Electronic Supplementary Information

Identification of 3,4-didehydrorhodopin as major carotenoid in *Rhodopseudomonas* species

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Contents

Identification of Cars found in *Rhodopseudomonas* sp. Rits by mass spectrometry

Table 1 lists the results of mass spectrometry of Cars #1 - #7. The molecular-ion peaks and their fragment peaks originating from the cleavage of terminal groups can be used to identify each Car. More specifically, the fragment peaks at $[MH-18]^+$, $[MH-32]^+$, $[MH-50]^+$ and $[MH-64]^+$ correspond to the cleavage of terminal hydroxy, methoxy, hydroxy-methoxy and two methoxy groups in the molecule. Car #1 possessing $(C=C)_{11}$ group exhibits the molecular-ion peak at 537.4 as the protonated form and no detectable fragment peak under present MS conditions. Car #2 possessing $(C=C)_{12}$ group exhibits the molecular-ion peak at 567.4 ($[MH]^+$) and the sole fragment peak at 535.4 ($[MH-32]^+$). This fragment peak is assigned to the cleavage of a terminal methoxy group in the molecule. Car #3 possessing $(C=C)_{13}$ group exhibits the molecular-ion peak at 597.3 ($[MH]^+$) and two fragment peaks at 565.4 ($[MH-32]^+$) and 533.3 ($[MH-64]^+$). These fragment peaks are assigned to the removal of one and two terminal methoxy groups in the molecule. Car #4 possessing $(C=C)_{11}$ group and Car #5 possessing $(C=C)_{12}$ group exhibit the molecular-ion peaks at 555.3 and 553.3 ($[MH]^+$) and the sole fragment peaks at 537.4 ($[MH-18]^+$) and 535.3 ($[MH-18]^+$), respectively. These fragment peaks are assigned to the cleavage of a terminal hydroxy group in the molecule. Car #6 possessing $(C=C)_{12}$ group and Car #7 possessing $(C=C)_{13}$ group exhibit the molecular-ion peaks at 585.4 and 583.3 ($[MH]^+$), respectively, and the three fragment peaks at 567.1 ($[MH-18]^+$), 553.4 ($[MH-32]^+$) and 535.3 ($[MH-50]^+$) for Car #6 and 565.2 ($[MH-18]^+$), 551.3 ($[MH-32]^+$) and 533.2 ($[MH-50]^+$) for Car #7. These fragment peaks are assigned to the cleavage of a terminal hydroxy, a methoxy and hydroxy-methoxy groups in the molecule.

Table S1. Electronic-absorption properties of carotenoids isolated from the cells of *Rhodopseudomonas* sp. Rits.

Peak # in HPLC	Carotenoid (number of conjugated double bonds)	λ_{max} in the eluent (nm)			ε at λ_{max} in the literature[a] ($M^{-1}\cdot cm^{-1}$)	ε at 450 nm in the eluent ($M^{-1}\cdot cm^{-1}$)
		0→2	0→1	0→0		
1	Lycopene (11)	445	484	504	184,900[b]	119,700
2	Anhydrorhodovibrin (12)	458	484	516	152,800[b]	96,600
3	Spirilloxanthin (13)	467	494	528	147,200[c]	68,600
4	Rhodopin (11)	445	472	504	165,600[c]	106,600
5	3,4-Didehydrorhodopin (12)	458	484	516	–	96,600
6	Rhodovibrin (12)	458	484	516	–	96,600
7	OH-Spirilloxanthin (13)	467	494	528	–	68,600

[a]Data taken from Britton (Ref.15). [b]In petroleum ether. [c]In benzene.

Table S2. The ^{1}H vicinal coupling constants[a] (Hz) for 3,4-didehydrorhodopin in $CDCl_3$.

C3H=C4H	16	C6H–C7H	11
C7H=C8H	15	C10H–C11H	11
C11H=C12H	16	C14H–C15H	11
C11’H=C12’H	16	C14’H–C15’H	11
C7’H=C8’H	16	C10’H–C11’H	12
		C6’H–C7’H	11

[a]15H=15’H coupling constant was not determined due to the contribution of long-range coupling via 14H (14’H).

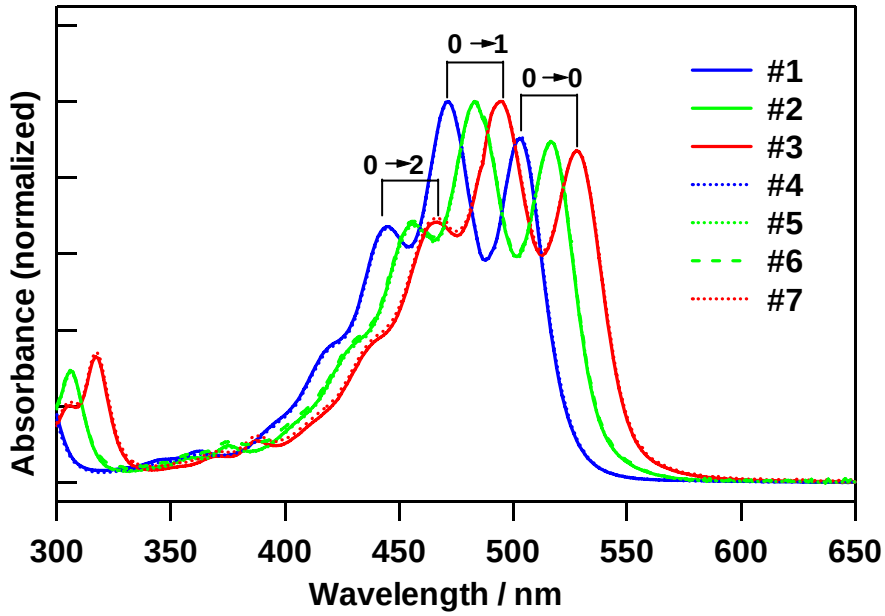

Figure S1. Electronic-absorption spectra of each Car found in *Rhodopseudomonas* sp. Rits obtained by on-line PDA. Numbers in the figure correspond to the HPLC elution order shown in Figure 1.

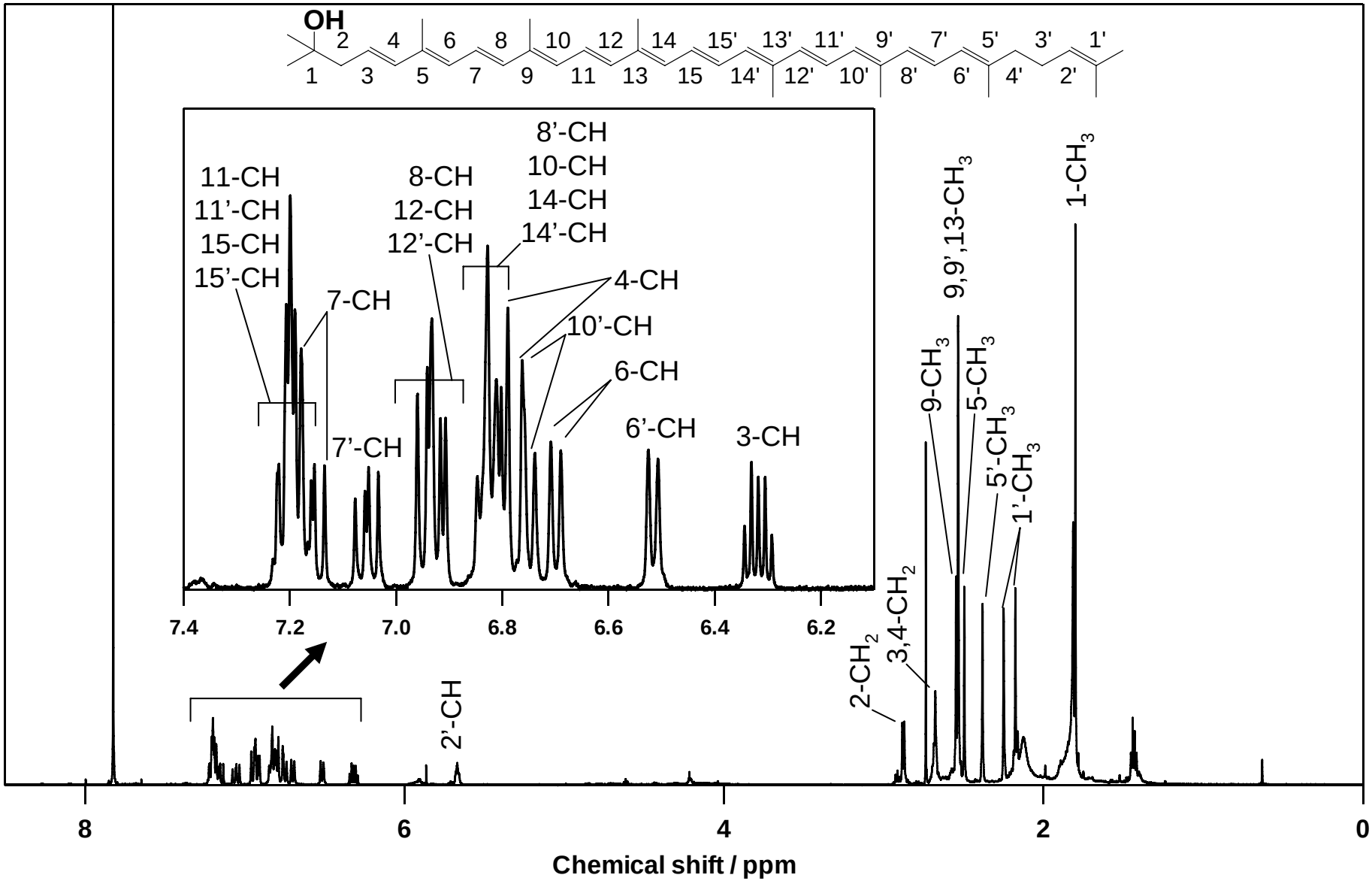

Figure S2. A representative ^{1}H-NMR spectrum of the isolated 3,4-didehydrorhodopin in $CDCl_3$ at room temperature.