SUPPORTING INFORMATION FOR:

Cacalol and Cacalol acetate as photoproducers of singlet oxygen and as free radical scavengers, evaluated by EPR spectroscopy and TBARS

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**A1.1 Quantum Yield for Production of Singlet Oxygen**

The $^1O_2$ radical quantum yield, $\phi^{^1O_2}$, can be determined from the generation rate of singlet oxygen, $R^{^1O_2}$, and the flux of absorbed photons, $I_a$ [1]:

$$\phi^{^1O_2} = \frac{R^{^1O_2}}{I_a}$$

For determining the absolute $^1O_2$ generation rate, the method of EPR spin-trapping with TEMP was employed. TEMP reacts with $^1O_2$ to give the adduct TEMPO [2].

**A1.2 Flux of Absorbed Photons.**
The methodology to determine $I_a$ is described in detail by Sun and Bolton [1]. The photon flux $I_a$ absorbed by a sample is the product of the incident photon flux $I_o$ and the integrated absorption fraction $F_S$ (for a sample S) over the wavelength range used in the experiment (300-800 nm) (eq.1):

$$I_a = I_o \cdot F_S \quad (1)$$

$F_S$ is given by eq. 2

$$\int_{\lambda_1}^{\lambda_2} I_\lambda T_\lambda f_\lambda^s \, d\lambda / \int_{\lambda_1}^{\lambda_2} I_\lambda T_\lambda \, d\lambda \quad (2)$$

where $I_\lambda$ is the relative incident photon flux in the wavelength band d$\lambda$, $T_\lambda$ is the transmittance of the filter at wavelength $\lambda$, and

$$f_\lambda^s = 1 - 10^{-A_\lambda^s} \quad (3)$$

is the fraction of light absorbed at wavelength $\lambda$, where $A_\lambda^s$ is the absorbance of the samples at wavelength $\lambda$. The integrals were determined by a sum over the wavelength range 300-800 nm.

The incident photon flux $I_o$ can be determined by a standard actinometer method, based on the photochemical conversion of the ferrioxalate salt. Irradiation with UV-vis light causes the reduction of Fe$^{3+}$ to Fe$^{2+}$ (reaction 1) [3, 4]:

$$2[Fe(C_2O_4)_3]^{3-} \xrightarrow{h\nu} 2Fe^{2+} + 5(C_2O_4)^{2-} + 2CO_2 \quad (1)$$

The generation rate of Fe$^{2+}$ ions $R_{Fe}^{2+}(M.s^{-1})$ can be determined spectrophotometrically at 510 nm after forming a complex with 1,10-phenanthroline (0.1%). The incident photon flux $I_o$ is then obtained from eq. 4:

$$I_o = R_{Fe}^{2+}/ \phi_{Fe}^{2+} F_S \quad (4)$$
\( \phi_{Fe^{2+}} \) is the quantum yield of \( Fe^{2+} \) generation by photochemical reaction, and \( F_{RS} \) is the integrated absorption fraction of the Ferrioxalate salt solution over the range of the wavelengths involved in the experiment. The weighted average of the quantum yield of \( Fe^{2+} \) production from \( Fe^{3+} \) salt over the bandwidth of the transmitting filter is known to be 1.0. According to our results, the formation rate of \( Fe^{2+} \) was found to be \( 1.5 \times 10^{-7} \pm 0.03 \) M s\(^{-1}\) and \( I_o \) was \( 1.5 \times 10^{-7} \pm 0.03 \) M s\(^{-1}\). C and CA concentrations were chosen in the range where the incident light is completely absorbed (fraction \( I_a/I_o = 1 \)). In our experiments, \( I_a \) was found to be \( 1.5 \times 10^{-7} \pm 0.03 \) M s\(^{-1}\).

**A2. Characterization of Compounds**

![Chemical structure of Cacalol](attachment:chemical_structure.png)

**Cacalol**

mp \( 92-94^\circ C \), \([\alpha]^{20}_D +10\), UV \( \lambda_{max} : 218 (\varepsilon 30400), 256 (\varepsilon 10500), 264 (\varepsilon 10000), 284 (\varepsilon 1840)\)

**IR (KBr):** 3580, 2966, 2934, 2870, 1450 cm\(^{-1}\).

**RMN \(^1H\) (CDCl\(_3\)) δ:** 1.18 (d, 3H, CH\(_3\), C-15), 3.22 (m, 1H, C-4) 1.75–1.90 (m, 4H, C-3, C-2), 2.92 - 3.03 (m, 2H, C-1), 2.36 (d, 3H, CH\(_3\), C-13), 2.52 (s, 3H, CH\(_3\), C-14), 7.24 (m, 1H, C-12).

**RMN \(^{13}C\) (CDCl\(_3\)) δ:** 136.4 (C-12), 117.2 (C-11), 120.2 (C-7), 118.9 (C-6), 135.6 (C-5), 29.8 (C-4), 30.2 (C-3), 16.7 (C-2), 23 (C-1), 126.2 (C-10), 142.2 (C-9), 140.8 (C-8), 11.3 (C-13), 13.8 (C-14), 21.4 (C-15).

**EM (IE) m/z:** 230 (M\(^+\), 71 %), 215 (M\(^+\)-15, 100 %).
Cacalol Acetate

mp 103-104°C; [α]₂⁰⁰° -9; UV λₘₐₓ: 218 (ε27000), 255 (ε12000), 280 (ε2100), 292 (ε1320).

IR (KBr): 1760, 1630, 1600 cm⁻¹.

RMN ¹H (CDCl₃) δ: 1.18 (d, 3H, CH₃, C-15), 3.24 (m, 1H, C-4), 1.75–1.90 (m, 4H, C-3, C-2), 2.77-2.88 (m, 2H, C-1), 2.38 (d, 3H, CH₃, C-13), 2.40 (s, 3H, CH₃-CO), 2.56 (s, 3H, CH₃, C-14), 7.22 (m, 1H, C-12).

RMN ¹³C (CDCl₃) δ: 168.6(CO-Me), 135.4 (C-8), 124.9 (C-11), 126.8 (C-7), 116.7 (C-6), 131.4 (C-5), 28.9 (C-4), 29.9 (C-3), 16.6 (C-2), 23.4 (C-1), 127.0 (C-10), 145.2 (C-9), 141.4 (C-12), 11.3 (C-13), 13.8 (C-14), 21.4 (C-15), 20.5 (CH₃-CO).

EM (IE) m/z: 272 (M⁺, 71 %), 215 (M⁺-15, 100 %).

References
