



Colorimetric and fluorescence signalling of thioesculetin in presence of oxidising agent

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Abstract. Thioesculetin (TE) is a sulfur analogue of esculetin. The UV-Vis absorption maximum of TE at 470 nm shifted to 357 nm in the presence of oxidising agent such as m-chloroperoxy benzoic acid (m-CPBA). With gradual increase in the m-CPBA concentration, the absorption band at 470 nm decreases while the band at 357 nm increases. The same system shows gradual increase in the fluorescence signal at 463 nm in the presence of m-CPBA. The fluorescence signal was unaffected in the presence of common anions and metal cations. The mechanism for optical signalling was due to the conversion of weakly fluorescent TE to fluorescent esculetin through desulfurization reaction. ¹³C-NMR shows strong evidence in support of the chemical conversion of TE to esculetin. TE may find applications to probe the redox environment in various chemical and biochemical processes.

Keywords. Thioesculetin; m-chloroperoxy benzoic acid; absorption; fluorescence; desulfurization.

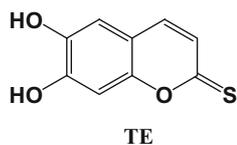
1. Introduction

Coumarins are a class of benzopyran compounds that exhibit exciting photophysical properties.^{1–6} These properties are sensitive to the surrounding solvent medium. The medium dependent photophysical properties of coumarin are often exploited to probe different physicochemical processes in condensed media.^{7–21} To name a few, investigation of solvatochromic properties,^{7–9} determination of the polarities of micro environments,^{10,11} investigation of photoinduced electron transfer processes,^{12–16} estimations of the solvent relaxation times, etc.^{8–17,17–21} Coumarin derivatives are also known to be very good sensors for various metal ions like, Ca(II), Mg(II), Al(III), Cr(III), Fe(III), Ni(II), Cu(II), Zn(II), Pb(II), Hg(II), and Ag(I).^{22–26} In the case of anions, like fluoride, phosphate, cyanide, acetate or benzoate, coumarin derivatives have served as good chemosensors.^{22–24} The recognition mechanisms of these chemosensors mainly involve photoinduced electron transfer, intramolecular charge transfer or fluores-

cence resonance energy transfer. Apart from these photophysical processes, on application of mild chemical stimulus, the probe molecule can be reversibly or irreversibly transformed to another chemical form. In such cases the recognition is achieved by ‘on-off’/‘off-on’ fluorescence signalling or through ratiometric analysis, where the probe molecule shows optical signalling in distinct wavelengths before and after addition of chemical stimulus.²³ Coordination of coumarin derivatives with metal ions or desulfurization under mild chemical stimulus are the two processes where such type of recognition is observed. It has been reported that the mild chemical processes have advantages in terms of selectivity and sensitivity. A large number of biochemical processes occur continuously in the human body under mild conditions and hence such probes find extensive application in this regard.^{23,27}

The functional analogue of coumarin, thiocoumarin is an interesting molecule which acts as redox indicator in the presence of various oxidants. In the presence of oxidant, thiocoumarin is readily transformed to coumarin.^{28,29} There is a distinct difference in the photophysical properties of coumarin and thiocoumarin.^{30,31}

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Scheme 1. Structure of thioesculetin (TE).

Coumarin and thiocoumarin have absorption in different wavelength regions. Coumarins are generally fluorescent but thiocoumarins are very weak fluorophores. Chang and his group, have studied conversion of different thiocoumarins to coumarins in the presence of various oxidising agents like hypochlorous acid (HOCl), *m*-chloroperoxy benzoic acid (*m*-CPBA), or trichloroisocyanuric acid.^{28,29,32} They have demonstrated that during the conversion of the thioketone group to ketone group, the fluorescence signal was increased substantially. Also, they have shown that fluorescence signalling was less affected in the presence of common interfering cations and anions. Apart from being redox indicators, thiocoumarin derivatives were also reported to show colorimetric and fluorescence signalling in the presence of trivalent gold ions.²⁶ Excellent selectivity for gold ions was achieved with the detection limit in the sub-micromolar level was reported. Thioesculetin (TE) is a thiocoumarin derivative of 6,7-dihydroxy coumarin commonly known as esculetin. The chemical structure of TE is shown in Scheme 1. With an aim to develop TE as a chemosensor in the presence of the oxidant, we have reported the optical signalling behaviour of TE in the presence of *m*-CPBA in this manuscript. The probable mechanism of signalling has been identified and the effect of interfering background ions during fluorescence signalling has been discussed. Signalling behaviour has also been studied with other oxidants like, hydroxyl radical, hydrogen peroxide and superoxide radical.

2. Experimental

2.1 Chemicals and reagents

Esculetin and *m*-chloroperoxy benzoic acid (*m*-CPBA) were purchased from Sigma Aldrich Chemicals. Lawesson's reagent was from Avra Synthesis Pvt. Ltd. India. All metal salts, hydrogen peroxide and phosphate buffer were of analytical grade. Anhydrous toluene, ethyl acetate, methanol, chloroform, petroleum ether, acetone were of synthetic grade. Acetonitrile used was of HPLC grade. Water from Millipore water purifier system was used for solution preparation and freshly prepared solutions were used for experiments. The

solutions for absorption and fluorescence studies were prepared in 10 mM phosphate buffer (pH 7) containing 10% acetonitrile. Acetonitrile was added in the phosphate buffer solution to overcome the solubility problem due to *m*-CPBA. Fluorescence quantum yields of TE and esculetin were determined by relative method using Coumarin-1 laser dye as a standard with a known quantum yield of 0.62 in acetonitrile.³³ Hydroxyl and superoxide radicals were generated by radiation chemical methods as reported in the literature.³⁴

2.2 Instrumentation

FTIR spectra of the solid samples were recorded in KBr pellets on a Bruker-Tensor 37 spectrometer. HRMS spectra were recorded on Impact II Ultra-High-Resolution Time-of-Flight Mass Spectrometer from Bruker Daltonik GmbH. ¹H NMR and ¹³C NMR were recorded on Bruker Ascend 500 NMR spectrometer. Melting point was determined manually from Buchi M-560 melting point apparatus. Steady state absorption and fluorescence spectra were recorded on JASCO V-650 spectrophotometer and JASCO FP-8500 spectrofluorometer, respectively. For steady state irradiation, cobalt-60 radiation source was used and the radiation dose was estimated by using standard Fricke dosimeter.³⁴

2.3 Synthesis of thioesculetin (TE)

A mixture of the esculetin (1 equivalent) and Lawesson's reagent [2,4-bis(4-thoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide] (2 equivalents) in anhydrous toluene was refluxed for about 30 h according to reported method.³⁵ After cooling, the solvent was evaporated under reduced pressure and the residue was extracted with ethyl acetate and water. The ethyl acetate extract was further dried over Na₂SO₄. The sticky residue was then separated by column chromatography with petroleum ether-acetone mixture (8:2). Yield: 65–70%; M.p. 231–234 °C, ¹H NMR (500 MHz, DMSO-*d*₆): (C₉H₆O₃S), 6.95(s, 1H), 7.04(s, 1H), 7.06(d, *J* = 3 Hz, 1H), 7.76(d, *J* = 9 Hz, 1H) ppm; ¹³C NMR (500 MHz, DMSO-*d*₆): (C₉H₆O₃S), 196.59, 152.66, 152.26, 144.95, 137.41, 125.64, 113.73, 112.09, 102.78 ppm; HRMS calculated for C₉H₆O₃S (+H): *m/z*: 195.0117, found: 195.0113. FTIR (C₉H₆O₃S): 3379, 2983, 2349, 1554, 1473, 1259, 1130, 1025, 937, 810, 638, 518, 432 cm⁻¹. The spectra for ¹H, ¹³C NMR, HRMS and FTIR (Figures S1–S4) are provided in electronic supporting information.

3. Results and Discussion

3.1 Steady state absorption and fluorescence spectra

Esculetin and TE have distinctive absorption bands in the UV–Visible region. Esculetin has absorption maximum around 357 nm whereas for TE the maximum

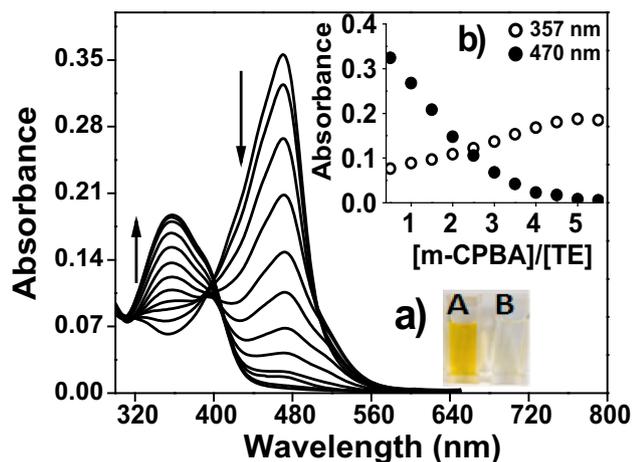


Figure 1. UV-Visible absorption spectra of TE (20 μM) with m-CPBA (10–110 μM) at pH 7.0 (10 mM phosphate buffer containing 10% acetonitrile). Inset (a) shows camera-ready pictures of TE (A) and TE in presence of m-CPBA (B). Inset (b) shows the change in absorbance at 470 and 357 nm for the same solution.

absorption appears at 470 nm. On addition of the m-CPBA in the concentration range of 10 to 100 μM to a solution of 20 μM TE, there was decrease in absorbance at 470 nm with concomitant increase at 357 nm through a crossover point at 400 nm (Figure 1). The color change can be visualized by the naked eye, from yellow to colorless as shown in Figure 1, inset (a).

Above 100 μM concentration of m-CPBA, the absorbance increase was not regular, in fact it starts to decrease (Figure S5 in SI). Inset (b) of Figure 1 represents the absorbance change of TE at 470 nm and 357 nm with respect to m-CPBA concentrations.

Thiocoumarins are generally weakly fluorescent in solution. The quantum yield for fluorescence emission of TE was 0.023 in the solvent system under investigation. The change in fluorescence spectra of TE solutions in the presence of m-CPBA were recorded by exciting at 400 nm (Figure 2). The fluorescence signal at 463 nm gradually increases with the increasing concentration of m-CPBA up to 100 μM (Inset (a) of Figure 2). In this situation the fluorescence of the solution can be visualized by the naked eye. The blue emission observed under UV lamp is shown in Figure 2 inset (b).

The reason for exciting at 400 nm was to minimise the contribution of fluorescence signal due to different amount of light absorption by TE solution with addition of m-CPBA. From the absorption and fluorescence spectra it was obvious that there was a change in the chemical nature of TE in the presence of m-CPBA. In the process of absorption and fluorescence changes, m-CPBA itself does not contribute directly absorption and fluorescence signal as shown in control absorption and

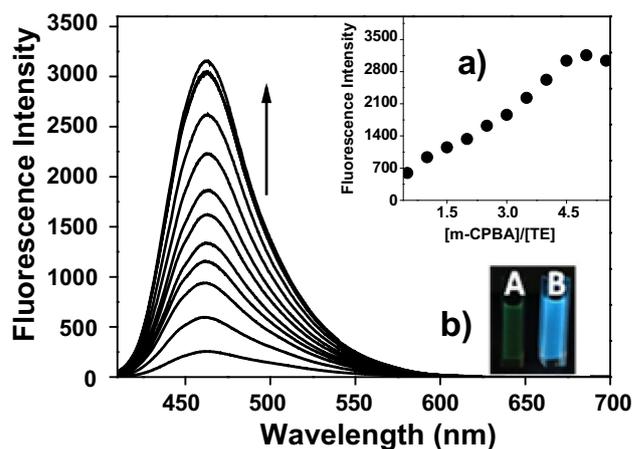


Figure 2. Fluorescence titration of TE (20 μM) solution with m-CPBA (10–110 μM) at pH 7.0 (10 mM phosphate buffer containing 10% acetonitrile). $\lambda_{\text{ex}} = 400 \text{ nm}$. Inset (a) shows the change in fluorescence intensity at 463 nm for the same solutions. Inset (b) shows camera-ready pictures of TE (A) and TE in presence of m-CPBA (B) under 366 nm UV lamp illumination.

fluorescence spectra of m-CPBA (Figure S6 in SI). The fluorescence spectrum of pure TE does not interfere in the fluorescence titration process, as TE emits at different wavelength (516 nm). The synthesized TE was free from any fluorogenic contamination as observed in the absorption, emission and excitation spectra of TE under similar experimental condition (Figure S7 in SI). In the context of ratiometric analysis of absorbance at 470 nm and 357 nm with m-CPBA concentration, there was a decrease in the ratio, suggesting possible conversion of TE to another species (Figure S8 in SI). It is very common that thioketones ($\text{C}=\text{S}$) are readily converted to ketone ($\text{C}=\text{O}$) upon oxidation through desulfurization process.^{27,29,32} m-CPBA has the unique property of oxygen atom donation during oxidation.³⁶ The conversion process for TE in the presence of m-CPBA was completed within 20 min and the product was stable upto 2 h as revealed from the time dependent fluorescence signal change (Figure S9 in SI). In order to establish the chemical conversion, ^{13}C NMR was recorded for pure TE and the reaction product of TE in the presence of m-CPBA. The reaction product of m-CPBA and TE was separated using a silica column for recording the NMR. The ^{13}C NMR signal of thioketone ($\text{C}=\text{S}$) group for TE was observed at 196.59 ppm. After addition of 5 equivalent of m-CPBA the signal appeared at 161.25 ppm which was identical to ketone ($\text{C}=\text{O}$) group of esculetin (Figure 3).

As mentioned earlier, TE has very low quantum yield ($\phi_f = 0.023$). However, with the addition of 5 equivalent of m-CPBA to TE, the fluorescence quantum yield of TE solution was found to be 0.15 which was very close

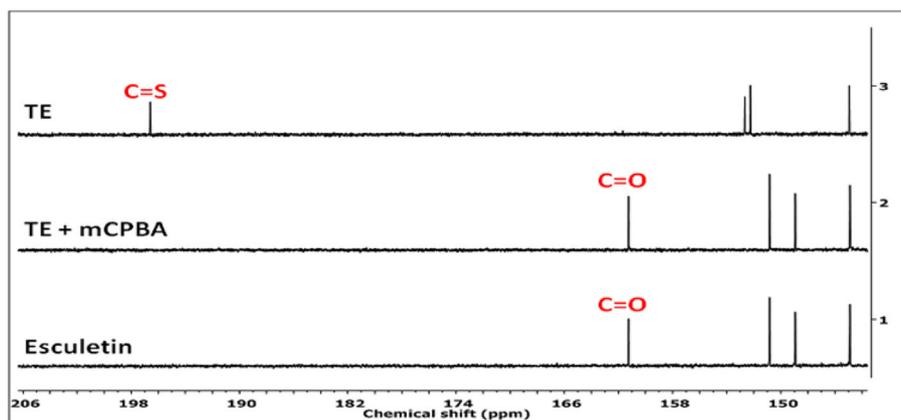


Figure 3. ^{13}C -NMR spectrum of TE, TE in presence of m-CPBA and esculetin. [TE] = 200 μM , [m-CPBA] = 1 mM, [esculetin] = 200 μM in DMSO- d_6 .

to esculetin ($\varphi_f = 0.14$) under similar conditions. From the above experimental evidences, the proposed mechanism for the conversion of TE to esculetin is shown in Scheme 2. Similar desulfurization mechanism was reported for thioamide and thioketone derivatives with high selectivity and yield by Bahrami *et al.*³⁷

Chang *et al.*, have performed signalling behaviour of thiocoumarin derivative in the presence of m-CPBA.²⁹ Compared to thiocoumarin, TE had achieved highest signalling at lower concentrations of m-CPBA. Also, the increase in fluorescence signal is almost two times higher in the case of TE compared to thiocoumarin derivative. At higher concentrations of m-CPBA (more than 5 equivalents), conversion of TE to esculetin was completed and further addition of m-CPBA probably led to the reaction with the phenolic OH groups of esculetin. Phenolic compounds yield Prussian blue colour in the presence of potassium ferricyanide and ferric chloride, which have absorption around 700 nm.³⁸ The addition of more than 5 equivalents of m-CPBA to TE solution was unable to develop any Prussian blue colour, which confirmed that indeed the phenolic groups of esculetin have undergone further reaction with m-CPBA (Figure S10 in SI).

3.2 Effect of interfering ions on fluorescence signalling

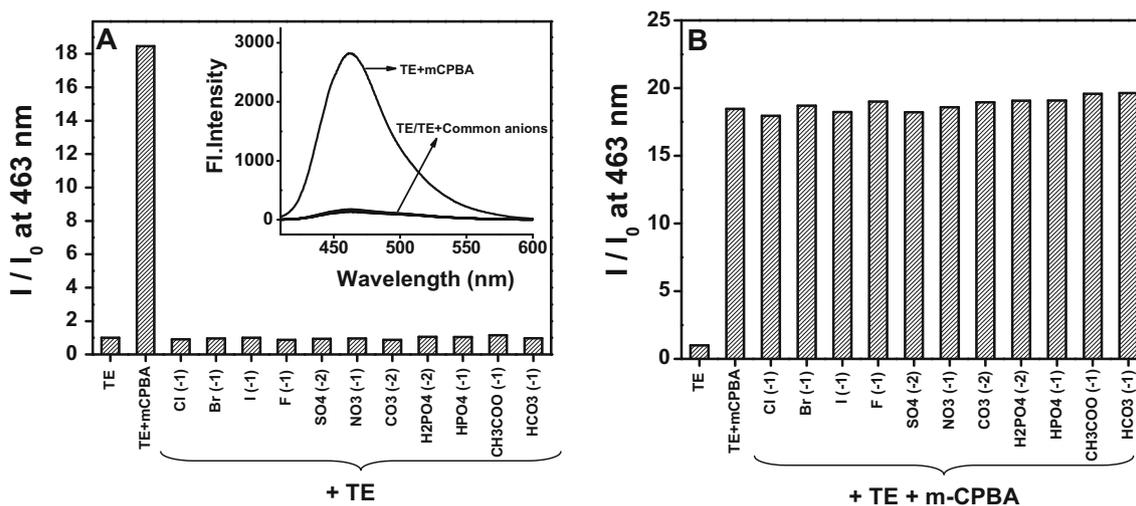
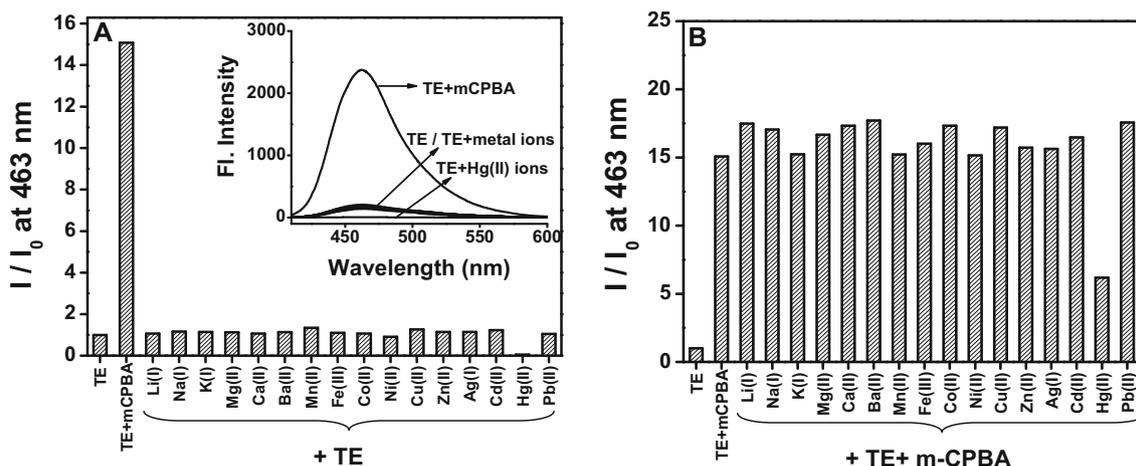
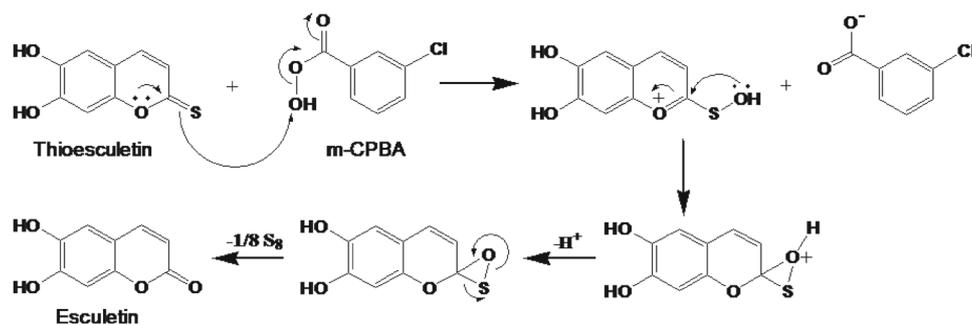
The fluorescence signalling process for TE with m-CPBA was monitored in the presence of common metal ions and anions to see the possible interference effect. The metal ions used are of alkali, alkaline earth, transition metals along with zinc, cadmium and mercury. There was no interference in the above signalling process of TE with m-CPBA, except mercury, which may be due to special affinity towards sulfur atom. Figure 4A shows that there was selective increase in fluorescence

intensity for TE solution in the presence of m-CPBA only.

The metal ions employed in the present system did not increase the fluorescence signal of TE solution. Inset of Figure 4A shows the representative fluorescence spectra of pure TE solution and TE solution in presence of the m-CPBA or metal ions. In order to understand the selective enhancement of fluorescence intensity of TE solution in the presence of m-CPBA, the same metal ions were used under competitive conditions. As mentioned earlier, except mercury, the enhancement of fluorescence intensity was not affected much and within the experimental error in the presence of other metal ions as shown in Figure 4B. The interference caused by mercury may be due to the oxidation of phenolic OH group of TE as reported in the literature for other molecules having phenolic OH group.³⁹ Likewise, there was no interference observed from anions in the above signalling process of m-CPBA. The anions used were halides, sulphate, carbonate, acetate, nitrate and phosphate. Figure 5A shows that there was selective increase in fluorescence intensity for TE solution in presence of the m-CPBA only and the anions were unable to influence the fluorescence signal of TE solution. Inset of Figure 5A shows the representative fluorescence spectra of TE solution alone and TE solution in the presence of m-CPBA or anions. Under competitive conditions, of the anions the enhancement of fluorescence intensity of TE solution in the presence of m-CPBA was not affected much and the small variations were within the experimental error (Figure 5B).

3.3 Comparison of signalling effect of TE in presence of other oxidants

The signalling effect of TE was compared with other oxidants like, hydroxyl radical, superoxide radical and



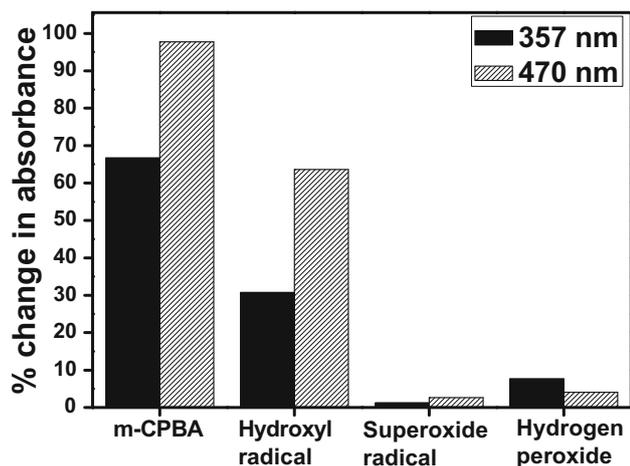


Figure 6. % change in absorbance of TE in presence of m-CPBA, hydroxyl radical, superoxide radical and hydrogen peroxide at 470 and 357 nm. [TE] = 20 μ M, [m-CPBA] = [hydroxyl radical] = [superoxide radical] = [peroxide] = 100 μ M at pH 7.0 (10 mM phosphate buffer).

hydrogen peroxide along with m-CPBA. The percentage change in absorbance for TE at 470 nm and 357 nm in the presence of different oxidants is shown in Figure 6.

From Figure 6, it is clear that m-CPBA shows better signalling efficiency in comparison to other oxidants. Apart from hydroxyl radical, the O-O bond in m-CPBA is the weakest, followed by hydrogen peroxide and superoxide. The bond dissociation energy of peracetic acid is 29.5 kcal/mol and the same for hydrogen peroxide is 48 kcal/mol in the gas phase.^{40,41} In many reactions, m-CPBA is more selective than hydrogen peroxide and other peracids.³⁶ The O-O bond dissociation energy in superoxide radical is expected to be higher than in hydrogen peroxide according to molecular orbital theory and also superoxide radical is a poor oxidant. On the contrary, though hydroxyl radical is a strong oxidant, the conversion of TE to esculetin was close to 50% compared to m-CPBA. The reaction of hydroxyl radical possibly proceeds through production of dimeric product of TE through S-S bond formation, which further hydrolysed to yield TE and esculetin. A similar type of reaction mechanism has been reported in the literature for hydroxyl radical reaction with ethylene trithiocarbonate.⁴²

4. Conclusions

Thioesculetin (TE) was tested for colorimetric and fluorescence signalling in the presence of m-CPBA. The signalling process was due to desulfurization reaction of TE. Colorimetric signalling in the presence of m-CPBA clearly indicated that there was transformation of TE which was evident from the change in absorption spectra. Fluorescence signalling confirms the transformation

of a weak fluorescent molecule, TE, to strongly fluorescent molecule, esculetin, in the presence of m-CPBA. ¹³C NMR clearly supported that the transformation of TE to esculetin was through desulfurization mechanism. In fact, TE acts as an ‘off-on’ type fluorescence switch under oxidizing condition. The signalling was selective in nature and negligibly affected in the presence of various metal ions and anions as background. TE may find applications as redox indicator in chemical and biochemical environment, in particular for designing suitable chemodosimetry for reactive oxygen species and reactive nitrogen species.

Supporting Information (SI)

Figures S1–S10 are available as Supplementary Information at www.ias.ac.in/chemsci.

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