## SUPPORTING INFORMATION FOR:

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

Virginia Gómez-Vidales,[a*] Gilma Granados-Oliveros,[a,b] Antonio Nieto-Camacho,[a] Mirna Reyes-Solís,[a] Manuel Jiménez-Estrada[a]

[a] Instituto de Química, Universidad Nacional Autónoma de México, Circuito exterior, Ciudad Universitaria, Coyoacán, D.F., C.P. 04510. México.
[b] GIADS, Facultad de Química Ambiental, Universidad Santo Tomás de Aquino, Bucaramanga, Colombia.

* Corresponding author: Tel. 52 55 56224617, Fax 52 55 5616 22 17. E-mail address: gomvidal@unam.mx (Virginia Gómez)

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**Figure A1 UV-vis spectra for Cacalol and Cacalol acetate**

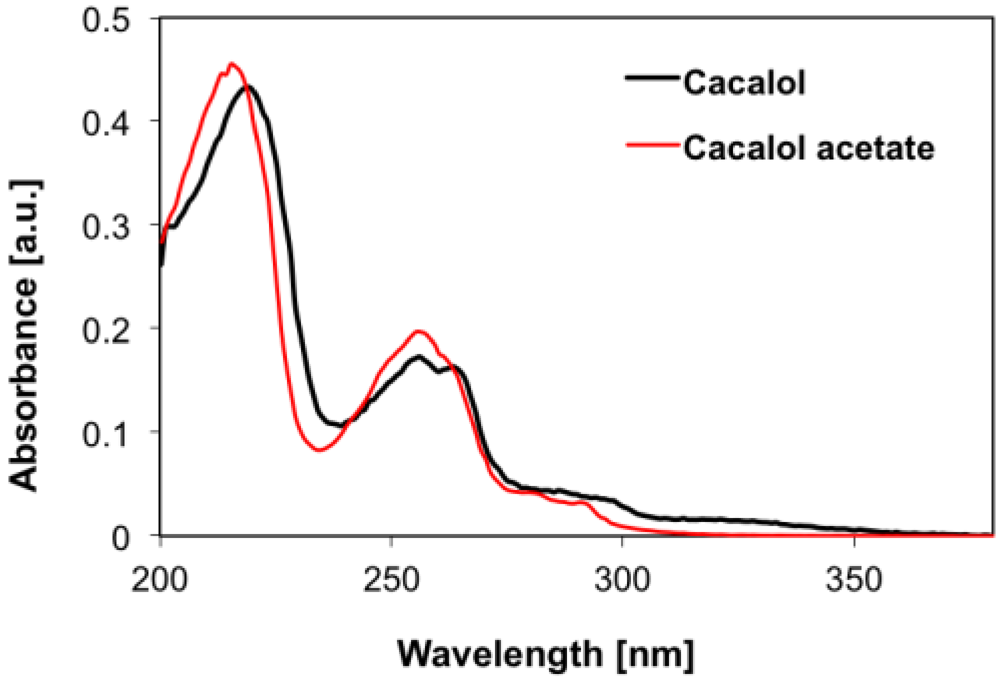



Figure A1. UV-vis spectra of Cacalol and Cacalol acetate in ethanol solution, [**C**] = 1.0 mM, [**CA**] = 1.4 mM

## 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]:

$$\phi^1O_2 = R^1O_2/I_a$$

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):

$I_a = I_o F_S$ (1)

$F_S$ is given by eq. 2

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

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

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

is the fraction of light absorbed at wavelength λ, where $A_\lambda^s$ is the absorbance of the samples at wavelength λ. 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]:

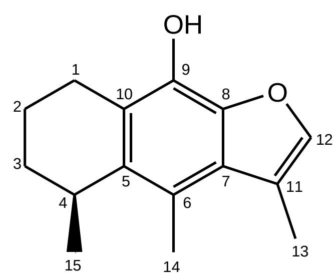
$$2[Fe(C_2O_4)_3]^{3-} \xrightarrow{h\vartheta} 2Fe^{2+} + 5(C_2O_4)^{2-} + 2CO_2 \qquad (1)$$

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:

$$I_o = R_{Fe}{}^{2+} / \phi_{Fe}{}^{2+} F_{RS} \qquad (4)$$

$\phi_{Fe}{}^{2+}$ 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 x $10^{-7}$ ± 0.03 $M.s^{-1}$ and $I_o$ was 1.5 x $10^{-7}$ ± 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 x $10^{-7}$ ± 0.03 M $s^{-1}$.

## A2. Characterization of Compounds




**Cacalol**

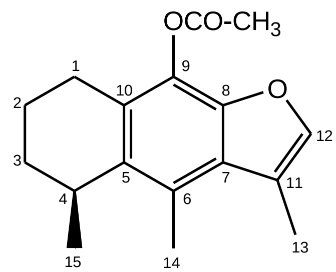
mp 92-94°C, $[\alpha]^{20}_D$ +10 , UV $\lambda_{max}$ : 218 (ε30400), 256 (ε10500), 264 (ε10000), 284 (ε1840)

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

**RMN $^1$H ($CDCl_3$) 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; $[\alpha]^{20}_D$ -9; UV $\lambda_{max}$: 218 (ε27000), 255 (ε12000), 280 (ε2100), 292 (ε1320).

**IR (KBr):** 1760, 1630, 1600 $cm^{-1}$.

**RMN $^1$H ($CDCl_3$) δ:** 1.18 (d, 3H, $CH_3$, 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, $CH_3$, C-13), 2.40 (s, 3H, $CH_3$-CO), 2.56 (s, 3H, $CH_3$, C-14), 7.22 (m, 1H, C-12).

**RMN $^{13}$C ($CDCl_3$) 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 ($CH_3$-CO)

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

## References

[1] L. Sun, J.R. Bolton, The Journal of Physical Chemistry 100 (1996) 4127-4134.

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