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Optical Spectra of Tocopheroxyl Model Radicals

Kazuo Mukai,* Yoshiko Watanabe, and Kazuhiko Ishizu
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790

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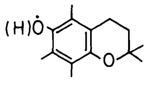
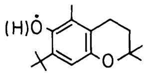
Synopsis. Tocopheroxyl model radicals have been prepared by the reaction between tocopherol models and stable phenoxyl radical in ethanol under nitrogen atmosphere. Optical spectra were recorded, and wavelength of absorption peaks (λ_{max}) and molar extinction coefficients (ε) were correctly determined.

The role of vitamin E (α-, β-, γ-, and δ-tocopherols) as an important biological antioxidant has been well recognized in recent years.[1] The antioxidant properties of the tocopherols have been ascribed to the initial oxidation of the phenolic hydroxyl group, producing tocopheroxyl radicals. Therefore, recently, several investigators including present authors have studied the ESR spectra of tocopheroxyl radicals, and determined the proton hyperfine splittings exactly.[2–4] By using pulse radiolysis technique, Packer et al. reported direct evidence for a free radical interaction between vitamin E (α-tocopherol) and vitamin C in vitro.[5] In the work, they observed the transient absorption spectrum of α-tocopheroxyl radical, showing an absorption peak (λ_{max}) at 425 nm. However, the value of molar extinction coefficient (ε) has not been reported, because of a rapid decrease in absorption at 425 nm.

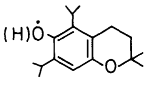
Structure



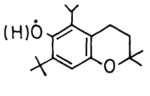
α-Tocopheroxyl Model 1



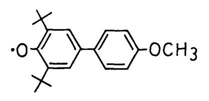
Tocopheroxyl 2



Tocopheroxyl 3



Tocopheroxyl 4



Phenoxyl 5

Recently, we have prepared the tocopherol model compounds **1**, **2**, **3**, and **4** having large alkyl substituents at both ortho positions (C-5 and C-7).[6] The tocopheroxyl radicals produced by the oxidation of the above tocopherols are fairly stable. Therefore, in the present work, we have succeeded in measuring the absorption spectra of the tocopheroxyls **2**, **3**, and **4**, and determined the values of λ_{max} and ε for these tocopheroxyls. However, in the case of α-tocopheroxyl model **1**, the radical is unstable, and thus we could only determine the wavelengths of absorption peaks.

Experimental

The preparation of tocopherol model compounds was reported in a previous paper.[6]

The 2,6-di-*t*-butyl-4-(4-methoxyphenyl)phenoxyl (abbreviated to phenoxyl **5** hereafter) was prepared according to the method of Müller et al.[7] Radical concentration of **5** was obtained from the results of the paramagnetic susceptibility measurements at 20 °C, after correcting for the diamagnetic contribution ($\chi_{dia}=-0.220\times10^{-3}$ emu mol^{-1}) calculated by the Pascal's method. The value was 100% for **5** assuming the Curie law.

Tocopheroxyl radicals **1**, **2**, **3**, and **4** have been prepared by the reaction between stable phenoxyl radical **5** and corresponding tocopherols in ethanol at 23 °C under nitrogen atmosphere.

The visible spectra were recorded with a Hitachi EPS-3T spectrophotometer.

Results and Discussion

The phenoxyl radical **5** is very stable in the absence of tocopherol, and shows absorption peaks at $\lambda_{max}=376$ nm ($\varepsilon=17600$) and 580 nm ($\varepsilon=4280$). Phenol precursor of **5** and tocopherol model **4** show absorption peaks at $\lambda_{max}=267$ nm ($\varepsilon=19500$) and $\lambda_{max}=295$ nm ($\varepsilon=3610$), respectively, in ethanol: no absorptions were observed in the visible absorption region. By adding the ethanol solution of tocopherol **4** (6.0×10^{-4} M) to the solution of phenoxyl **5** (4.0×10^{-4}M)(1:1 in volume) at 23 °C, the absorption spectrum of phenoxyl **5** immediately changed to that of tocopheroxyl **4** (see Fig. 1). Here, new absorptions at visible region ($\lambda_{max}=341$, 400, and 419 nm) are due to tocopheroxyl **4**, and the weak absorption at 580 nm is due to remaining phenoxyl **5** (5.0%). The tocopheroxyl **4** is considerably stable at 23 °C, and the absorption intensity only gradually decreases with time. There-

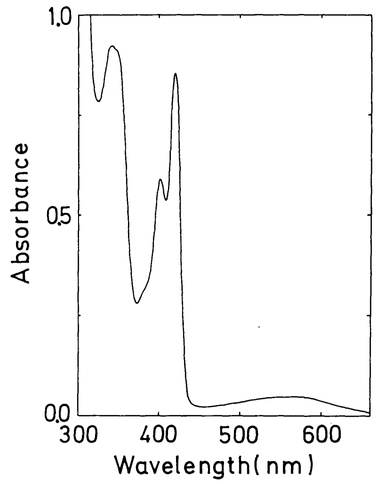


Fig. 1. Absorption spectrum of tocopheroxyl **4** in ethanol.
The weak absorption at 580 nm and the shoulder at 376 nm are due to remaining phenoxyl **5** (5.0%).

Table 1. Absorption Peaks (λ_{max}) and Molar Extinction Coefficients (ε) of Tocopheroxyl Radicals **1**, **2**, **3**, and **4** in Ethanol

1	λ_{max} (nm)	340	405	427
	ε (M^{-1} cm^{-1})	—	—	—
2	λ_{max}	338	398	419
	ε	3720	2390	3910
3	λ_{max}	338	401	420
	ε	4100	2490	4010
4	λ_{max}	341	400	419
	ε	3990	2510	3990

fore, the molar extinction coefficients are calculated to be ε=3990 M^{-1} cm^{-1} at 341 nm, ε=2510 M^{-1} cm^{-1} at 400 nm, and ε=3990 M^{-1} cm^{-1} at 419 nm for tocopheroxyl **4**, after correcting for the remaining phenoxyl **5** (5.0%). Similarly, tocopherols **1**, **2**, and **3** were reacted with phenoxyl **5**, and the optical spectra of tocopheroxyls **1**, **2**, and **3** were observed. The remaining phenoxyl radical **5** was 4.4% for **1**, 9.5% for **2**, and 11.9% for 3. The values of λ_{max} and ε obtained are listed in Table 1. However, in the case of α-tocopherol model **1**, the tocopheroxyl radical **1** produced is unstable, and absorption decreases rapidly with time.[6] Therefore, the value of ε cannot be determined.

As it is clear from the results listed in Table 1, the values of λ_{max} in tocopheroxyls **1**, **2**, **3**, and **4** are similar to each other as expected. Further, the values of ε obtained for tocopheroxyls **2**, **3**, and **4** are very similar to each other at three absorption peaks, where the difference in the ε value is 9% at most. The result suggests that the ε value of α-tocopheroxyl model is also similar to those of tocopheroxyls **2**, **3**, and **4**. As described in a previous section, Packer et al. have observed the absorption peak at 425 nm in water-2-propanol-acetone mixtures. In the present work, we have observed three absorption peaks (340, 405, and 427 nm) at visible region for α-tocopherol model **1**. The value of λ_{max} at the longest wavelength (427 nm) in α-tocopheroxyl model shows good accordance with that (425 nm) of α-tocopheroxyl reported by Packer et al.

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