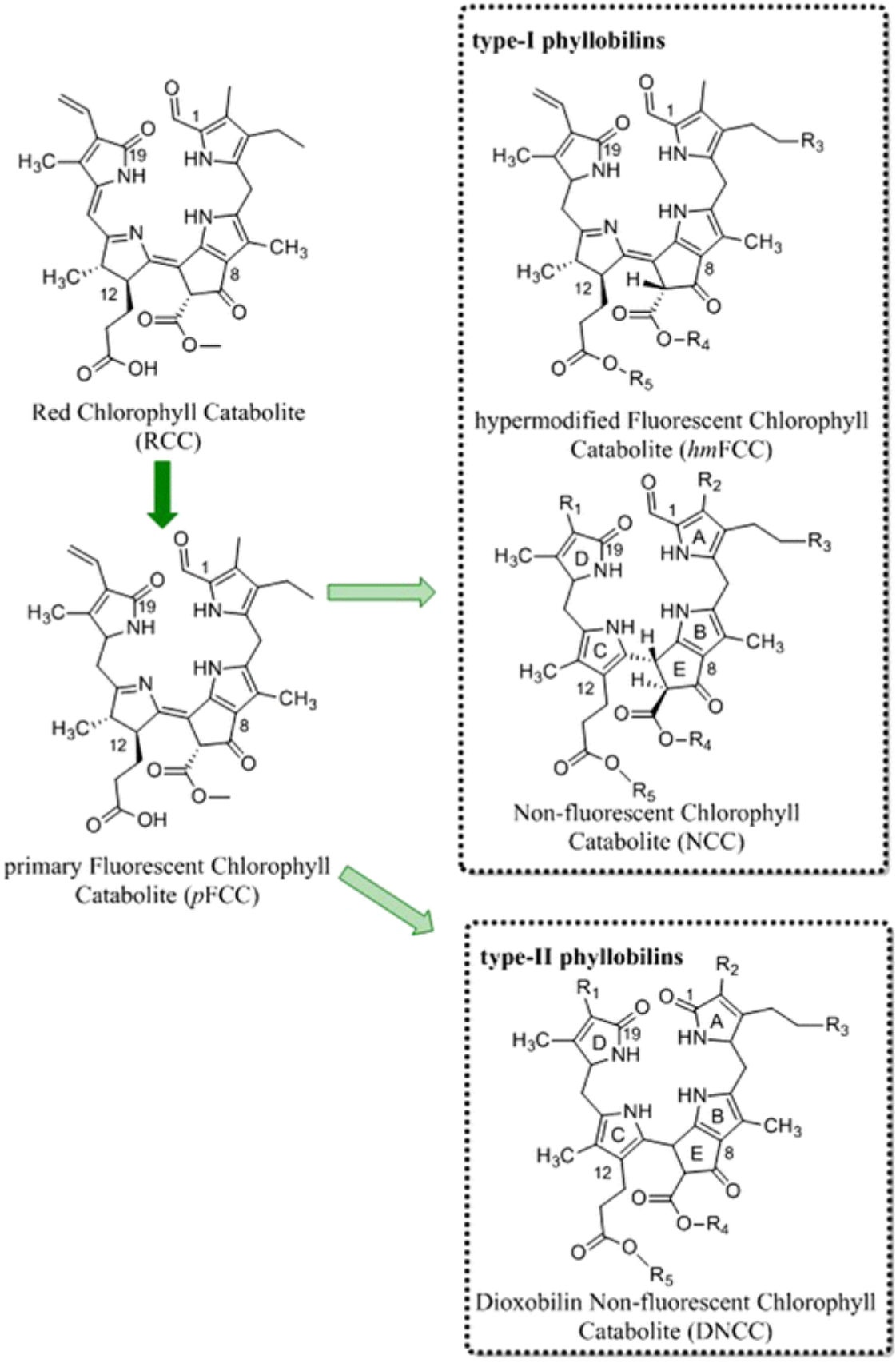

type-I phyllobilins
Red Chlorophyll Catabolite (RCC)
hypermodified Fluorescent Chlorophyll Catabolite (hmFCC)
primary Fluorescent Chlorophyll Catabolite (pFCC)
Non-fluorescent Chlorophyll Catabolite (NCC)
type-II phyllobilins
Dioxobilin Non-fluorescent Chlorophyll Catabolite (DNCC)

Figure 2

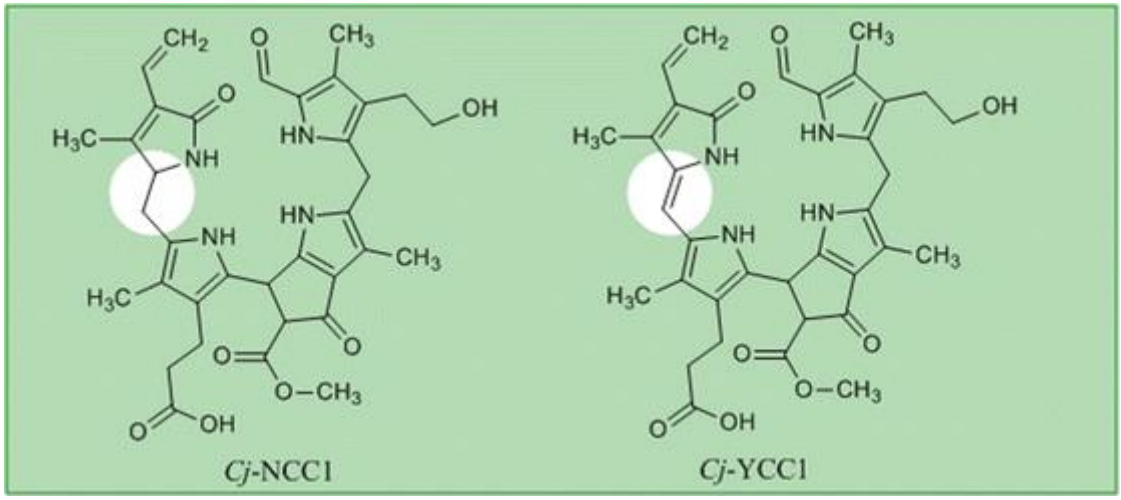
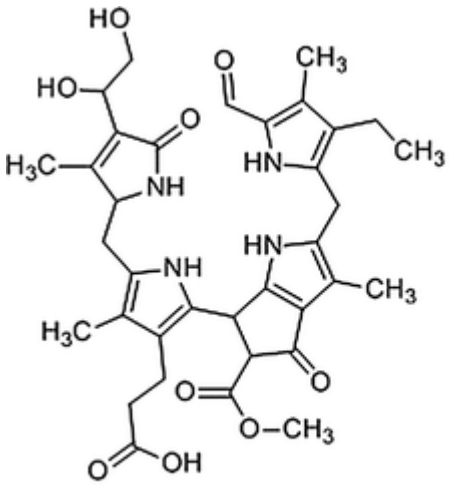
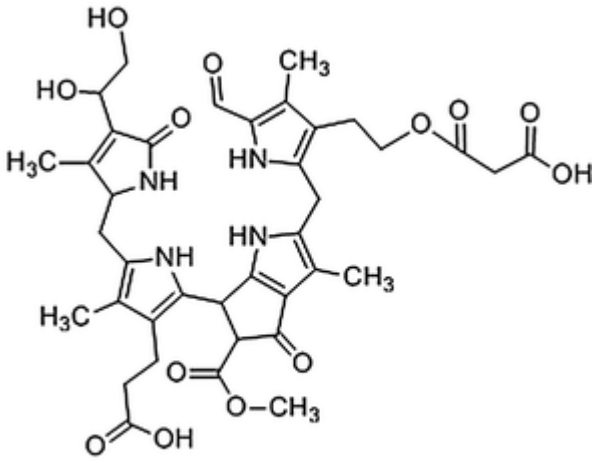


Figure 3

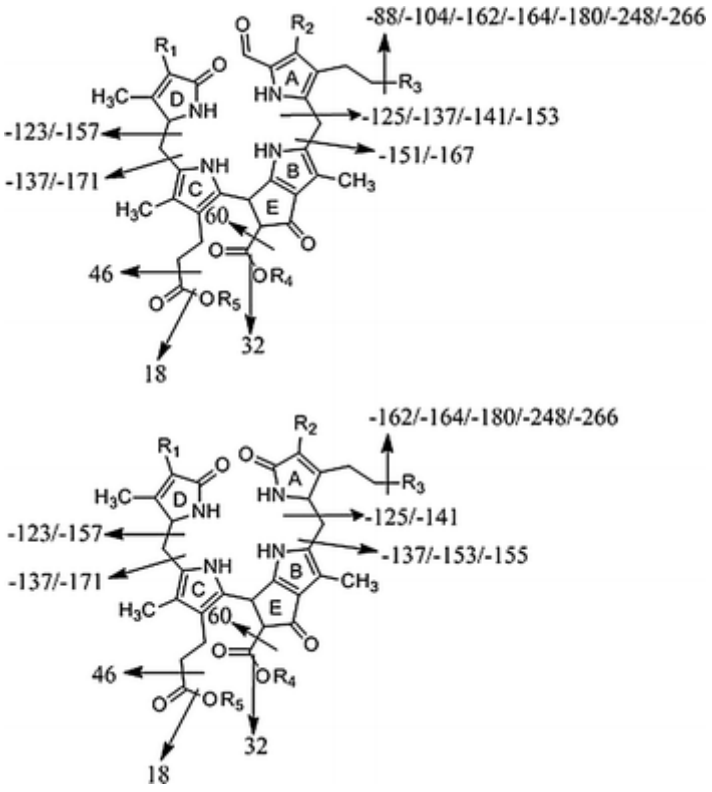


Unknown 1



Unknown 2

Figure 4


-88/-104/-162/-164/-180/-248/-266
-125/-137/-141/-153
-151/-167
-123/-157
-137/-171
46
32
18
-162/-164/-180/-248/-266
-125/-141
-137/-153/-155
-123/-157
-137/-171
46
32
18

Appendix

Figure Legends

Figure 5. MS^2 of $[M + H]^+$ at *m/z* = 807.3447 Da (*Zm*-NCC2 and its structural equivalents in Table 1). Some of the structural features arise from the characteristic fragmentations described in Table 2: 32 Da, methylation at $O8^4$ (at *m/z* = 775 Da $[M + H\text{-}MeOH]^+$); 123 Da, ring D presents the 18^1,18^2-vinyl arrangement (at *m/z* = 683 Da $[M + H\text{-ring D}]^+$); 155 Da, ring A is hydroxylated at $C3^2$; 285 Da, presence of ring D-β-glucopyranoyl

Figure 6. MS^2 of $[M + H]^+$ at *m/z* = 731.29237 Da (*Ej*-NCC2 in Table 1). Some of the structural features arise from the characteristic fragmentations described in Table 2: 88 Da, The structure presents a malonyl group and it is hydroxylated at $C3^2$ (at *m/z* = 643 Da $[M + H\text{-malonyl}]^+$); 209 Da, ring D presents the 18^1,18^2-vinyl arrangement and it is hydroxylated at $C3^2$ (at *m/z* = 522 Da $[M + H\text{-ring D-malonyl}]^+$)

Figure 7. MS^2 of $[M + H]^+$ at *m/z* = 667.2974 Da (UCC and its structural equivalents in Table 1). Some of the structural features arise from the characteristic fragmentations described in Table 2: 18 Da, presence of hydroxyl group (at *m/z* = 649 Da $[M + H\text{-}H_2O]^+$); 32 Da, structure is methylated at $O8^4$ (at *m/z* = 649 Da $[M + H\text{-}MeOH]^+$); 157 Da, ring D presents the 18^1,18^2-dihydroxyethyl arrangement (at *m/z* = 510 Da $[M + H\text{-ring D}]^+$)

Figure 5

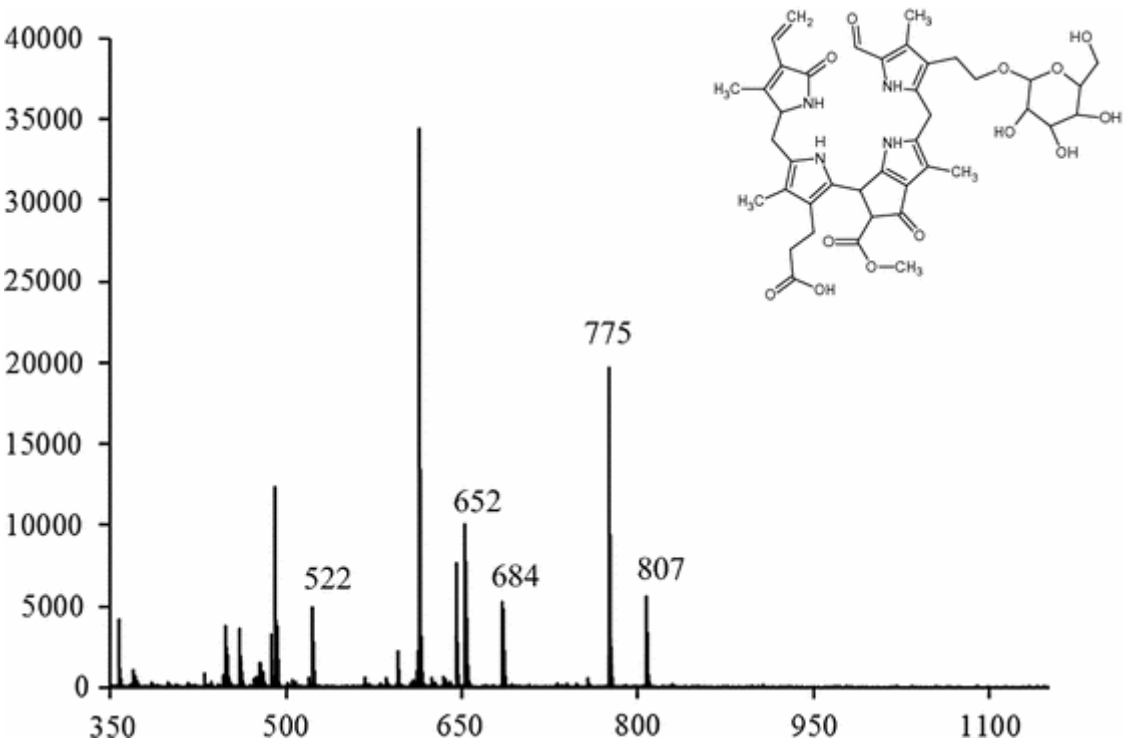

40000
35000
30000
25000
20000
15000
10000
5000
0
350
500
650
800
950
1100
775
652
522
684
807

Figure 6

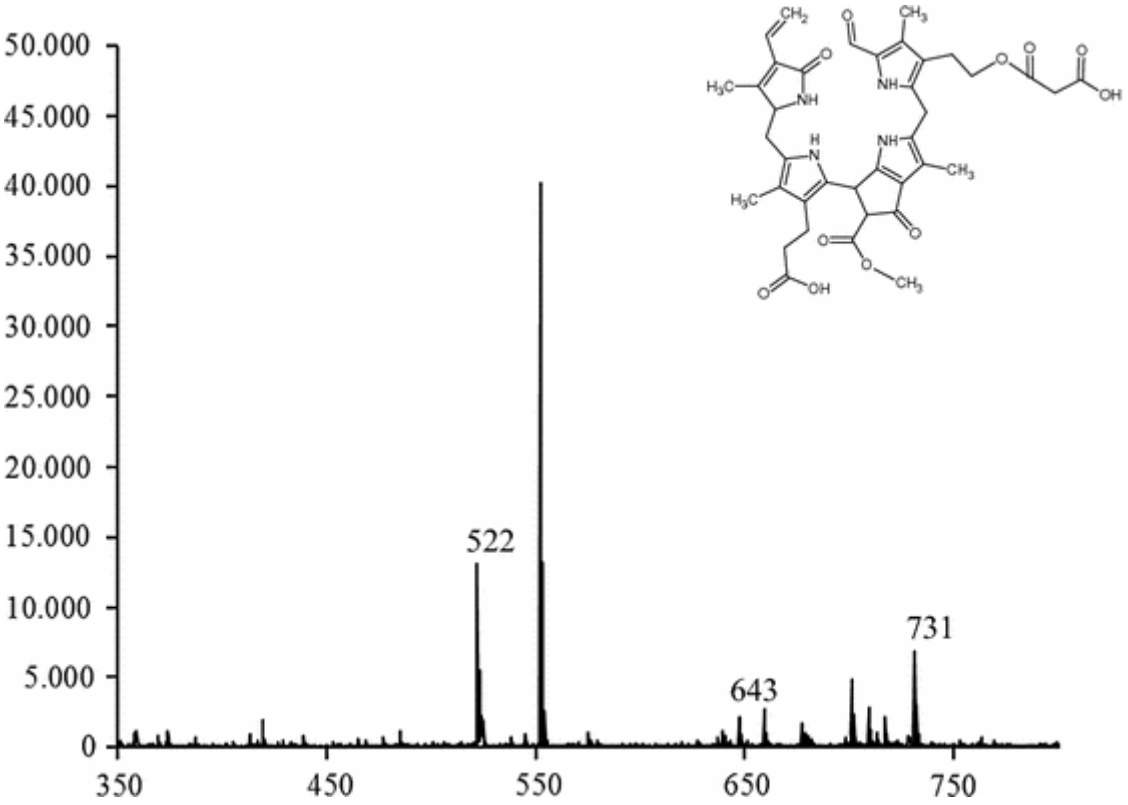

50.000
45.000
40.000
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0
350
450
550
650
750
522
643
731

Figure 7