

# Sensitized Photooxygenation of Tinosponone, a Clerodane Diterpene from *Tinospora Cordifolia*

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## Abstract

The reaction of tinosponone (**1**) with singlet oxygen was studied by using different combinations of photosensitizers (i.e. rose bengal, methylene blue, riboflavin and benzophenone), solvents (i.e. benzene, chloroform, acetone, acetonitrile and methanol) and singlet oxygen scavengers (i.e. DABCO and sodium azide). Two major products (3S,4aS,4bS,8R,8aR,10aR)-8-Hydroxy-3-(5'-hydroxy-2'-oxo-2',5'-dihydrofuran-3'-yl)-4a,8a-dimethyl-3,4,8,8a,9,10-hexahydro-10aH-benzo[f]isochromene-1,5(4aH,4bH)-dione (**2**) and (3S,4aS,4bS,8R,8aR,10aR)-8-Hydroxy-4a,8a-dimethyl-3-((1'R)-3'-oxo-4',6'-dioxo-bicyclo[3.1.0]hexan-1'-yl)-3,4,8,8a,9,10-hexahydro-10aH-benzo[f]isochromene-1,5(4aH,4bH)-dione (**3**) were isolated in all the solvents except methanol. In methanol a single product (3S,4aS,4bS,8R,8aR,10aR)-8-Hydroxy-3-(5'-hydroperoxy-2'-methoxy-2',5'-dihydrofuran-3'-yl)-4a,8a-dimethyl-3,4,8,8a,9,10-hexahydro-10aH-benzo[f]isochromene-1,5(4aH,4bH)-dione (**4**) was obtained. All products were characterized on the basis of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis studies. The formation of products was explained by photooxidation of tinosponone. Effects of different solvents with the variation of added singlet oxygen sensitizers and singlet oxygen scavengers were observed on the yield of photooxidation products and were correlated to the rate of singlet oxygen formation.

**Key words:** photooxygenation, tinosponone, clerodane diterpene, *Tinospora cordifolia*, benzo[f]isochromene

## Introduction

The photoreactivity of synthetic drugs have been intensively studied in the recent past for their phototoxicity and phototherapeutic value.<sup>1,2</sup> In contrast photochemical studies on biologically active natural products are very limited. Plant materials are well known for their biological activity and medicinal values.<sup>3–5</sup> Hence it is of importance to study the photoreactivity of biologically active plant metabolites for a correlation to their possible *in vivo* photoreactions and phototoxicity. The photochemical study is expected to through light on improving the stability of these compounds in medicinal formulations derived from natural plant extracts.

Within the context we have investigated the photooxidation of tinosponone (**1**), a clerodane diterpene isolated from *Tinospora cordifolia*. *T. cordifolia* is a plant of recognized medicinal values and is widely used as anti-bacterial, analgesic, antipyretic and also for the treatment of jaundice, skin diseases, diabetes, anemia etc.<sup>6–10</sup> Several compounds containing 3-substituted furan moiety have been isolated from this plant species.<sup>11–13</sup> In spite of immense medicinal use of this plant extract the photochemical sensitivity of their bioactive constituents has not been described in the literature. The 3-substituted furan moiety is quite

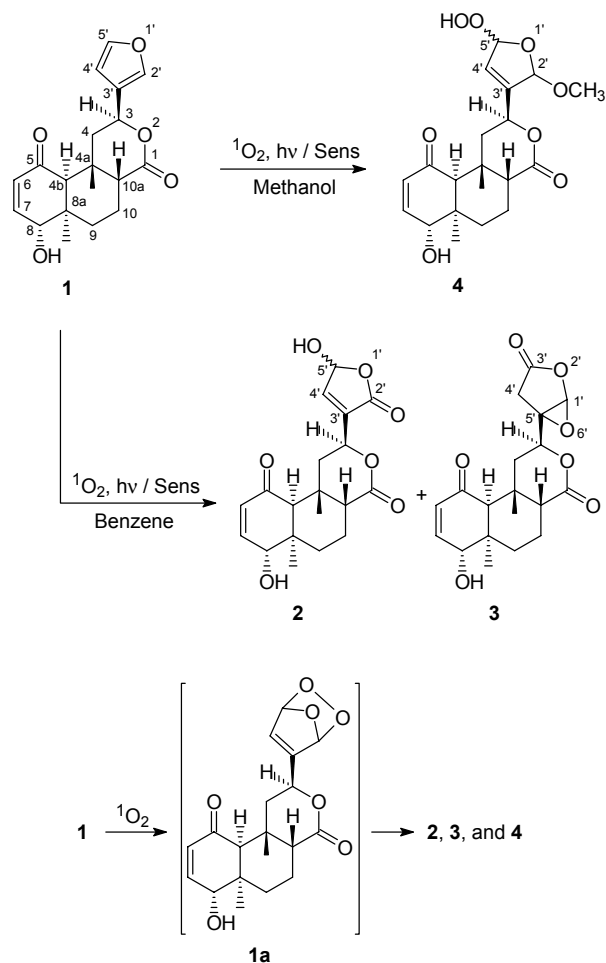
susceptible to attack by biological oxygens; we therefore, have investigated photooxygenation of tinosponone under different combinations of sensitizer dyes and solvents.

## Results and discussion

Irradiation of air-saturated benzene solution of tinosponone with methylene blue as sensitizer in a water-cooled immersion well type photoreactor equipped with medium pressure mercury vapour lamp and purification of the crude product by silica gel column chromatography afforded two compound **2** and **3**. When tinosponone was irradiated with methylene blue in methanol, the chromatographic analysis (TLC) of irradiated mixture did not show the presence of any of the previously identified products (**2** and **3**), rather a new product **4** was observed (Scheme 1). When these photoreactions were carried out in the absence of sensitizer same products were obtained but the reaction was observed to be slow.

The effect of nature of solvent on photooxidation was studied by using different solvents. The amount of substrate could not be kept same, as the solubility of substrate was different in different solvents. Therefore, relative yield of products was determined in these

cases. For this purpose, different reaction mixtures were irradiated under standard conditions for the same time period. Then 15 ml of each solution was taken out, concentrated and subjected to preparative TLC for the isolation of the products, and correlation of their yields. Yields of products in different solvents were found to vary with the polarity of the solvent. The yield was higher in polar solvents in comparison to non-polar solvents (Table 1). This observation may be attributed to longer lifetime of  $^1\text{O}_2$  in polar solvents.<sup>14,15</sup> Owing to the solubility problem, the concentration of **1** was not same in all the solutions, as it was of methylene blue therefore, the possibility of energy transfer for different yields of products cannot be discarded. To confirm whether energy transfer or longer lifetime of  $^1\text{O}_2$  is responsible for different yields of products, we conducted experiments by varying the concentration of sensitizer ( $5 \times 10^{-3}$ – $2 \times 10^{-2}$  mol L<sup>-1</sup>) to the concentration of tinosponone in different solvents. Similar product patterns were obtained in these cases also, which supports the fact that lifetime of  $^1\text{O}_2$  and in turn polarity of solvent is responsible for the observed difference in the yields.



Scheme 1

The dependence of percentage yield of products on triplet energies of various sensitizers has also been studied. It was observed that rose bengal and methylene blue was much more efficient than riboflavin and benzophenone in the photosensitized decomposition of **1** (Table 2). This may be due to the fact that rose bengal and methylene blue, with lower triplet energies, produce singlet oxygen in large amount<sup>16,17</sup> by type II mechanism.<sup>18</sup>

**Table 1.** Yields of products, by methylene blue photosensitized reaction of Tinosponone with different solvents.

Solvent	Lifetime of $^1\text{O}_2$ <sup>a</sup> (μs)	Yields of products (%) <sup>b</sup> (2+3)
Benzene	24	32.3 (19.6+12.7)
Acetone	26	31.6 (18.9+12.7)
Acetonitrile	30	35.2 (22.8+12.4)
Chloroform	60	40.4 (27.1+13.3)

Concentration of tinosponone = 100 mg/200mL, 1.5 mM. Concentration of Methylene blue = 10% wt/wt of tinosponone. Time of irradiation = 4 hours. <sup>a</sup> See refs. 14, and 15. <sup>b</sup> Yields of the products were determined after isolation according to experimental part.

**Table 2.** Effect of Triplet energies of different sensitizers on the yields of products.

Sensitizer	Triplet energy <sup>a</sup> (Kcal/mole)	Yields of products (%) <sup>b</sup> (2+3)
Methylene blue	33.5–34.0	31.7 (19.1+12.6)
Rose bengal	39.2–42.2	30.3 (17.1+13.2)
Riboflavin	57.8	21.2 (11.3+9.9)
Benzophenone	68.6–69.1	19.9 (9.9+10.0)

Concentration of tinosponone = 100 mg/200mL, 1.5 mM. Concentration of Dye = 10% wt/wt of tinosponone. Time of irradiation = 4 hours. <sup>a</sup> See ref. 25. <sup>b</sup> Yields of the products were determined after isolation according to experimental part. Benzene was used as solvent.

On other hand riboflavin and benzophenone (higher triplet energies) act mainly by type I photosensitized photooxidation, do not produce significant amount of  $^1\text{O}_2$ .<sup>19</sup> The participation of  $^1\text{O}_2$  in the reaction was confirmed by studying the effect of some scavengers on the yield of this photooxidation reaction. The drastic lowering of the yield of products in presence of scavengers (DABCO-17%; sodium azide-14%) confirms that  $^1\text{O}_2$  is active oxidizing species in this photoreaction. Also no reaction was observed on conducting experiments under nitrogen atmosphere, which further support the involvement of  $^1\text{O}_2$  in this photoreaction. When irradiations were carried out by using silica bound rose bengal,<sup>20</sup> same products were obtained but the reaction was observed to be slow.

The structure of the photoproducts was assigned on the basis of IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and elemental analysis studies. The spectral data of photoproducts **2**, **3** and **4** were found to be similar with that of **1** except for the furan signals. The furan ring had been site of

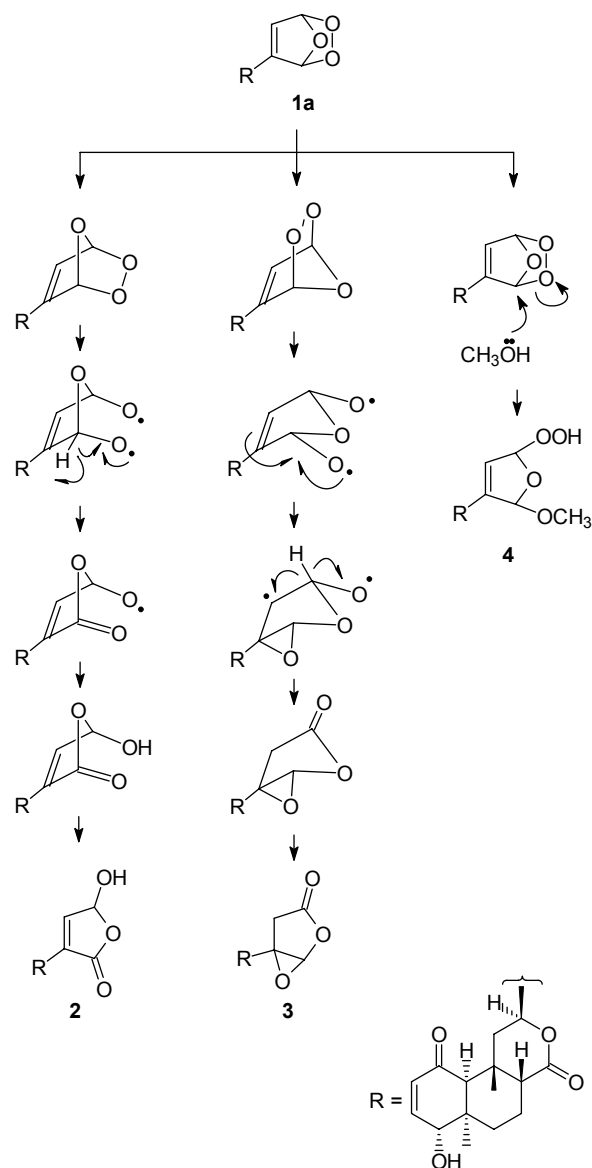
attack is evident from absence of carbon/hydrogen signals due to furan moiety in the spectral data of all the identified photoproducts. The spectral study suggested that product **2** now poses  $\delta$ -hydroxy butenolide moiety instead of furan moiety. The additional IR bands at  $3390\text{ cm}^{-1}$  (hydroxy group),  $1670\text{ cm}^{-1}$  ( $\alpha,\beta$ -unsaturated ketone) and extra carbonyl resonance at  $\delta 175.7$  suggested an extra lactone carbonyl compared to that of parent compound. The  $^{13}\text{C}$  NMR signal at  $\delta 97.5$  indicate that carbon must be attached to two oxygen atoms. This proton is in split with the proton of  $\alpha,\beta$ -unsaturated carbon at  $\delta 6.94$  suggested that carbon attached to two oxygen atoms must be adjacent to  $\alpha,\beta$ -unsaturated carbon. The change of furan ring to  $\delta$ -hydroxy butenolide moiety is also evident from the two carbon signals at  $\delta 136.5$  and  $175.7$  instead of the olefinic signals of furan at  $\delta 121.5$  and  $139.7$ . The appearance of double signals for C-5' indicated that compound **2** to be an epimeric mixture at C-5'.

The spectral data for compound **3** was also found to be similar with that of **1** except for the furan signals. On the basis of following spectral data we conclude the presence of epoxy lactone in **3**. The  $^{13}\text{C}$  NMR spectrum indicated an additional lactone carbonyl resonance at  $\delta 171.1$ . A signal at  $\delta 120.4$  was assigned to a dioxygenated carbon of the epoxy lactone ring, with additional support from its  $^1\text{H}$  NMR signal at  $\delta 5.23$ . Of the other carbons of the lactone ring, a carbon resonance value at  $\delta 36.2$  along with a proton resonance at  $\delta 2.2$  was assigned to the methylene carbon and at  $\delta 59.2$  assigned to the quaternary carbon. The formation of lactone ring gets additional support from the IR spectrum of **3**, which shows characteristic absorption for two lactone carbonyl at  $1750$  and  $1710\text{ cm}^{-1}$  and for the epoxide ring at  $3150$ ,  $1210$ ,  $950$  and  $745\text{ cm}^{-1}$ . The appearance of double signals for C-5' indicated compound **3** to be an epimeric mixture at C-5'.

The compound **4** was having a comparably similar spectral data to **1**, with a basic difference in furan ring values. It was shown to contain a 2,5-dihydrofuran ring with an allylic hydroperoxy and a methoxy group. The  $^1\text{H}$  NMR spectrum recorded a highly deshielded signal at  $\delta 8.1$  (brs, exch., 1H) and a three proton singlet at  $\delta 3.32$ , which were assigned to the allylic -OOH group (at C-5') and -OMe group (at C-2') respectively. This regiostructure gets support from the  $^1\text{H}$  NMR signals as a singlet at a low value of  $\delta 5.84$  for C-2' proton and a doublet at a high value of  $\delta 6.21$  for C-5' proton. Of olefinic carbons a carbon resonance at  $\delta 114.7$  was assigned to C-4' and at  $\delta 141.4$  was assigned to C-3'. The signals for the protons at C-4' and  $\text{OCH}_3$  were appropriately observed at  $\delta 5.72$  and  $3.32$  respectively. Additional structural information for the compound **4** was inferred from its following chemical properties: 1) with  $\text{Pb}(\text{OAc})_4$ , gas was evolved, as it is characteristic

of compounds containing -OOH group; 2) With potassium iodide-acetic acid solution it liberate iodine (suggested presence of O-O bond).<sup>21</sup>

The formation of photoproducts **2**, **3** and **4** can be envisaged to occur from unstable cyclic peroxide **1a**, which initially results by the  $[4\pi + 2\pi]$  cycloaddition of  $^1\text{O}_2$  to furan ring (Scheme 1). This unstable cyclic peroxide (**1a**) undergoes homolytic cleavage of O-O bond and afforded product **2** and **3** by following two competing processes:<sup>22,23</sup> elimination of proton from bridgehead position and a subsequent rearrangement gives product **2**; and 1,2 hydrogen shift gives product **3**, as mechanistically rationalized in Scheme 2. In the presence of polar methanol solvent, the solvolysis induced transformation of intermediate **1a** leads to the formation of product **4**.



Scheme 2

## Experimental

### Apparatus and chemicals

Irradiations were carried out in a photoreactor equipped with medium pressure mercury vapour lamp inserted in a water-cooled immersion well with continuous supply of water. IR spectra were recorded as KBr discs on a Perkin Elmer model spectrum RX1.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance DRX-300 spectrometer using  $\text{SiMe}_4$  as internal standard and  $\text{CDCl}_3$  as solvent. Elemental analyses were carried on a Carlo Erba model 1108 Elemental analyzer. High-resolution mass spectra were determined with a VG-ZAB-BEQ9 spectrometer. All solvents and chemicals used were of HPLC and pharmaceutical grade. Tinosponone was isolated from stem of *Tinospora cordifolia* according to literature procedure.<sup>24</sup> The purity of **1** was determined by comparison of its melting point and  $^1\text{H}$  NMR with that of literature value. Merck silica gel 60  $F_{254}$  plates were used for analytical TLC; column chromatography was performed on Merck silica gel 60 (70–230 mesh).

### Irradiation procedure

Irradiation of air-saturated solution of tinosponone (**1**) (100mg/200mL, 1.5 mM) in benzene with methylene blue (0.01 gm, 10% wt/wt of tinosponone) as sensitizer was carried out with medium pressure mercury vapour lamp (125 W) for 8 hours. Complete decomposition of **1** was monitored by thin layer chromatography (ethyl acetate: hexane; 3 : 7). Removal of solvent under reduced pressure and column chromatography of the resulting photoproduct on silica gel yielded compound **2** and **3**. This photoreaction was also carried out under nitrogen atmosphere. The solutions to be irradiated were saturated with air/nitrogen prior to irradiation and were continuously bubbled during irradiation.

Similar experiments were carried out by using different combinations of solvents and sensitizers (Table I and II). Two different sets of reactions were also carried out in similar way by using DABCO/sodium azide (10% wt/wt of tinosponone) with methylene blue as sensitizer.

### Characterization of products

**(3S,4aS,4bS,8R,8aR,10aR)-8-Hydroxy-3-(5'-hydroxy-2'-oxo-2',5'-dihydrofuran-3'-yl)-4a,8a-dimethyl-3,4,8,8a,9,10-hexahydro-10aH-benzo[f]isochromene-1,5(4aH,4bH)-dione (2)**: mp 177 °C.  $R_f$  0.83.  $[\alpha]_D^{23}$  -93.7 (c 0.92,  $\text{CHCl}_3$ ). IR (KBr)  $\nu$  3500, 3390, 1745, 1715, 1678, 1450  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.94 (d, 1H,  $J$  7.1 Hz), 6.67 (dd, 1H,  $J$  10.8, 5.2 Hz), 6.15 (d, 1H,  $J$  7.0 Hz), 5.91 (d, 1H,  $J$  10.8 Hz), 4.91 (dd, 1H,  $J$  12.2, 3.6 Hz), 4.82 (brs, exch., -OH), 4.28 (d, 1H,  $J$  5.1 Hz), 2.42 (dd, 1H,  $J$  14.8, 3.4 Hz), 2.38 (brs, 1H), 2.21 (m, 1H), 2.20 (brs, 1H), 2.18 (m, 1H), 1.65 (dd, 1H,  $J$  15.4, 12.2

Hz), 1.61 (m, 1H), 1.42 (s, - $\text{CH}_3$ ), 1.1 (dt, 1H,  $J$  13.8, 4.5 Hz), 0.80 (s, - $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  204.5, 176.2, 175.7, 141.5, 143.1, 136.5, 127.5, 97.1, 97.5, 74.5, 60.5, 52.6, 49.2, 42.9, 40.1, 34.8, 30.9, 29.9, 26.6, 19.2. HRMS-FAB (m/z):  $[\text{M}^+]$  calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_7$ , 362.3738; found, 362.3731; m/z (relative intensity): 345 ( $\text{C}_{19}\text{H}_{21}\text{O}_6^+$ , 14), 318 ( $\text{C}_{18}\text{H}_{22}\text{O}_5^+$ , 100), 303 ( $\text{C}_{18}\text{H}_{23}\text{O}_4^+$ , 15), 274 ( $\text{C}_{17}\text{H}_{22}\text{O}_3^+$ , 10), 263 ( $\text{C}_{15}\text{H}_{19}\text{O}_4^+$ , 17), 261 ( $\text{C}_{17}\text{H}_{25}\text{O}_2^+$ , 9). Anal. Calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_7$ : C 62.97, H 6.12, O 30.91. Found: C 62.84, H 6.08, O 30.98.

**(3S,4aS,4bS,8R,8aR,10aR)-8-Hydroxy-4a,8a-dimethyl-3-((1'R)-3'-oxo-4',6'-dioxo-bicyclo[3.1.0]hexan-1'-yl)-3,4,8,8a,9,10-hexahydro-10aH-benzo[f]isochromene-1,5(4aH,4bH)-dione (3)**: mp 164 °C.  $R_f$  0.62.  $[\alpha]_D^{23}$  -84.6 (c 0.47,  $\text{CHCl}_3$ ). IR (KBr)  $\nu$  3430, 1750, 1710, 1660, 1210, 950, 745  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.52 (dd, 1H,  $J$  10.6, 4.8 Hz), 5.75 (d, 1H,  $J$  10.4 Hz), 5.23 (s, 1H), 4.87 (dd, 1H,  $J$  12.4, 3.8 Hz), 4.30 (d, 1H,  $J$  5.1 Hz), 4.12 (brs, exch., -OH), 2.28 (dd, 1H,  $J$  14.2, 2.9 Hz), 2.22 (brs, 1H), 2.36 (m, 1H), 2.2 (s, 1H), 2.16 (brs, 1H), 1.98 (m, 1H), 1.71 (m, 1H), 1.58 (dd, 1H,  $J$  15.3, 11.8 Hz), 1.38 (s,  $\text{CH}_3$ ), 1.12 (dt, 1H,  $J$  13.6, 4.4 Hz), 0.80 (s,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  202.6, 175.2, 171.1, 145.2, 130.7, 120.4, 75.2, 59.2, 56.8, 52.5, 48.1, 44.2, 41.7, 36.6, 36.2, 31.3, 18.6, 25.4, 18.8. HRMS-FAB (m/z):  $[\text{M}^+]$  calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_7$ , 362.3738; found, 362.3751; m/z (relative intensity): 318 ( $\text{C}_{18}\text{H}_{22}\text{O}_5^+$ , 20), 290 ( $\text{C}_{17}\text{H}_{22}\text{O}_4^+$ , 100), 278 ( $\text{C}_{15}\text{H}_{18}\text{O}_5^+$ , 11), 276 ( $\text{C}_{17}\text{H}_{24}\text{O}_3^+$ , 11), 263 ( $\text{C}_{15}\text{H}_{19}\text{O}_4^+$ , 9), 221 ( $\text{C}_{14}\text{H}_{21}\text{O}_2^+$ , 16), 84 ( $\text{C}_4\text{H}_4\text{O}_2^+$ , 19). Anal. Calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_7$ : C 62.97, H 6.12, O 30.91. Found: C 62.74, H 6.34, O 31.05.

**(3S,4aS,4bS,8R,8aR,10aR)-8-Hydroxy-3-(5'-hydroperoxy-2'-methoxy-2',5'-dihydrofuran-3'-yl)-4a,8a-dimethyl-3,4,8,8a,9,10-hexahydro-10aH-benzo[f]isochromene-1,5(4aH,4bH)-dione (4)**: mp 169 °C.  $[\alpha]_D^{23}$  -77.8 (c 0.34,  $\text{CHCl}_3$ ). IR (KBr)  $\nu$  3520, 3500, 1670, 1250  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.12 (brs, exch.), 6.61 (dd, 1H,  $J$  10.7, 5.2 Hz), 6.21 (d, 1H,  $J$  7.4 Hz), 5.84 (s, 1H), 5.72 (d, 1H,  $J$  7.2 Hz), 5.62 (d, 1H,  $J$  10.8 Hz), 4.94 (dd, 1H,  $J$  12.1, 3.2 Hz), 4.64 (brs, exch., -OH) 4.26 (d, 1H,  $J$  4.8 Hz), 3.22 (s, 3H), 2.48 (dd, 1H,  $J$  13.8, 3.2 Hz), 2.30 (brs, 1H), 2.22 (m, 1H), 2.20 (brs, 1H), 2.12 (m, 1H), 1.68 (dd, 1H,  $J$  15.2, 12.8 Hz), 1.65 (m, 1H), 1.48 (s, 3H), 1.1 (dt, 1H,  $J$  13.8, 4.0 Hz), 0.82 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  200.5, 173.4, 143.7, 141.4, 129.4, 114.7, 111.8, 112.2, 98.4, 73.8, 58.1, 53.8, 51.3, 47.6, 43.1, 42.5, 39.2, 33.7, 26.1, 25.2, 18.4. HRMS-FAB (m/z):  $[\text{M}^+]$  calcd for  $\text{C}_{20}\text{H}_{26}\text{O}_8$ , 394.4156; found, 394.4152; m/z (relative intensity): 301 ( $\text{C}_{18}\text{H}_{21}\text{O}_4^+$ , 100), 363 ( $\text{C}_{19}\text{H}_{23}\text{O}_7^+$ , 18), 361 ( $\text{C}_{20}\text{H}_{25}\text{O}_6^+$ , 21), 331 ( $\text{C}_{19}\text{H}_{23}\text{O}_5^+$ , 13), 288 ( $\text{C}_{17}\text{H}_{20}\text{O}_4^+$ , 11), 206 ( $\text{C}_{14}\text{H}_{22}\text{O}^+$ , 15), 84 ( $\text{C}_4\text{H}_4\text{O}_2^+$ , 21). Anal. Calcd for  $\text{C}_{20}\text{H}_{26}\text{O}_8$ : C 60.90, H 6.64, O 32.45. Found: C 60.98, H 6.45, O 32.52.

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## Povzetek

Raziskovana je bila reakcija tinosponona (**1**) s singletnim kisikom v prisotnosti različnih kombinacij vzbujevalcev, topil in ponorov singletnega kisika. V vseh toipilih, razen v metanolu, smo izolirali dva glavna produkta: (3S,4aS,4bS,8R,8aR,10aR)-8-Hidroksi-3-(5'-hidroksi-2'-okso-2',5'-dihidrofuran-3'-il)-4a,8a-dimetil-3,4,8,8a,9,10-heksahidro-10aH-benzo[f]isokromen-1,5(4aH,4bH)-dion (**2**) in (3S,4aS,4bS,8R,8aR,10aR)-8-hidroksi-4a,8a-dimetil-3-((1'R)-3'-okso-4',6'-dioksa-biciklo[3.1.0]heksan-1'-il)-3,4,8,8a,9,10-heksahidro-10aH-benzo[f]isokromen-1,5(4aH,4bH)-dion (**3**). V metanolu smo dobili le (3S,4aS,4bS,8R,8aR,10aR)-8-hidroksi-3-(5'-hidroperoksi-2'-metoksi-2',5'-dihidrofuran-3'-il)-4a,8a-dimetil-3,4,8,8a,9,10-heksahidro-10aH-benzo[f]isokromen-1,5-(4aH,4bH)-dion (**4**). Strukture spojin smo potrdili na osnovi njihovih IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR spektrov in elementne analize. Nastanek produktov razlagamo s fotooksidacijo tinosponona. Ugotovili smo, da izbrana kombinacija reagentov vpliva na izkoristek fotooksidacijskih produktov in da sledi hitrosti tvorbe singletnega kisika.