Phyllobilins – the Abundant Tetrapyrrolic Catabolites of the Green Plant Pigment Chlorophyll

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Supporting Information

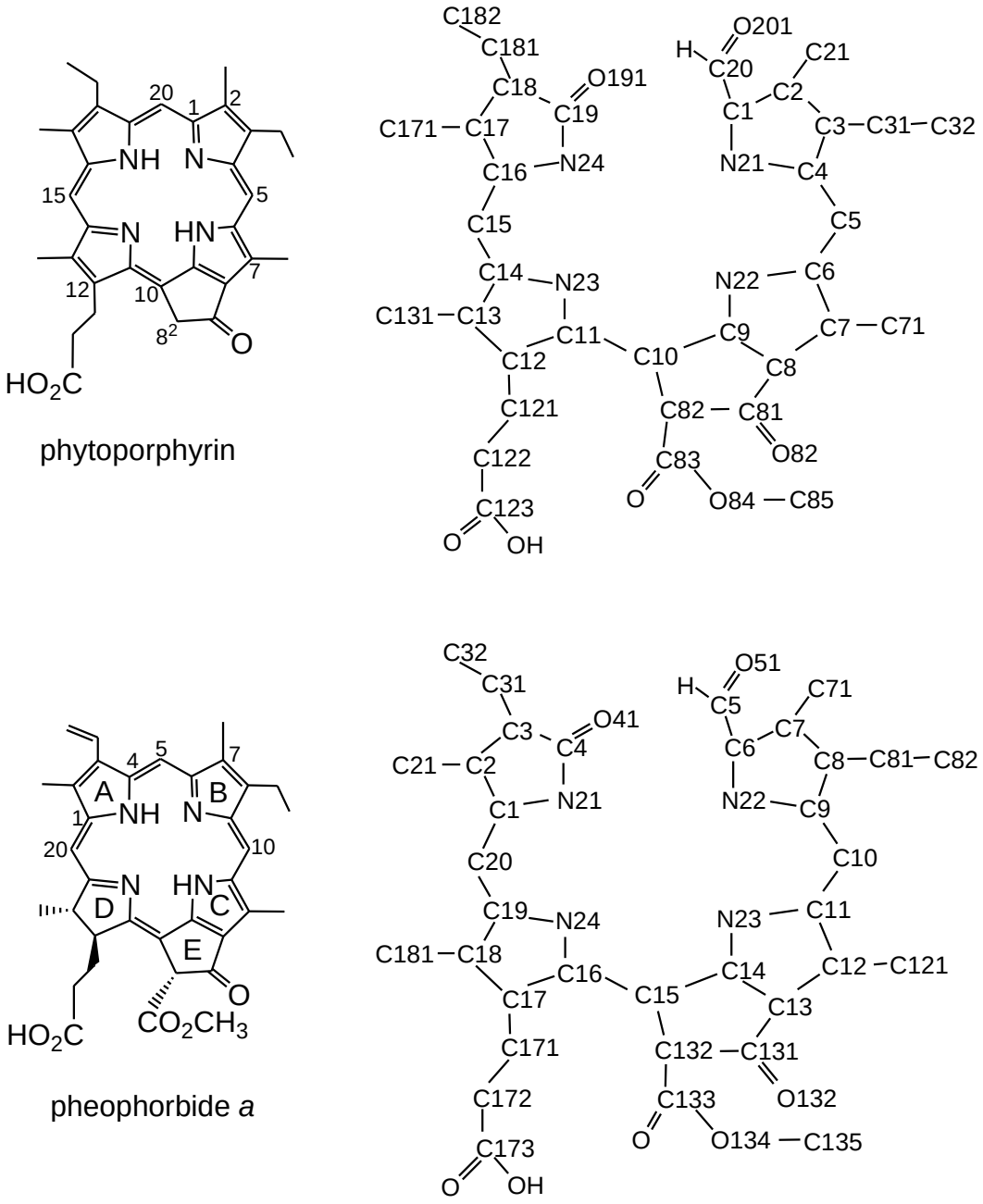
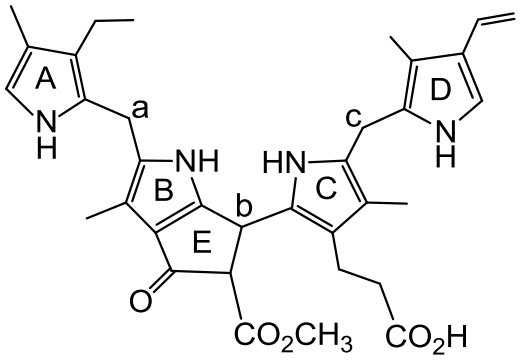


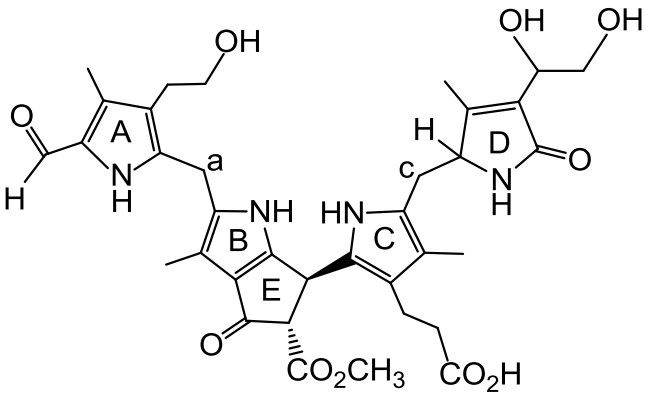
Figure S1. Atom numbering for phyllobilins.

Top. Phytoporphyrin formula with adapted atom numbering (left) and deduced atom numbering system used here for phyllobilin skeleton (right).

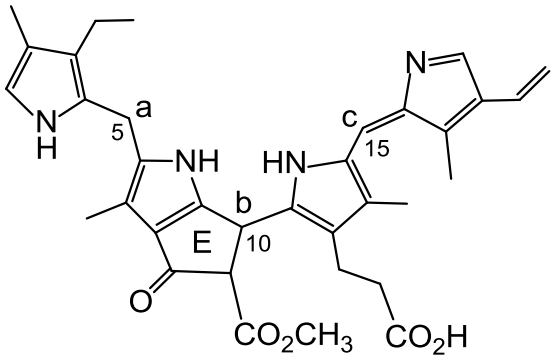
Bottom. Formula of pheophorbide *a* (Pheo *a*) with conventional atom numbering (left) and corresponding atom numbering for Chl-catabolites, used in earlier publications (right).



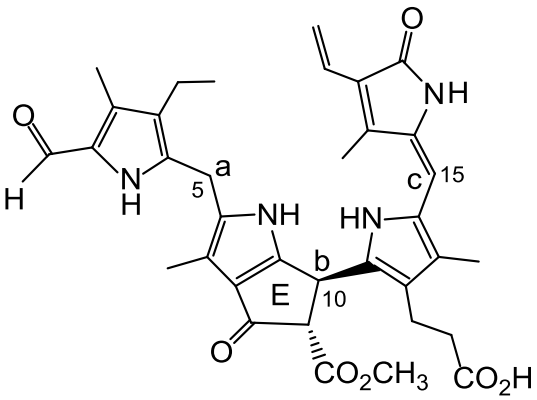
phyllobilane



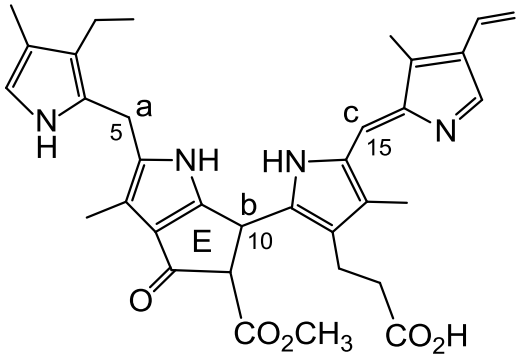
Hv-NCC-1



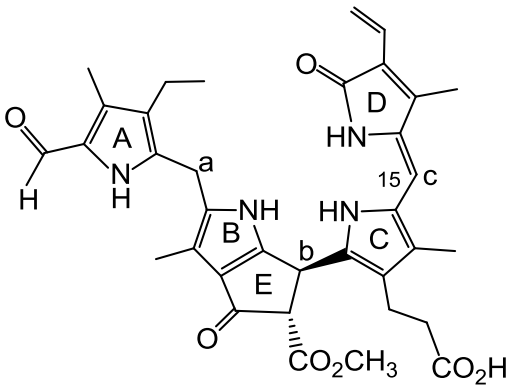
(15*E*)-phyllobilene-c



(15E)-YCC

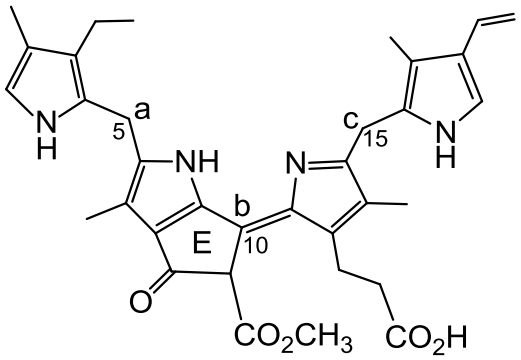


(15*Z*)-phyllobilene-c

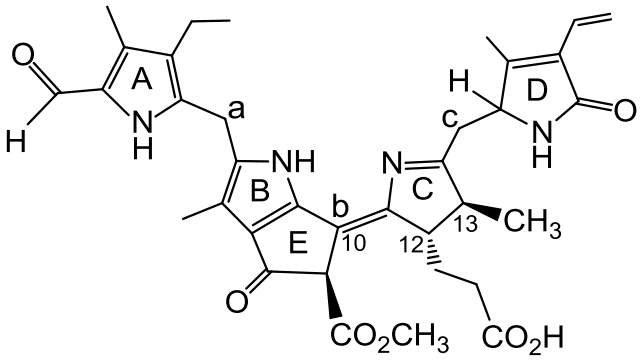


(15*Z*)-YCC

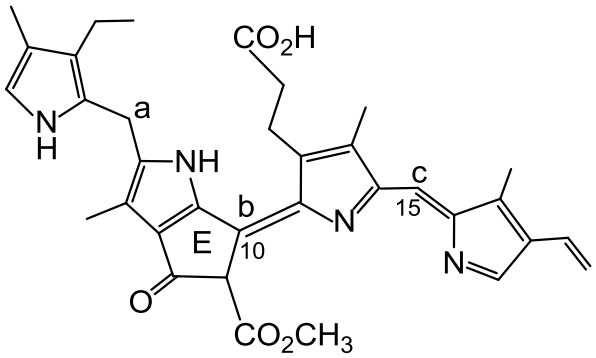
Figure S2a. Phyllobilin nomenclature (part a): phyllobilane, two isomeric phyllobilenes-c, and corresponding examples of three natural phyllobilins.



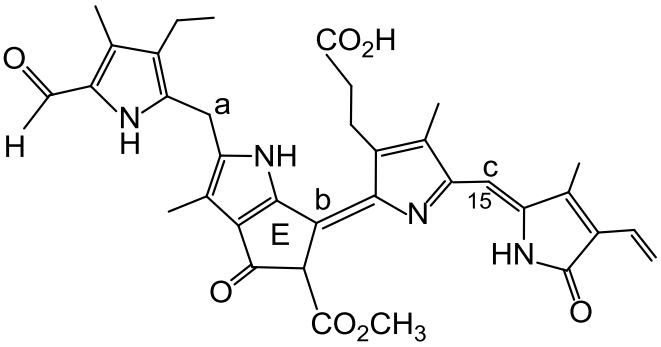
(10*Z*)-phyllobilene-b



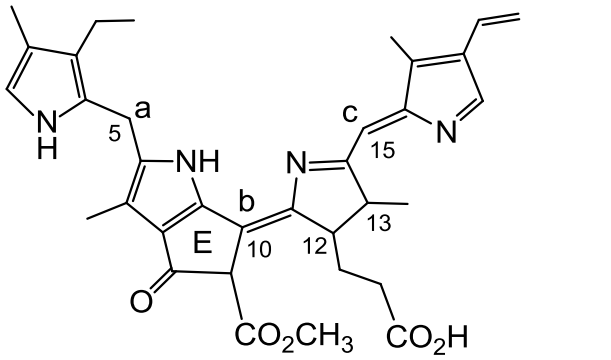
*p*FCC



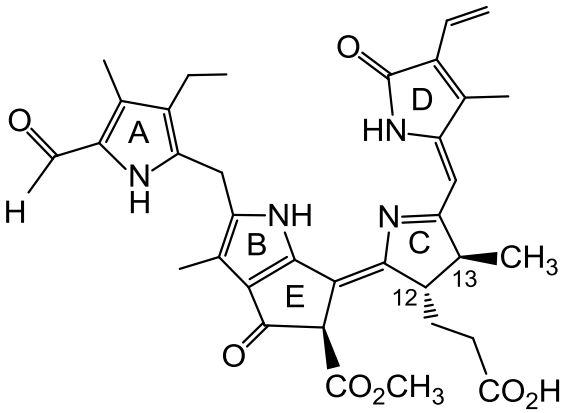
(10*E*, 15*Z*)phyllobiladiene-b,c



PiCC



(10*Z*,15*Z*)-12,13-dihydro-phyllobiladiene-b,c



RCC

Figure S2b. Phyllobilin nomenclature (part b): phyllobilene-b and two phyllobiladienes-b,c, and corresponding examples of three natural phyllobilins.

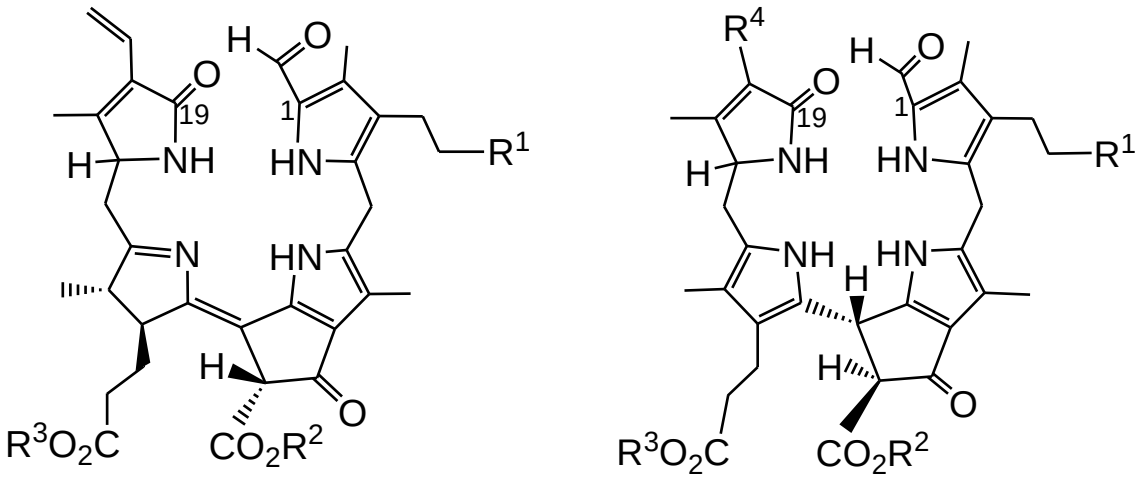


Figure S3. Generalized formulas for FCCs and NCCs, two type-I phyllobilins (for specifications of R^1 to R^4 in known natural type-I phyllobilins, see Tables S1 and S2).

Table S1: Structures of natural non-fluorescent Chl-catabolites (NCCs): labels **R^1** to **R^4** refer to the generalized formula of NCCs (Figure S3); atom numbering, as shown in Figure S1.

R^1 [a]	**R^2**	**R^3**	**R^4**	**C16** [b]	**provisional names** [c]	**Ref.**
OH	CH_3	OH	$CH(OH)CH_2OH$	n	*Hv*-NCC-1	1, 2
OH	CH_3	OH	$CH(OH)CH_2OH$	epi	*So*-NCC-2 (*Mc*-NCC-42)	3-5
OH	CH_3	OH	$CH=CH_2$	n	*Sw*-NCC-58	6
OH	CH_3	OH	$CH=CH_2$	epi	*Cj*-NCC-1 (*So*-NCC-4 / *Pc*-NCC-2 / *Md*-NCC-2 / *Mc*-NCC-61)	4, 5, 7-9
H	CH_3	OH	$CH=CH_2$	epi	*Cj*-NCC-2 (*So*-NCC-5)	4, 8
O-Glc	CH_3	OH	$CH=CH_2$	epi	*Nr*-NCC-2 (*Zm*-NCC-2 / *Pc*-NCC-1 / *Md*-NCC-1 / *Tc*-NCC-2 / *Mc*-NCC-59 / *Ug*-NCC-43)	5, 9-13
O-Glc	CH_3	OH	$CH(OH)CH_2OH$	epi	*Zm*-NCC-1 (*Tc*-NCC-1 / *Ug*-NCC-27)	11-13
O-(6´-O-Mal)-Glc	CH_3	OH	$CH=CH_2$	epi	*Nr*-NCC-1	10
H	H	OH	$CH=CH_2$	n	*Bn*-NCC-4 (*At*-NCC-5)	14, 15
OH	H	OH	$CH=CH_2$	n	*Bn*-NCC-3 (*At*-NCC-2)	14, 16
OH	H	OH	$CH=CH_2$	epi	*So*-NCC-3 (*Mc*-NCC-49)	4, 5
OH	H	OH	$CH(OH)CH_2OH$	epi	*So*-NCC-1 (*Mc*-NCC-26)	4, 5
O-Mal	H	OH	$CH=CH_2$	n	*Bn*-NCC-1	16, 17
O-Glc	H	OH	$CH=CH_2$	n	*Bn*-NCC-2 (*At*-NCC-1)	14, 16
OH	CH_3	[d]	$CH = CH_2$	epi[e]	*Mc*-NCC-58	5
OH	CH_3	[d]	$CH = CH_2$	epi[f]	*Mc*-NCC-55	5

[a] abbreviations: Mal = malonyl; Glc = β-glucopyranosyl; [b] configuration at C16 from correlation with NCCs derived from *p*FCC (n = 'normal') or from *epi-p*FCC (epi = 'epimeric'), the absolute configuration at C16 is still unknown; [c] for specific provisional names see references: *Hv*-NCC-1 (from barley, *Hordeum vulgare*)[1, 2], *So*-NCC s (from spinach, *Spinacia oleracea*), [3, 4] *Cj*-NCCs (from Katsura tree, *Cercidiphyllum japonicum*),[7, 8] *Sw*-NCC-58 (from Peace Lily, *Spathiphyllum wallisii*),[6] *Pc*-NCCs (from *Pyrus communis*),[9] *Md*-NCCs (from *Malus domestica*),[9] *At*-NCCs (from *Arabidopsis thaliana, At*-NCC-3 carries a HO-CH_2-group at C2, see ref. [18]),[14, 18] *Nr*-NCCs (from tobacco, *Nicotiana rustica*),[10] *Zm*-NCCs (from maize, *Zea mays*)[11], and *Bn*-NCCs (from oilseed rape, *Brassica napus*),[15-17] *Tc*-NCCs (from Lime tree, *Tilia cordata*),[12]), *Ug*-NCCs (from Dutch Elm tree, *Ulmus glabra* [13]) and *Mc*-NCCs (from banana peels, *Musa acuminata*, Cavendish cultivar).[5] [d] R^3 = daucic acid;); [e] *R*-configuration at C10; [f] *S*-configuration at C10 (configuration derived from CD-spectra [5]).

Table 2. Structures of natural fluorescent Chl-catabolites (FCCs): labels R^1 to R^3 refer to the generalized formula of FCCs (Figure S3); atom numbering, as shown in Figure S1.

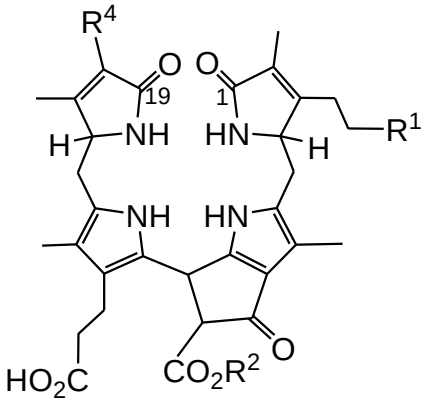
R^1	**R^2**	**R^3**	**C16[a]**	**provisional names [b]**	**Ref.**
H	CH_3	H	n	*Bn*-FCC-2 *(p*FCC*)*	19
H	CH_3	H	epi	*Ca*-FCC-2 *(epi-p*FCC*)*	20
H	H	H	n	*At*-FCC-2	14
OH	H	H	n	*At*-FCC-1	14
OH	CH_3	H	epi	*Mc*-FCC-62	5
OH	CH_3	CH_3	epi	*Mc*-FCC-71 [d]	5
OH	CH_3	5‘-daucyl [e]	epi	*Mc*-FCC-56	21
OH	CH_3	4‘-daucyl [f]	epi	*Mc*-FCC-53	22
O-Glc [c]	CH_3	5‘-daucyl [e]	epi	*Mc*-FCC-49	22
O-Glc [c]	CH_3	4‘-daucyl [f]	epi	*Mc*-FCC-46	22
OH	CH_3	[g]	n	*Sw*-FCC-62	6
OH	CH_3	[h]	epi	*Ma*-FCC-61	23
OH	CH_3	[g]	epi	*Ma*-FCC-69	24
OH	CH_3	[i]	epi	*Ma*-FCC-63	24
OH	CH_3	[j]	epi	*Ma*-FCC-64	24

[a] relative configuration at C16: n = ‘normal’, i.e. derived from *p*FCC, or epi = ‘epimeric’, i.e. derived from *epi-p*FCC; [b] *Bn*-FCC-2 (from oilseed rape, *Brassica napus*);[19] *Ca*-FCC-2 (from sweet pepper, *Capsicum annuum*);[20] *At*-FCCs (from *Arabidopsis thaliana*);[14] *Mc*-FCCs (from banana peels, *Musa acuminata*, Cavendish cultivar,[5, 6, 21, 22]); *Ma*-FCCs (from banana leaves, *Musa acuminata*, Cavendish cultivar,[23, 24]); *Sw*-FCC-62 (from senescent leaves of *Spathiphyllum wallisii*, [6]). [c] Glc = *β*-glucopyranosyl; [d] apparently an artefact, from methanolysis of 'persistent' FCC-daucyl-esters, such as *Mc*-FCC-56 and *Mc*-FCC-53; [e] daucic acid bound at 5’-OH; [f] daucic acid bound at 4’-OH; [5] [g] R^3 = 6β-glucopyranosyl-(1-1’)-2-[3,4-dihydroxyphenyl]-ethyl; [6] [h] R^3 = 6α-galactopyranosyl-(1-6)-β-galactopyranosyl-(1-1)-glyceryl; [23] [i] R^3 = 6-(1*β*)-glucopyranosyl; [24] [j] R^3 = 6-(1*α*)-glucopyranosyl [24].

Table 3. Structures of natural dioxobilane-type non-fluorescent Chl-catabolites (DNCCs): labels R^1, R^2 and R^4 refer to the general constitutional formula of DNCCs, shown below; atom numbering, as shown in Figure S1.

R^1	**R^2**	**R^4**	**C16[a]**	**provisional names [b]**	**Ref.**
OH	CH_3	CH(OH)-CH_2OH	n	-	25
OH	CH_3	CH(OH)-CH_2OH	n	-	25
OH	CH_3	CH_2=CH_2	[c]	UNCC-*Pvir*	26, 27
				UNCC-*Pp*	
H	H	CH_2=CH_2	n	*At*-DNCC	28
OH	CH_3	CH(OH)-CH_2OH	epi	*Ap*-DNCC	29
OH	H	CH_2=CH_2	n	*At*-DNCC-33	28
OH	CH_3	CH_2=CH_2	n	*At*-DNCC-38	30
H	CH_3	CH_2=CH_2	n	*At*-DNCC-47	30

[a] relative configuration at C16: n = 'normal', if derived for *p*FCC or epi = 'epimeric', if derived for *epi-p*FCC; [b] for specific provisional names see references: e.g. *Ap*-DNCC (from *Acer platanoides* [29]); *At*-DNCCs (from *Arabidopsis thaliana*); [28, 30] [c] relative configuration at C16 not determined.



DNCCs

Generalized constitutional formula of DNCCs
(type-II phyllobilins)

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