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Tetrahedron Letters
Tetrahedron Letters 47 (2006) 1663–1668

# Demethoxycarbonylation and oxidation of $13^2(S/R)$-hydroxy-chlorophyll *a* to $13^2$-demethoxycarbonyl-$13^2$-oxo-chlorophyll *a* and Mg-purpurin-18 phytyl ester

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Received 24 October 2005; revised 13 December 2005; accepted 20 December 2005
Available online 23 January 2006

**Abstract**—The conversion of $13^2(S/R)$-hydroxy-chlorophyll (Chl) *a* to $13^2$-demethoxycarbonyl-$13^2$-oxo-Chl *a* in a yield of 40%, utilizing a simple pyrolysis technique, is described. About 10% of the phytyl ester of Mg-purpurin-18 was formed as a side product. The completely assigned $^1$H and $^{13}$C NMR spectra are presented for $13^2$-demethoxycarbonyl-$13^2$-oxo-Chl *a* and a likely mechanism for its formation is proposed. A slight extension of this mechanism also explains the formation of the Mg-purpurin-18 side product. The proposed mechanism has several features comparable with those previously suggested for the allomerization of $13^2(R/S)$-Chl *a*. Attempts to apply the same pyrolysis method to prepare $13^2$-demethoxycarbonyl-$13^2$-oxo-Chl *b* from $13^2(S/R)$-hydroxy-Chl *b* were unsuccessful.
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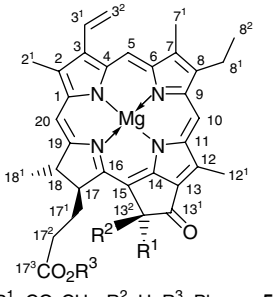
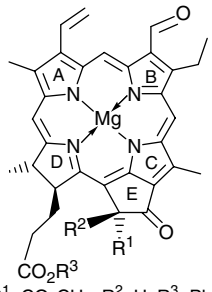
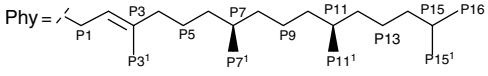
Recently,[1] we described the oxidation of $13^2(R/S)$-chlorophyll (Chl) *a* (**1**/**2**) and $13^2(R/S)$-Chl *b* (**5**/**6**) to $13^2(S/R)$-HO-Chl *a* (**3**/**4**) and $13^2(S/R)$-HO-Chl *b* (**7**/**8**), respectively, using the (−)- or (+)-enantiomer of (10-camphorsulfonyl)oxaziridine as an oxidant and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. $13^2(S/R)$-HO-Chl *a* has been postulated to be an early intermediate from which other allomers are formed.[2–5] On the basis of kinetic studies, the Bristol chemometrics group[2] has proposed an allomerization reaction pathway, where the phytyl ester of Mg-$15^1(S/R)$-methoxy-purpurin-7 lactone (**9**/**10**) [Mg-$3^1$,$3^2$-didehydro-$15^1$-hydroxy-$15^1$-methoxy-rhodochlorin-15-acetic acid $15^1(S/R)$-δ-lactone][6–10] is formed from $13^2(S/R)$-HO-Chl *a* (**3**/**4**). The results of our group are contradictory to this: After storing $13^2(S/R)$-HO-Chl *a* in methanol for 1 year, the only reaction we observed was some pheophytinization, that is, loss of the central magnesium.[11,12] A similar result has been reported by Woolley and co-workers,[13] who employed even more forcing conditions by raising the temperature to 50 °C. Also, Schaber and co-workers[14] kept $13^2$-HO-Chl *a* under methanolic allomerization conditions without observing any significant further reaction.





**1** $R^1$=$CO_2CH_3$; $R^2$=H; $R^3$=Phy;
**2** $R^1$=H; $R^2$=$CO_2CH_3$; $R^3$=Phy;
**3** $R^1$=$CO_2CH_3$; $R^2$=OH; $R^3$=Phy;
**4** $R^1$=OH; $R^2$=$CO_2CH_3$; $R^3$=Phy;
**5** $R^1$=$CO_2CH_3$; $R^2$=H; $R^3$=Phy;
**6** $R^1$=H; $R^2$=$CO_2CH_3$; $R^3$=Phy;
**7** $R^1$=$CO_2CH_3$; $R^2$=OH; $R^3$=Phy;
**8** $R^1$=OH; $R^2$=$CO_2CH_3$; $R^3$=Phy;



*Keywords*: Oxidation; Decarboxylation; Chlorophyll; Photosynthesis; 1,2-Diketone; Enolate; Free-radical; Mechanism.
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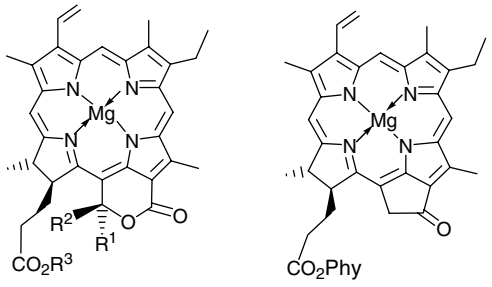
doi:10.1016/j.tetlet.2005.12.106



**9** $R^1$=$CO_2CH_3$; $R^2$=$CH_3O$; $R^3$=Phy; **11**
**10** $R^1$=$CH_3O$; $R^2$=$CO_2CH_3$; $R^3$=Phy;

$13^2(R/S)$-Chl *a* (**1/2**) is converted quantitatively into $13^2$-demethoxycarbonyl-Chl *a* (**11**, pyroChl *a*), when its deaerated pyridine solution is heated overnight at 100 °C in a sealed tube.[15–17] We have developed a facile procedure to carry out this 'pyrolysis' reaction in a Thunberg-tube, which can easily be deaerated using a freeze–pump–thaw method and thereafter sealed air-tight with adhesive tape for heating in an oven.[16,17] We were interested in applying the same pyrolysis technique to $13^2(S/R)$-HO-Chl *a* to obtain direct information on its stability as compared with Chl *a*. $13^2(S/R)$-HO-Chl *a* does not have an aptitude to enolize and is therefore expected to be appreciably more stable than $13^2(R/S)$-Chl *a*, which enolizes very easily in all polar organic solvents.[9] However, there should be no restriction for $13^2(S/R)$-HO-Chl *a* to undergo base-catalyzed ester hydrolysis of the $13^2$-methoxycarbonyl group and decarboxylation of the β-keto acid[18] formed might still be possible at elevated temperatures, even though the $13^2$-hydroxy group is expected to hinder enolization in the isocyclic ring E. In this letter, we report the isolation and structure determination of the products from $13^2(S/R)$-HO-Chl *a* on applying the pyrolysis technique developed by us. The oxidized products obtained are quite unexpected and the mechanism of their formation, considered here in detail, poses an interesting problem.

The application of our pyrolysis technique to $13^2(S/R)$-HO-Chl *a* (**3/4**) afforded, after a 92 h reaction time and work-up, $13^2$-demethoxycarbonyl-$13^2$-oxo-Chl *a* (**12**) in a yield of ca. 40% (Scheme 1).[19] About 10% of the phytyl ester of Mg-purpurin-18 (**13**) [Mg-chlorin $p_6$ anhydride = Mg-$3^1$,$3^2$-didehydro-15-carboxy-rhodochlorin anhydride] was found to form as a side product and about an equal amount of the starting compounds (**3/4**) was recovered from the product mixture. Due to the long reaction time at 100 °C, small amounts of dephytylated $13^2$-HO-Chl derivatives were formed as well. The main product **12** was characterized by $^1$H and $^{13}$C NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and electronic absorption spectroscopy (UV–vis).[20–22] The electronic absorption spectrum of **12** contained a shoulder of low intensity on the right side of the Soret band (Fig. 1). This shoulder was interpreted as belonging to compound **12** and not to an impurity in the preparation.

For the oxidation of $13^2(S/R)$-HO-Chl *a* (**3/4**) to products **12** and **13**, we propose the mechanism shown in Scheme 2. The C-$13^2$ methoxycarbonyl group of **3/4** first undergoes base-catalyzed ester hydrolysis (water content of pyridine ⩽0.1%), producing the β-keto acid intermediate **14**. Due to the long reaction time of 92 h, hydrolysis of the 17-propionate phytyl ester group also

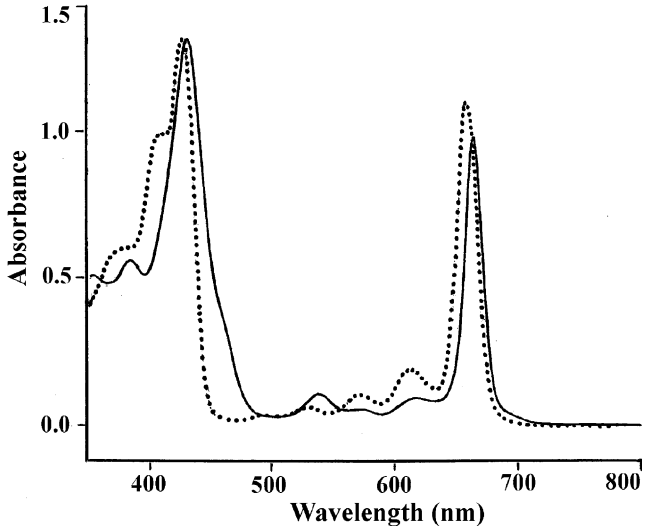
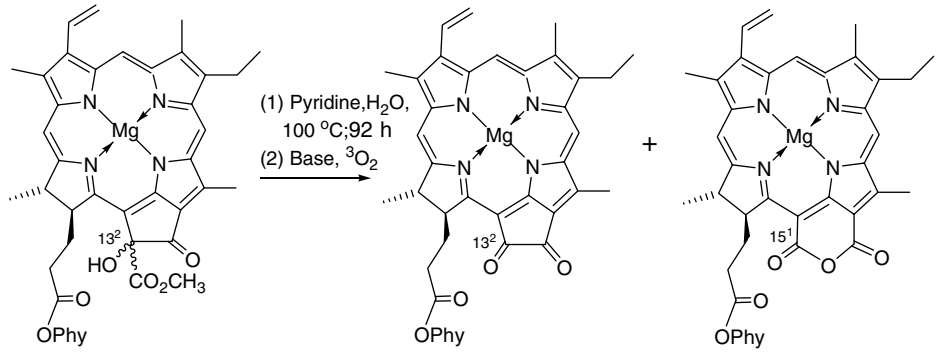



**Figure 1.** Electronic absorption spectra of $13^2(S/R)$-HO-Chl *a*, **3/4** (···) and $13^2$-demethoxycarbonyl-$13^2$-oxo-Chl *a*, **12** (—) in $Et_2O$.

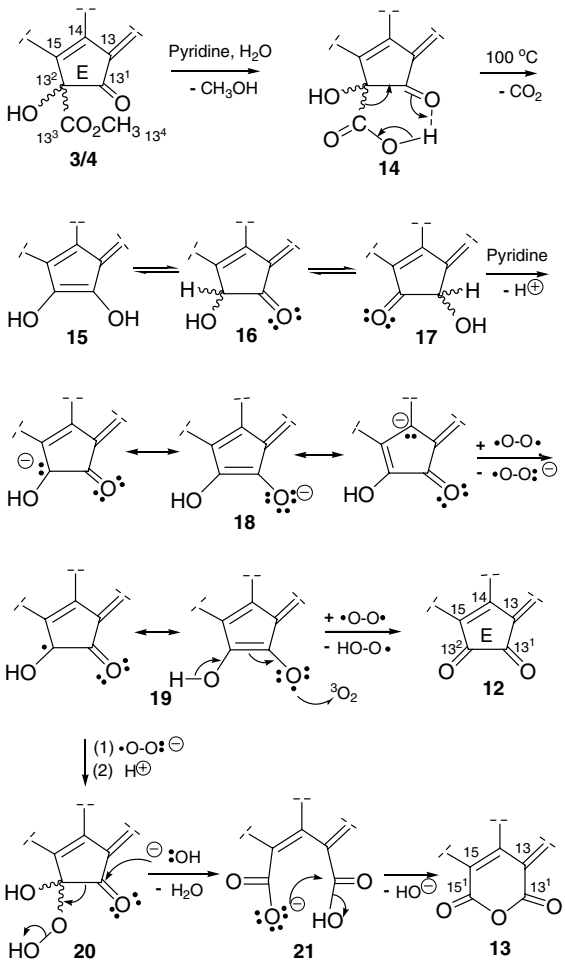



**3/4** $13^2(S/R)$-HO-Chl *a*

**12** $13^2$-Demethoxycarbonyl-$13^2$-oxo-Chl *a* (ca.40%)

**13** Mg-purpurin 18 phytyl ester (ca.10%)

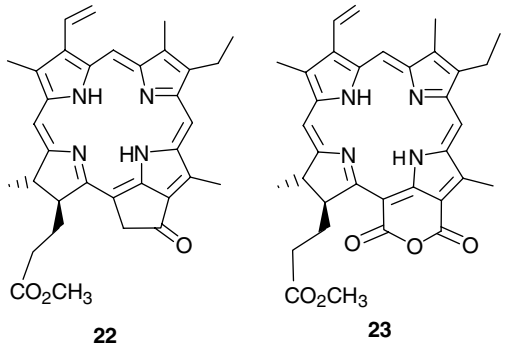
**Scheme 1.**




**Scheme 2.**

occurred to a minor extent, yielding water-soluble pheophorbide side products, which were entirely immobile in sucrose TLC[23] or medium-pressure liquid chromatography (MPLC).[1] The β-keto acid then decarboxylates, producing the enediol intermediate **15**. Evidence for the formation of **15** was obtained by measuring an ESI-MS of a sample taken from the reaction mixture, which showed a molecular ion at *m/z* 850.7 and a fragment ion at *m/z* 833.5, formed by the loss of the $13^2$-hydroxy group. The enediol **15**, which can tautomerize to **16** and **17**, deprotonates in pyridine solution, thus producing the enolate anion **18**, which is stabilized by partial delocalization of the free electron pair (negative charge) over the macrocyclic π-system.[9,22] Electron transfer from the enolate anion **18** to triplet molecular oxygen ($^3O_2$) affords the enol radical **19**, where the unpaired electron is conjugated with the macrocyclic π-system. After electron transfer to $^3O_2$ and deprotonation (these reactions are shown in Scheme 2 as a concerted reaction), $13^2$-demethoxycarbonyl-$13^2$-oxo-Chl *a* (**12**) is formed.

Alternatively, the enol radical **19** can react with a hydroperoxide ('superoxide') anion radical, to yield after protonation the $13^2$-hydroperoxide intermediate **20**; this reaction is equivalent to the reaction with another molecule of $^3O_2$, yielding the $13^2$-hydroperoxyl radical, which is hydrogenated by a suitable molecular species in the reaction mixture, for example, $H_2O$. The $13^2$-hydroperoxide intermediate **20** can then undergo nucleophilic attack by hydroxide, resulting in opening of the isocyclic ring and elimination of $H_2O$. The resulting phytyl ester of deprotonated Mg-chlorin $p_6$ (**21**, Mg-$3^1$, $3^2$-didehydro-rhodochlorin-15-carboxylate ion) undergoes an intramolecular nucleophilic substitution, yielding finally the phytyl ester of Mg-purpurin-18 (**13**), which was found to form as a side product in the pyrolysis procedure. Kozyrev and co-workers[24] have claimed that the methyl ester of $13^2$-demethoxycarbonyl-pheophorbide *a* (**22**) is converted to the methyl ester of purpurin-18 (**23**) through the action of LiOH and molecular oxygen ($O_2$). The lithium enolate and the $13^2$-oxo derivative of **22** were suggested to form as intermediates in the conversion. They did not specify in further detail the oxygen species and neither did they propose a detailed mechanism for the reaction.




The oxidation of the enolate anion **18** and the enol radical **19** by $^3O_2$ occurred possibly because some $^3O_2$ remained in the reaction mixture despite the thorough deaeration. However, it appears more likely that the oxidation occurred largely after the reaction tube was opened and air was allowed to flow into the solution. To some extent, oxidation might have also occurred during or after the evaporation of pyridine. In addition, it should be noted that the well-known $Cu^{++}$ promoted oxidation of α-hydroxy-ketones to α-diketones in hot pyridine[25] is unlikely in the present case, because the pyridine used was of analytical quality (Cu $\leqslant$0.000002%).

To improve the yield of the main product **12**, several variations of the reaction conditions were tested. With a shorter reaction time (41 h), the yield of the product was 35%, while 49% of the starting material, including a small amount of the side product **13**, was recovered. This result indicates that the first steps in the reaction sequence, that is, hydrolysis of the $13^2$-methoxycarbonyl group and decarboxylation of the β-keto acid formed, may be the primary reasons for the modest yield of the main product. Knowing that decarboxylation reactions are dependent on temperature, we undertook a pyrolysis experiment (under deaerated conditions), where pyridine was replaced with collidine (2,4,6-trimethylpyridine, bp 171 °C)[26] and the temperature was raised to 120 °C; however, this experiment afforded a

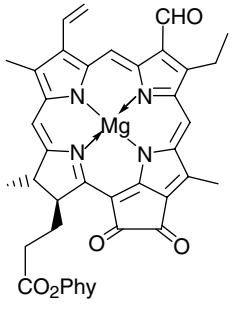
somewhat lower yield of the desired product. Hence, the pyrolysis temperature did not seem to be a limiting factor for the modest yield. Further, the pyrolysis experiments, which were performed under deaerated conditions at 100 °C in pyridine solution, containing a small amount of DBU, potassium *tert*-butoxide or the proton sponge, 1,8-bis(dimethylamino)naphthalene, did not improve the yield of **12**. On the contrary, the addition of bases seemed to promote dephytylation (hydrolysis of the phytyl group) and other side reactions as well. When pyrolysis was carried out in pyridine solution under normal atmosphere in an open Thunberg-tube at 100 °C, the yield of **12** was only 13% after 51 h and the usual work-up. Hence, it seems likely that triplet molecular oxygen, which is needed to oxidize the enolate anion **18**, is not a major limiting factor for the yield of **12**.

The results from the above attempts, taken together, lead us to the conclusion that the most likely limiting factor for the yield of **12** is decarboxylation of the β-keto acid **14**. The transition state involved in this reaction requires the formation of a hydrogen-bonded cyclic structure, which is not easily formed because $13^2(S/R)$-HO-chlorophylls do not have a tendency to enolize. In this regard, the $13^2(S/R)$-HO-chlorophylls differ from intact $13^2(R/S)$-chlorophylls, which have a high tendency to enolize in polar organic solvents. Apparently, the enolization aptitude of $13^2(R/S)$-chlorophylls promotes the formation of the hydrogen-bonded cyclic transition state, corresponding to structure **14** with the $13^2$-HO substituent replaced by a hydrogen atom. Owing to the high enolization tendency, the intact $13^2(R/S)$-Chl *a* or *b* undergoes pyrolysis very easily, affording almost quantitatively, $13^2$-demethoxycarbonyl-Chl *a* or *b*. In this connection, it is interesting to note that, apparently, the $13^2$-demethoxycarbonylation of $13^2(R/S)$-pheophorbide *a* occurs in plant senescence as catalyzed by two enzymes: pheophorbidase and $13^2$-demethoxycarbonylase.[27] Pheophorbidase is an esterase that occurs in higher plants and catalyzes the hydrolysis of the $13^2$-methoxycarbonyl group, resulting in the β-keto acid, which spontaneously decarboxylates to give the pyro derivative. $13^2$-Demethoxycarbonylase has been found in some algae and seems to catalyze both the ester hydrolysis and decarboxylation of the β-keto acid. The mechanism of this enzyme reaction is still unclear.

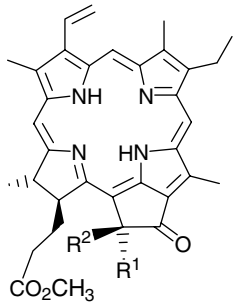
The attempts to oxidize $13^2(S/R)$-HO-Chl *b* (**5/6**)[1] to $13^2$-demethoxycarbonyl-$13^2$-oxo-Chl *b* (**24**) using the same pyrolysis technique were unsuccessful, even when the pyrolysis time was extended to 114 h. This result is not surprising, considering the previously observed differences in reactivity between Chl *a* and Chl *b* in reactions such as the oxidation of Chl *b* by triplet oxygen, $^3O_2$, (Willstätter allomerization)[11,12,22] or by (10-camphorsulfonyl)oxaziridines.[1] These differences in reactivity reflect the influence of the C-7 formyl group, whose electron-withdrawing effect is mediated by the conjugated π-system down to the isocyclic ring E of the *b*-series compounds.[1] It is also noteworthy that the oxidation potential of Chl *b* has been reported to be significantly higher than that of Chl *a*.[28,29] This implies that detachment of an electron is more difficult from the macrocyclic π-system of Chl *b* than from that of Chl *a*. Apparently, the possible higher oxidation potential of the *b*-series compounds is not the main reason responsible for the non-reactivity of these compounds under the same conditions as those used for the *a*-series compounds. A more likely explanation for the non-reactivity of HO-Chl *b* is the C-7 formyl group, whose electron-withdrawing effect reaches down to the isocyclic ring E, inducing structural alterations that hinder the formation of the cyclic transition state, which is necessary for decarboxylation of the β-keto acid.

The possible difference in reactivity between $13^2(S)$- and $13^2(R)$-HO-Chl *a* was studied by first determining the ratio of the epimers in the starting material [$13^2(S)$-HO-Chl *a*/$13^2(R)$-HO-Chl $a = \rho = 45/55$], using normal-phase HPLC.[1] Then, the ratio of the epimers was determined in the residual starting material, recovered after the reaction. We found that more $13^2(S)$-epimer remained at the end of the reaction ($\rho = 57/43$), even though the starting material contained more $13^2(R)$-epimer. This implies a higher reactivity for the $13^2(R)$-epimer. This result is expected, because in the $13^2(R)$-epimer, there is more steric strain between the $13^2$-methoxycarbonyl and 17-propionate phytyl ester groups. As $13^2(S/R)$-HO-Chl *a* is not enolizable, the $13^2$-epimerization of the starting material is impossible under the reported reaction conditions employed.

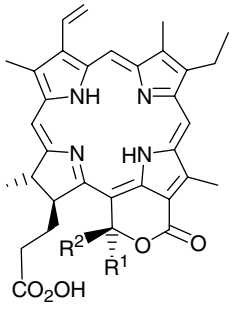
Fischer[30,31] has reported that agitation of an ethereal solution of $13^2(S/R)$-HO-pheophorbide *a* methyl ester (**25/26**) with 10% NaOH results in the formation of unstable chlorin (**27/28**), which can be converted with diazomethane into purpurin-7 trimethyl ester (**29**). Also,



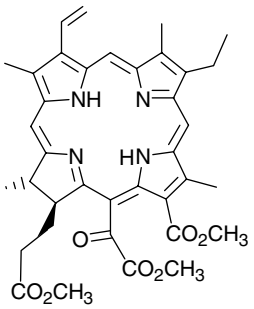

**24**




**25** $R^1$=$CO_2CH_3$; $R^2$=OH;
**26** $R^1$=OH; $R^2$=$CO_2CH_3$




**27** $R^1$=$CO_2H$; $R^2$=OH;
**28** $R^1$=OH; $R^2$=$CO_2H$




**29**

Ma and Dolphin[32] have claimed that the treatment of **25/26** with methanolic alkali at room temperature for 12 h under $N_2$ resulted in the hydrolytic cleavage of ring E, generating unstable chlorin 7. However, we find it difficult to envisage what would be the reaction mechanism for such a transformation under the reported reaction conditions.

In conclusion, the mechanism proposed in Scheme 2 has several features comparable with those previously suggested for the allomerization mechanism of $13^2(R/S)$-Chl *a*.[22] In both mechanisms, enolization is an important reaction step. It is the enolate anion of the Chl derivative concerned, which is reactive with triplet oxygen (˙O–O˙), producing a reactive C-$13^2$ radical species that plays an important role in the free-radical chain reaction. It is also interesting that, in both reaction mechanisms, the delocalized π-electron system of the chlorin macrocycle contributes, to a certain extent, to the electronic structure of the enolate anion, which is an ambident nucleophile. Via this macrocyclic contribution, there is an obvious connection of the foregoing reaction mechanisms to the photosynthetic reaction centre (RC) mechanism, where the excited RC chlorophyll ejects an electron, to form a delocalized π-cation radical.[33–37] An intriguing question is: What is the precise relationship between the Chl C-$13^2$ radical and the Chl π-cation radical? Are they interconvertible? Several other questions can be addressed: Why is there an enolizable β-keto ester system in the RC chlorophylls of all oxygenic photosynthetic organisms? What prevents the RC chlorophyll from reacting with triplet oxygen ($^3O_2$) or singlet oxygen ($^1O_2$)? The non-reactivity of the RC chlorophylls with the molecular oxygen species seems at first sight paradoxical, considering that all oxygenic photosynthetic organisms photolyze $H_2O$ and evolve $O_2$ at a site that is quite close to the RC II. At the moment, we find it very difficult to obtain satisfactory answers to these questions. It seems to us that a more complete understanding regarding the RC events of photosynthesis inevitably demands a thorough organic chemical approach, which, regrettably, has so far been quite rare in photosynthesis research.

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19. $13^2(S/R)$-Hydroxy-Chl *a* (**3/4**)[1] (15 mg, $0.17 \times 10^{-4}$ mol) was dissolved in 6.0 mL pyridine (Merck, analytical grade) in a dried Thunberg-tube and the pyridine solution was deaerated using the freeze–pump–thaw technique (three cycles). Vacuum (0.05 mbar) was applied to the tube, which was sealed with strong adhesive tape and heated at 100 ± 5 °C in an oven for 92 h (41 h gave only a 35% yield; due to the vacuum, the sealed tube was sufficiently resistant against the gas pressure of pyridine at 100 °C). Next, the tube was cooled to room temperature and opened under a normal atmosphere. The pyridine solution was evaporated to dryness at reduced pressure. The product was purified by MPLC on a semi-preparative sucrose column[1] with 2-propanol–THF–hexane (1.0:0.5:98.5, v/v/v) as the eluent. The sample was prepared by dissolving the product in 2.0 mL of $Et_2O$ (Merck, analytical grade) and 6.0 mL of the eluent. A small amount of starting material (**3/4**) was eluted fastest and was overlapped partly by the major side product **13**, which was then followed by the desired product **12**. The effluent fractions, containing each pure component, were combined and the solvents evaporated. The residue was dehydrated by chloroform co-distillation (three times). After solvent evaporation in vacuum, the yield of **12** was 5.2 mg (37%). The total amount of the major side product **13**, also containing some starting material **3/4**, was 2.7 mg (18%). The side product **13** was characterized by ESI-MS and UV–vis as $3^1$,$3^2$-didehydro-15-carboxy-rhodochlorin anhydride $17^3$-phytyl ester (**13**, trivial name: Mg-purpurin-18 phytyl ester). In addition, small amounts of dephytylated/demetallated Chl *a* derivatives were observed by means of sucrose TLC analyses.[23]
$13^2$-Demethoxycarbonyl-$13^2$-oxo-chlorophyll *a* (**12**). $^1$H NMR (acetone-$d_6$), $\delta_H$ [ppm]: 10.03 (s, 10-CH), 9.77 (s, 5-CH), 8.97 (s, 20-CH), 8.19 (dd, $^3J_{cis} = 11.6$ Hz, $^3J_{trans} = 17.8$ Hz, $3^1$-CH), 6.27 (dd, $^2J_{gem} = 1.5$ Hz, $^3J_{trans} = 17.8$ Hz, $3^2$-$CH_2$, $H_{trans}$), 6.05 (dd, $^2J_{gem} = 1.5$ Hz, $^3J_{cis} = 11.6$ Hz, $3^2$-$CH_2$, $H_{cis}$), 5.10 (tq, $^3J_{P2-P1} = 6.8$ Hz, P2–CH), 5.02 (m, 17-CH), 4.73 (dq, $^3J_{18-18^1} = 7.5$ Hz, 18-CH), 4.35 (m, P1–$CH_2$, $H_a$, $H_b$), 3.89 (q, $^3J_{8^1-8^2} = 7.6$ Hz, $8^1$-$CH_2$), 3.77 (s, $12^1$-$CH_3$), 3.42 (s, $2^1$-$CH_3$), 3.37 (s, $7^1$-$CH_3$), ~2.75 (m, $17^2$-$CH_2$, $H_b$),† ~2.30 (m, $17^2$-$CH_2$, $H_{b'}$),† ~2.50 (m, $17^1$-$CH_2$, $H_a$),† ~2.30 (m, $17^1$-$CH_2$, $H_{a'}$),† 1.88 (m, P4–CH), 1.74 (t, $^3J_{8^2-8^1} = 7.6$ Hz, $8^2$-$CH_3$), 1.87 (d, $^3J_{18^1-18} = 7.5$ Hz, $18^1$-$CH_3$), 1.55 (br s, P3$^1$–$CH_3$); † Requires spin simulation for the fragment 17-CH–$17^1$-$CH_2$–$17^2$-$CH_2$; The assignments of the phytyl P5–P16 proton signals were similar to those reported previously.[12,21] $^{13}$C NMR (acetone-$d_6$), $\delta_C$ [ppm]: 194.05 ($13^1$), 187.15 ($13^2$), 173.41 ($17^3$), 169.67 (19), 164.21 (14,

16), 155.19 (1), 150.39 (6), 147.95 (9), 149.09 (4), 146.27 (11), 144.59 (8), 142.48 (P3), 140.62 (3), 136.09 (7), 135.72 (2), 135.10 (12), 131.34 ($3^1$), 129.71 (13), 120.62 ($3^2$), 119.47 (P2), 109.16 (10), 105.39 (5), 105.20 (15), 97.47 (20), 61.38 (P1), 52.76 (17), 48.93 (18), 40.30 (P4), 31.83 ($17^2$), 31.54 ($17^1$), 24.54 ($18^1$), 20.05 ($8^1$), 18.14 ($8^2$), 16.22 ($P3^1$), 13.05 ($12^1$), 12.62 ($2^1$) 11.23 ($7^1$); the assignments of the phytyl P5–P16 carbon signals were similar to those reported earlier.[12,21] ESI-MS: *m/z* 849.5036 $(M+1)^+$; $C_{53}H_{68}$-$N_4O_4Mg$ requires 848.5091. UV–vis in $Et_2O$: $\lambda_{max}$ at 665.0 (0.747), 618.0 (0.072), 538.7 (0.084), ≅460 (sh, ≅0.270), 431.0 (1.000) and 384.0 (0.426) nm (Fig. 1).
Mg-purpurin-18 phytyl ester (**13**). ESI-MS: *m/z* 865.6 $(M+1)^+$; $C_{53}H_{68}N_4O_5Mg$ requires 864.5085. UV–vis in 2-PrOH–THF–hexane, 1.0:0.5:98.5, v/v/v: $\lambda_{max}$ at 676 (0.552), 628 (0.121), 565 (0.068), 525 (0.033), 490 (0.022) and 422 (1.000) nm.

20. The $^1H$ and $^{13}C$ spectra were recorded on a 500 MHz Bruker Avance FT spectrometer and fully assigned using two-dimensional $^1H$,$^{13}C$ HSQC (heteronuclear single quantum coherence) and HMBC (heteronuclear multiple quantum multiple bond coherence) techniques.[21] The ESI-MS were measured on a Mariner time-of-flight (TOF) mass spectrometer using positive mode electrospray ionization.[22] Electronic absorption spectra were recorded in $Et_2O$ (Merck, analytical grade, SeccoSolv, stabilized with butylated hydroxytoluene, BHT) using a Cary-5E UV–vis–NIR spectrophotometer or, in the case of Mg-purpurin-18 phytyl ester (**13**), directly from the HPLC effluent (2-PrOH–THF–hexane, 1.0:0.5:98.5, v/v/v) using the photodiode-array detector of the HPLC equipment.
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