Chemical Methodologies 3(2019) 481-493

Chemical Methodologies

Journalhomepage:http://chemmethod.com

Original Research article

Improved Photostabilization of Chlorpyrifos Insecticide with Novel Benzil Derivatives

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ARTICLE INFORMATION

Received:9October 2018
Received in revised:29 November 2018
Accepted27 January 2019
Available online11 March 2019

DOI:10.22034/chemm.2018.151723.1101

KEYWORDS

Photostabilizer
UV absorber
Chlorpyrifos
Benzils

ABSTRACT

Chlorpyrifos, an organophosphorus insecticide, is widely used in agricultural and non-agricultural areas all over the world. During field application, it readily undergoes degradation due to microbial decomposition, hydrolysis, volatilization and photolysis. Among these, photodegradation is one of the major pathways for its decomposition on field. In the present study, eight novel benzil derivatives and their application for the photostabilization of chlorpyrifos under UV light are reported. The percentage recovery of chlorpyrifos after UV irradiation (in the presence and absence of the benzil derivatives) is obtained by HPLC analysis. Results indicate significant enhancement in the photostabilization of chlorpyrifos using these benzil derivatives (96.63% recovery) in comparison to 2,4-dihydroxy benzophenone taken as a reference photostabilizer (78.80% recovery). Enhanced photostabilization, in case of benzil derivatives, is attributed to the assembly of two hydroxy and keto pairs in a single structure.

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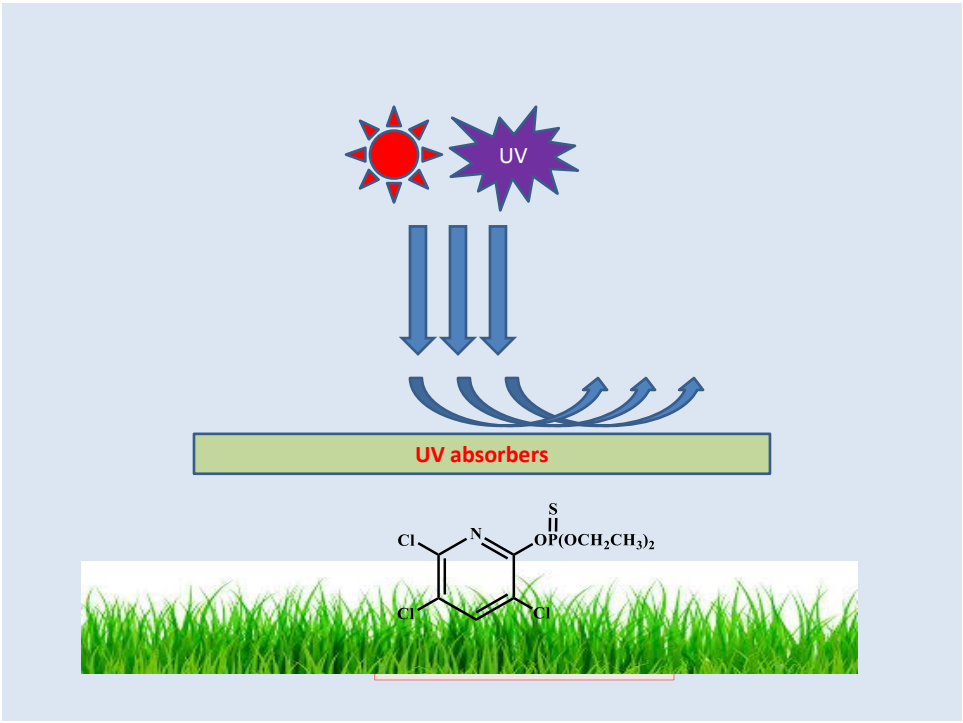
Graphical Abstract



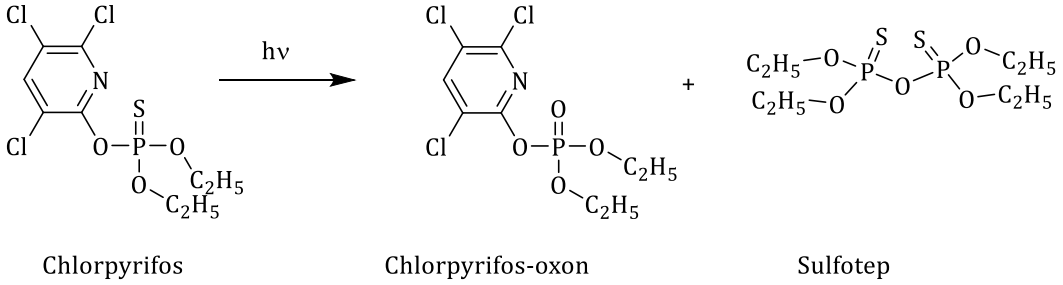
Introduction

A long-standing problem in agricultural field is the menace of various pests damaging the useful crops. Use of insecticides in agriculture is continuously increasing with simultaneous addition of new types of insecticides every year. Developing effective insecticides for controlling the ruinous attack by the pests has been a major activity in the past decades. A wide range of insecticides including organophosphorus, carbamates, pyrethroids and other class of insecticides has been used for this purpose.

Many factors affect activity of the insecticides when they are exposed to external environment like microbial decomposition, hydrolysis, volatilization and photolysis. Photodegradation due to sunlight is one of the major pathways that lessen insecticidal activity in the field. On exposure to sunlight, the insecticide molecules undergo a variety of primary processes such as isomerization, decarboxylation, dehalogenation, dealkylation, C-oxidation, S-oxidation, rearrangement, cyclization, *etc.*, often resulting in their degradation[1]. To overcome this problem, chemical modification were attempted [2] which seriously affected the insecticidal activity and caused ecological problems[3]. Alternatively, the UV absorbing molecules, also known as photostabilzers were used in the formulations to extend the environmental life of the insecticides [4-7].

Chlorpyrifos, *O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate ($C_9H_{11}Cl_3NO_3PS$), is most widely used insecticide all over the world for the protection against variety of pests [8]. It is used both for agriculture and household purposes [9]. US alone use almost 5-8 million pounds per year [10]. While in Europe, more than 50,000 kg/year of the insecticide are used [11]. It is generally used for various crops such as corn, alfalfa, cotton, soybeans, cereals, tobacco, peaches, vegetables and citrus fruits to control a wide spectrum of chewing, sucking and boring insects like aphids, caterpillars, helicoverpaspp, mites, moths, jassids, budworm, stem borer and locusts.

Chlorpyrifos degrades on exposure to sunlight resulting in the formation of various photoproducts which are more stable to UV radiation than chlorpyrifos itself. Chlorpyrifos-oxon is one such photoproduct which is more persistent and about 3000 times more toxic to humans than chlorpyrifos (Scheme 1)[12].



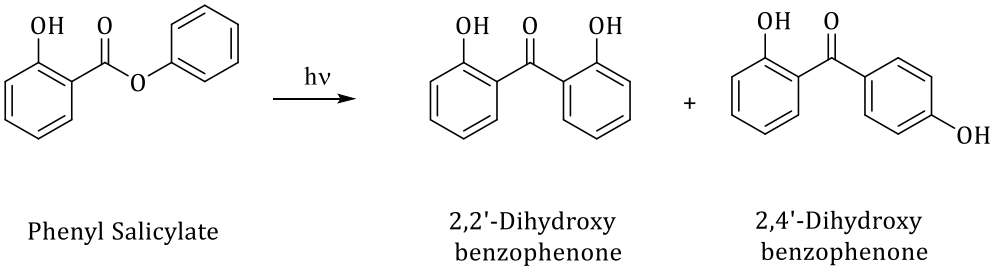
Scheme 1. Photodegradation of chlorpyrifos

On exposure to UV light, sulfotep is also formed from chlorpyrifos (Scheme 1) which is highly toxic and often co-exists as an impurity in chlorpyrifos [13]. In addition, 3,5,6-trichloro-2-pyridinol is also formed on photodecomposition of chlorpyrifos [14]. Photosensitivity of chlorpyrifos restricts its use in forestry because it should remain intact on the foliage for sufficient time to allow the insects to ingest it and cause mortality. Therefore, the insecticide must be stabilized for its effective use in agriculture.

Extending the life of chlorpyrifoscan also minimize the formation of the toxic photoproducts. Addition of UV absorbing compounds to formulations is often an attractive alternative to protect the photosensitive insecticides [15]. UV absorbers absorb UV radiation and dissipate the absorbed energy harmlessly and also persist in the matrix for the expected lifetime. Photostabilization of the insecticide takes place either by preferential absorption of light by photostabilizer, thereby preventing photo-excitation of the insecticide molecules or transfer of excess energy from the excited insecticide molecules to the photostabilizers through various energy transfer mechanisms such as excited-state intramolecular proton transfer (ESIPT) or keto-enol tautomerism [16, 17].

Intramolecularly *H*-bonded photostabilizers such as 2-hydroxybenzophenones, 2-(2-hydroxyaryl)-benzotriazoles, oxanilides and 2-(2-hydroxyaryl)-1,3,5-triazines are widely used for the protection of various products against photodegradation [18-20].

Previously we reported the effect of photostabilization of azadirachtin-A on exposure to UV light in the presence ofstructurally different photostabilizers, namely 4-aminobenzoic acid, 2,4-dihydroxybenzophenone, 4,4'-dihydroxybenzophenone and phenyl salicylate [21, 22]. Amongst the four photostabilizers studied, phenyl salicylate provided the best photostabilization. It was proposed that on exposure to UV light, phenyl salicylate does not dissipate absorbed energy by direct absorption of UV light but instead undergoes photo-Fries type rearrangement to form strongly absorbing 2,2'- and 2,4'-dihydroxy benzophenones (Scheme 2). These two molecules then dissipate absorbed energy through ESIPT.

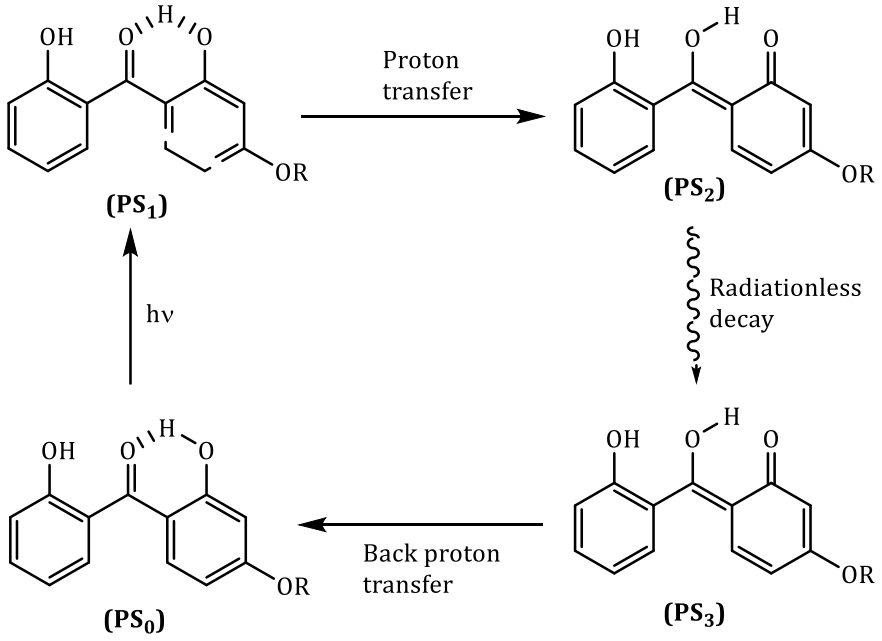


Scheme 2. Photo-Fries type rearrangement of phenyl salicylate

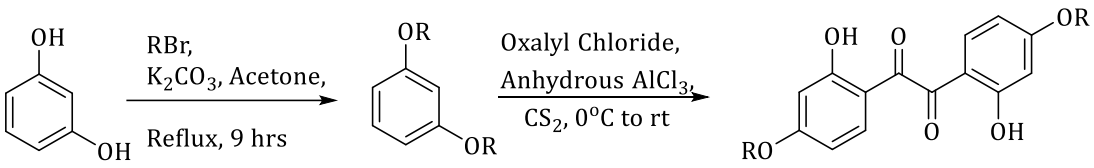
2-Hydroxybenzophenones act as photostabilizers *via* ESIPT mechanism involving dissipation of absorbed light energy through non-photochemical pathways. These compounds possess an efficient radiationless mechanism (*keto-enol*tautomerism) of energy dissipation. The molecule in the first excited state $\mathbf{PS_1}$ undergoes ESIPT to generate another species in its first excited singlet state $\mathbf{PS_2}$. This excited proton-transferred species loses its energy by a nonradiative decay process to form $\mathbf{PS_3}$. It should be noted that the contribution of this energy towards thermal degradation of the compound is negligible compared to the much stronger thermal energy reaching the compound from the solar radiation [23]. The original form of the photostabilizer$\mathbf{PS_0}$ is regenerated by a reverse proton transfer mechanism (Scheme 3)[24-26]. In 2-hydroxybenzophenone, it is the proximity of hydroxyl and keto groups in the molecule which is thought to be responsible for such photostabilization.

In continuation with our search for novel photostabilizers, we envisioned benzil derivatives having structures of the type **3** (Scheme 4) with two hydroxy and keto pairs assembled into a single structure. It was thought that these benzil derivatives would possess enhanced efficiency and

usefulness as photostabilizers due to their inherent structural features. To ascertain our contemplation, novel 2,2'-dihydroxy-4,4'-dialkoxy benzils **3(a-h)** were synthesized from various 1,4-dialkoxy benzenes **2(a-h)** (Scheme 4) by intermolecular Friedel-Crafts acylation with oxalyl chloride in CS_2 as solvent. The photostability of chlorpyrifos in the presence of benzils was compared with that using the reference photostabilizer*i.e.,* 2,4-dihydroxybenzophenone.



Scheme 3. Excited State Intramolecular Proton Transfer (ESIPT) of o-hydroxy benzophenones



2(a-h) **3(a-h)**

a: R= CH_3; b: R= C_2H_5; c: R= n-C_3H_7; d: n-C_4H_9; e: R= n-C_6H_{13}; f: R= n-C_8H_{17}; g: R= n-$C_{10}H_{21}$; h: R= n-$C_{12}H_{25}$

Scheme 4. Synthesis of novel benzil derivatives

Experimental

Chemicals

Chlorpyrifos (99%) was obtained from United Phosphorus Limited (India) as a gift while the rest of the chemicals and HPLC solvents were purchased from Glaxo (Qualigens) India Ltd.

Standard Solutions

Standard solutions of pure chlorpyrifos (0.5 mg / mL) were prepared along with photostabilizers in the mole ratio of 1:1 (Chlorpyrifos:photostabilizer) and 1:0 (no photostabilizer) in dry methanol. The solutions were stored in amber colored bottles between 0-4 °C and the chlorpyrifos content was determined by analytical HPLC.

HPLC instrumentation

Shimadzu LC 20AT equipped with a variable wavelength detector (SPD 20A), flow controller and Class-VP software was used in the HPLC study. The instrument employed dual solvent system and dual pump heads with common drive which gave stable and reproducible flows. The Class-VP software provided the chromatogram, percent area and retention time (t_R) for each peak.

Irradiation experiments

Standard solutions of pure chlorpyrifos prepared as above with and without photostabilizers in methanol (20 mL) were placed in a Pyrex immersion–well type photochemical reactor and irradiated separately using a high-pressure mercury vapor lamp (HPMV, 250 W, Bajaj India) at a distance of 3.8 cm from the light source. The solutions were withdrawn after irradiation for 10 h and analyzed for their chlorpyrifos content by analytical HPLC. Control samples were irradiated and analyzed similarly.

General experimental

IR spectra were recorded on a Shimadzu 8400S FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-400 FT NMR spectrometer (400 MHz) using $CDCl_3$ with TMS as an internal standard. Mass spectra were obtained on a Shimadzu QP-5050 mass spectrometer. Column chromatography was performed on Acme's silica gel (60-120 mesh) using mixtures of light petroleum (60 °C-80 °C) and ethyl acetate. Thin layer chromatography was performed using Acme's silica gel for TLC and spots were visualized in iodine vapor. Identification and quantitative analysis of chlorpyrifos in the sample solution was done using methanol as mobile phase by high performance liquid chromatography (HPLC) equipped with a SPD 20A UV-Vis detector. The HPLC column was fitted with a 4.6 mm ID, 250 mm length, Hypersil ODS and 5 micron particle size.

General procedure for the synthesis of dialkoxy benzenes

A mixture of 1,3-dihydroxy benzene **1 (**45 mmol), appropriate alkyl bromide (108 mmol) and powdered anhydrous potassium carbonate (135 mmol) was stirred in dry acetone (50 mL) for 9 h under reflux. After completion of the reaction (TLC), the reaction mixture was allowed to cool to

room temperature, filtered through a celite pad and acetone was distilled off. Water was added to the residue and the aqueous layer was extracted with ethyl acetate (4×25 mL) and the combined organic layer was washed with water (2×20 mL), brine (2×20 mL), dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the resulting residue was chromatographed over silica gel using a mixture of light petroleum and ethyl acetate as eluents.

General procedure for the synthesis of dialkoxy benzils

To a mechanically stirred suspension of dialkoxy benzenes (7.2 mmol) and anhydrous aluminium chloride (7.9 mmol) in carbon disulfide (100 mL) at 0 °C was added a solution of oxalyl chloride (4.7 mmol) in carbon disulfide (50 mL) over a period of 4 h under a constant stream of nitrogen. Stirring was continued for 18 h after which the resulting mixture was poured onto ice and carbon disulfide was distilled off. The aqueous mixture was extracted with ethyl acetate (4×25 mL) and the combined organic layer was washed with water (2×20 mL), brine (2×20 mL), dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the resulting residue was chromatographed over silica gel using a mixture of light petroleum and ethyl acetate as eluents.

The selected spectral data

1,3-Diethoxybenzene 2(b)

Colorless liquid, λ_{max} (EtOAc)/nm: 270; IR (ν_{max} /cm^{-1}): 2980 (CH), 1047 (C-O); ^{1}H NMR: δ_H1.44 (t, 6H, *J* = 7.2 Hz, CH_3), 4.04 (q, 4H, CH_2), 6.51(m, 3H, Ar H), 7.19 (t, 1H, *J* = 8.4 Hz, Ar H).

1,3-Di-*n*-propyloxybenzene 2(c)

Colorless liquid, λ_{max} (EtOAc)/nm: 274; IR (ν_{max}/cm^{-1}): 2964 (CH), 1012 (C-O); ^{1}H NMR: δ_H 1.07 (t, 6H, *J* = 7.2 Hz, CH_3), 1.84 (m, 4H, CH_2), 3.93 (t, 4H, *J* = 6.8 Hz, O-CH_2), 6.52 (m, 3H, Ar), 7.19 (t, 1H, *J* = 8.4 Hz, Ar H).

1,3-Di-*n*-butyloxybenzene 2(d)

Colorless liquid, λ_{max} (EtOAc)/nm: 274; IR (ν_{max} /cm^{-1}): 2968 (CH), 1031 (C-O); ^{1}H NMR: δ_H 1.04 (t, 6H, *J* = 7.6 Hz, CH_3) , 1.55 (m, 4H, CH_2), 1.82 (m, 4H, CH_2), 4.0 (t, 4H, *J* = 6.8 Hz, O-CH_2), 6.55 (m, 3H, Ar), 7.20 (t, 1H, *J* = 8.4 Hz, Ar H).

1,3-Bis-*n*-(hexyloxy)benzene 2(e)

Colorless liquid, λ_{max} (EtOAc)/nm: 274; IR (ν_{max} /cm^{-1}): 2965 (CH), 1045 (C-O); ^{1}H NMR:δ_H 0.96 (t, 6H, *J* = 7.2 Hz, CH_3), 1.36 (m, 8H, CH_2), 1.50 (m, 4H, CH_2), 1.81 (m, 4H, CH_2), 3.96 (t, 4H, *J* = 6.8 Hz, O-CH_2), 6.52 (m, 3H, Ar), 7.20 (t, 1H, *J* = 8.0 Hz, Ar H).

1,3-Bis-*n*-(octyloxy)benzene 2(f)

White crystalline solid, λ_{max} (EtOAc)/nm: 274; IR (ν_{max}/cm^{-1}):2953 (CH), 1043 (C-O); ^{1}H NMR: δ_H0.99 (t, 6H, *J* = 7.2 Hz, CH_3), 1.35 (m, 16H, CH_2), 1.45 (m, 4H, CH_2), 1.78 (m, 4H, CH_2), 3.94 (t, 4H, *J* = 6.4 Hz, O-CH_2), 6.49 (m, 3H, Ar H), 7.20 (t, 1H, *J* = 8.0 Hz, Ar H).

1,3-Bis-*n*-(decyloxy)benzene (2g)

White crystalline solid, λ_{max} (EtOAc)/nm: 274; IR (ν_{max}/cm^{-1}): 2961 (CH), 1022 (C-O); ^{1}H NMR: δ_H 0.90 (t, 6H, *J* = 7.2 Hz, CH_3), 1.35 (m, 24H, CH_2), 1.45 (m, 4H, CH_2), 1.75 (m, 4H, CH_2), 3.94 (t, 4H, *J* = 6.8 Hz, O-CH_2), 6.49 (m, 3H, Ar), 7.17 (t, 1H, *J* = 8.4 Hz, Ar H).

1,3-Bis-*n*-(dodecyloxy)benzene (2h)

White crystalline solid, λ_{max} (EtOAc)/nm: 274; IR (ν_{max}/cm^{-1}): 2955 (CH), 1045 (C-O); ^{1}H NMR: δ_H 0.90 (t, 6H, *J* = 7.2 Hz, CH_3), 1.29 (m, 32H, CH_2), 1.46 (m, 4H, CH_2), 1.78 (m, 4H, CH_2), 3.94 (t, 4H, *J* = 6.8 Hz, O-CH_2), 6.49 (m, 3H, Ar), 7.17 (t, 1H, *J* = 8.4 Hz, Ar H).

1,2 –Bis(2-hydroxy-4-methoxyphenyl)ethane-1,2-dione 3(a)

White crystalline solid; mp 150 °C; λ_{max} (EtOAc)/nm: 284; IR (ν_{max}/cm^{-1}): 1024 (C-O), 1629 (C=O), 3076 (CH); ^{1}H NMR (400MHz, $CDCl_3$): δ_H 3.89 (s, 6H, O-CH_3), 6.45 (dd, 2H, J_1 = 2.4 Hz, J_2 = 2.4 Hz, Ar), 6.52 (d, 2H, *J* = 2.4 Hz, Ar H), 7.42 (d, 2H, *J* = 8.8 Hz, Ar H), 11.86 (s, 2H, OH); ^{13}C NMR (100MHz, $CDCl_3$): δ_C 55.86 (O-CH_3), 101.17, 109.03, 110.95, 134.04, 166.80 (C-OH), 167.76 (C-OR), 194.47 (keto carbon); MS: m/z 301.13(M^+). Found: C, 63.4; H, 4.8. Calc. for $C_{16}H_{14}O_6$: C, 63.6; H, 4.7%.

1,2-Bis(4-ethoxy-2-hydroxyphenyl)ethane-1,2-dione 3(b)

White crystalline solid; mp 130 °C; λ_{max} (EtOAc)/nm: 287; IR (ν_{max}/cm^{-1}):1043 (C-O), 1633 (C=O), 2983 (CH); ^{1}H NMR: δ_H 1.43 (t, 6H, *J* = 7.2 Hz, CH_3), 4.14 (q, 4H, O-CH_2), 6.42 (dd, 2H, J_1 = 2.4 Hz, J_2 = 2.4 Hz, Ar H), 6.49 (d, 2H, *J* = 2.4 Hz, Ar H), 7.42 (d, 2H, *J* = 8.8 Hz, Ar H), 11.86 (s, 2H, -OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.49 (CH_3), 64.33 (O-CH_2), 101.55, 109.33, 110.81, 134.04, 166.76 (C-OH), 167.18 (C-OR), 194.45 (keto carbon); MS: m/z 330.22 (M^+). Found: C, 65.3; H, 5.5. Calc. for $C_{18}H_{18}O_6$: C, 65.4; H, 5.5 %.

1,2-Bis(2-hydroxy-4-*n*-propoxyphenyl)ethane-1,2-dione 3(c)

White crystalline solid, mp 117^{o}C; λ_{max} (EtOAc)/nm : 285; IR (ν_{max}/cm^{-1}): 1018 (C-O), 1622 (C=O), 2966 (CH); ^{1}H NMR: δ_H 0.89 (t, 6H, *J* = 6.8 Hz, CH_3), 1.80 (m, 4H, CH_2), 4.04 (t, 4H, *J* = 6.8 Hz, O-CH_2), 6.44 (dd, 2H, J_1 = 2.4 Hz, J_2 = 2.4 Hz, Ar), 6.49 (d, 2H, *J* = 2.4 Hz, Ar), 7.40 (d, 2H, *J* = 8.8 Hz, Ar), 11.86 (s, 2H, OH); ^{13}C NMR (100MHz, $CDCl_3$): δ_C 14.14 (CH_3), 22.69 (CH_2), 68.77 (O-CH_2), 101.57, 109.35,

110.79, 134.00, 166.76 (C-OH), 167.38 (C-OR), 194.45 (keto carbon); MS: m/z 358.11 (M^+). Found: C, 67.1; H, 6.3. Calc. for $C_{20}H_{22}O_6$: C, 67.0; H, 6.2%.

1,2-Bis(4-*n*-butoxy-2-hydroxyphenyl)ethane-1,2-dione 3(d)

White crystalline solid, mp 107 °C; λ_{max} (EtOAc)/nm: 287; IR (ν_{max} /cm^{-1}):1058 (C-O), 1630 (C=O), 2962 (CH); ^{1}H NMR: δ_H 1.49 (t, 6H, *J* = 7.2 Hz, CH_3), 1.52 (m, 4H, CH_2), 1.80 (m, 4H, CH_2), 4.04 (t, 4H, *J* = 6.8 Hz, O-CH_2), 6.44 (dd, 2H, J_1 = 2.4 Hz, J_2 = 2.4 Hz, Ar H), 6.49 (d, 2H, *J* = 2.0 Hz, Ar H), 7.40 (d, 2H, *J* = 8.8 Hz, Ar H), 11.86 (s, 2H, OH); ^{13}C NMR (100MHz, $CDCl_3$): δ_C 13.77 (CH_3), 19.12, 30.86 (CH_2), 68.45 (O-CH_2), 101.55, 109.37, 110.78, 134.01, 166.76(C-OH), 167.39 (C-OR), 194.46 (keto carbon); MS: m/z 385.88 (M^+). Found: C, 68.6; H, 6.7. Calc. for $C_{22}H_{26}O_6$: C, 68.4; H, 6.8 %.

1,2-Bis(4-*n*-hexyloxy-2-hydroxyphenyl)ethane-1,2-dione 3(e)

White crystalline solid, mp 94 °C; λ_{max} (EtOAc)/nm: 287; IR (ν_{max} /cm^{-1}): 1022 (C-O), 1633 (C=O), 2964 (CH); ^{1}H NMR: δ_H 0.93 (t, 6H, *J* = 6.8 Hz, CH_3), 1.34 (m, 8H, CH_2), 1.46 (m, 4H, CH_2), 1.80 (m, 4H, CH_2), 4.03 (t, 4H, *J* = 6.8 Hz, O-CH_2), 6.44 (dd, 2H, J_1 = 2.4 Hz, J_2 = 2.4 Hz, Ar H), 6.49 (d, 2H, *J* = 2.4 Hz, Ar), 7.40 (d, 2H, *J* = 8.8 Hz, Ar), 11.86 (s, 2H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.04 (CH_3), 22.57, 25.57, 28.82, 31.47 (CH_2), 68.76 (O-CH_2), 101.56, 109.35, 110.78, 134.01, 166.76 (C-OH), 167.38 (C-OR), 194.45 (keto carbon); MS : m/z 441.93 (M^+). Found: C, 70.7; H, 7.6. Calc. for $C_{26}H_{34}O_6$: C, 70.6; H, 7.7 %.

1,2-Bis(2-hydroxy-4-*n*-octyloxyphenyl)ethane-1,2-dione 3(f)

White crystalline solid, mp 98 °C; λ_{max} (EtOAc)/nm : 287; IR (ν_{max} /cm^{-1}): 1030 (C-O), 1620 (C=O), 2945 (CH); ^{1}H NMR: δ_H 0.91 (t, 6H, *J* = 6.8 Hz, CH_3), 1.34 (m, 16H, CH_2), 1.46 (m, 4H, CH_2), 1.80 (m, 4H, CH_2), 4.03 (t, 4H, *J* = 6.8 Hz, O-CH_2), 6.44 (dd, 2H, J_1 = 2.4 Hz, J_2 = 2.4 Hz, Ar H), 6.49 (d, 2H, *J* = 2.4 Hz, Ar H), 7.40 (d, 2H, *J* = 8.8 Hz, Ar H), 11.86 (s, 2H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.12 (CH_3), 22.66, 25.90, 28.85, 29.20, 29.26, 31.79 (CH_2), 68.77 (O-CH_2), 101.56, 109.36, 110.78, 134.04, 166.76 (C-OH), 167.38 (C-OR), 194.45 (keto carbon); MS: m/z 497.84 (M^+). Found: C, 72.3; H, 8.3. Calc. for $C_{30}H_{42}O_6$: C, 72.2; H, 8.5 %.

1,2-Bis(4-*n*-decyloxy-2-hydroxyphenyl)ethane-1,2-dione 3(g)

White crystalline solid, mp 105 °C; λ_{max} (EtOAc)/nm: 287; IR (ν_{max} /cm^{-1}): 1018 (C-O), 1633 (C=O), 3082 (CH); ^{1}H NMR: δ_H 0.89 (t, 6H, *J* = 6.8 Hz, CH_3),1.34 (m, 24H, CH_2),1.45 (m, 4H, CH_2), 1.80 (m, 4H, CH_2),4.0 (t, 4H, *J* = 6.8 Hz, O-CH_2),6.44 (dd, 2H, J_1 = 2.4 Hz, J_2 = 2.4 Hz, Ar H), 6.49 (d, 2H, *J* = 2.4 Hz, Ar H), 7.40 (d, 2H, *J* = 8.8 Hz, Ar H), 11.77 (s, 2H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.14 (CH_3), 22.69, 25.89, 28.85, 29.30, 29.31, 29.54, 31.89, 68.77 (O-CH_2), 101.58, 109.35, 110.79, 134.00, 166.76 (C-

OH), 167.38 (C-OR), 194.45 (keto carbon); MS: m/z 553.99 (M^+). Found: C, 73.4; H, 9.2. Calc. for $C_{34}H_{50}O_6$: C, 73.6; H, 9.1 %.

1,2-Bis(4-*n*-dodecyloxy-2-hydroxyphenyl)ethane-1,2-dione 3(h)

White crystalline solid, mp 90 °C; λ_{max} (EtOAc)/nm: 285; IR (ν_{max}/cm^{-1}): 1026 (C-O), 1635 (C=O), 2955 (CH); ^{1}H NMR: δ_H 0.80 (t, J = 6.8 Hz, 6H, CH_3), 1.21 (m, 32H, CH_2), 1.35 (m, 4H, CH_2), 1.71 (m, 4H,CH_2), 4.0 (t, J = 6.8 Hz, 4H, O-CH_2), 6.35 (dd, 2H, J_1 = 2.4 Hz, J_2 = 2.4 Hz, Ar H), 6.40 (d, 2H, J = 2.4 Hz, Ar H), 7.31 (d, 2H, J = 8.8 Hz, Ar H), 11.77 (s, 2H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.13 (CH_3), 22.69, 25.89, 28.85, 29.29, 29.35, 29.52, 29.57, 29.63, 29.64, 31.92, 68.77 (O-CH_2), 101.58, 109.34, 110.80, 134.00, 166.76 (C-OH), 167.38 (C-OR), 194.45 (keto carbon); MS: m/z 610.63 (M^+); Found: C, 74.6; H, 9.7. Calc. for $C_{38}H_{58}O_6$: C, 74.7; H, 9.6%.

Results and Discussion

For photostabilization studies, the standard solution of pure chlorpyrifos with and without benzil photostabilizers were irradiated in a Pyrex immersion–well type photochemical reactor using a highpressure mercury vapor (HPMV) lamp. After 10h of irradiation, the solutions were analyzed for their chlorpyrifos content by analytical HPLC. An optimization study was carried out with different mole ratio of benzil to chlorpyrifos (Table 1). It was found that 1:1 mole ratio gave maximum photostabilization in 10h of exposure of UV light in case of benzil derivative **3h**.

Table 1. Optimization of mole ratio of chlorpyrifos to benzil **3h**

Sr. No.	Mole ratio chlorpyrifos : benzil (3h)	Recovery of chlorpyrifos (%)
1	1 : 0.1	66.12
2	1 : 0.3	67.60
3	1 : 0.5	70.07
4	1 : 0.7	78.23
5	1 : 1	96.63

The recovery of chlorpyrifos was found to be only 66.12% in the absence of photostabilizers when exposed to UV light while that in the presence of a known photostabilizer, 2,4-dihydroxybenzophenone was 78.80%. Thus the photostabilization of chlorpyrifos induced by 2,4-dihydroxybenzophenone was found to be upto 12.68%. We further found that benzil derivatives (**3a-h**), provided photostabilizing effect up to 30.51% *i.e.,* up to 96.63% of chlorpyrifos was recovered after irradiation experiments as compared to that of UV exposure of bare chlorpyrifos (Table 2).

Absorption spectra of chlorpyrifos and photostabilizers

Figure 1 shows the absorption spectra of pure chlorpyrifos, 2,4-dihydroxybenzophenone and benzil derivatives in methanol. The UV spectra of pure chlorpyrifos and benzil derivatives show that both the molecules absorb strongly near 289 nm and 287 nm respectively. Effective photostabilization of chlorpyrifos by benzil derivatives appears to be due to competitive energy absorption of UV photons which cause degradation of chlorpyrifos.

Table 2. Percentage recovery of chlorpyrifos in presence and absence of photostabilizer on exposure to UV-Radiation (chlorpyrifos: photostabilizer, 1:1)

Sr. No.	Samples	Recovery of chlorpyrifos (%)
1	Chlorpyrifos (no stabilizer)	66.12
2	2,4-dihydroxy benzophenone $C_{13}H_{10}O_3$	78.80
3	$C_{16}H_{14}O_6$ **(3a)**	89.83
4	$C_{18}H_{18}O_6$ **(3b)**	89.00
5	$C_{20}H_{22}O_6$ **(3c)**	95.53
6	$C_{22}H_{26}O_6$ **(3d)**	94.42
7	$C_{26}H_{34}O_6$ **(3e)**	96.44
8	$C_{30}H_{42}O_6$ **(3f)**	96.62
9	$C_{34}H_{50}O_6$ **(3g)**	89.90
10	$C_{38}H_{58}O_6$ **(3h)**	96.63

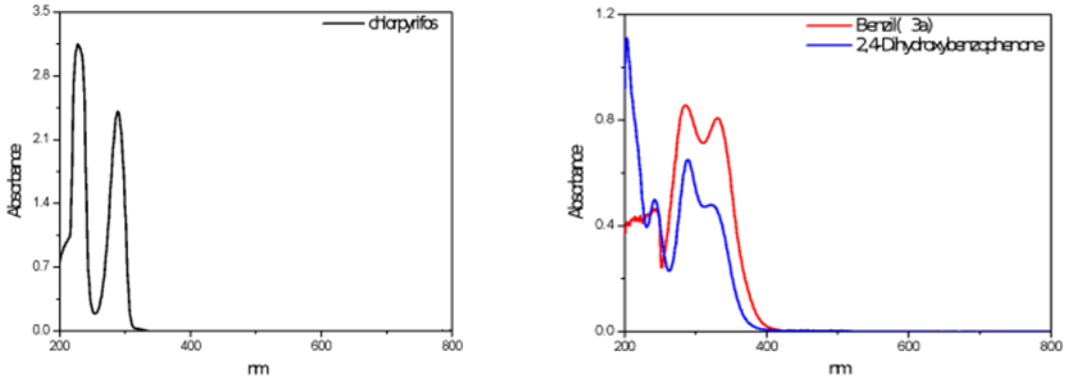


Figure 1. UV spectra of chlorpyrifos, benzil and 2,4-dihydroxybenzophenone

The UV spectra of 2,4-dihydroxybenzophenone and benzil derivatives are almost identical and absorb strongly near 287 nm. Less recovery of chlorpyrifos was observed in case of 2,4-dihydroxybenzophenone which has one hydroxy-keto pair that can photostabilizechlorpyrifos through ESIPT. However in case of benzil derivatives there are two such hydroxy-keto pairs which are perhaps responsible for more efficient photostabilization of chlorpyrifos. Formulations of expensive pesticides such as chlorpyrifos, having such photostabilizers as additives, may require

lower quantities during actual field applications on large scale thereby adding attractive economical benefits.

Conclusions

A systematic photostabilization study of the known and widely used insecticide, chlorpyrifos, was carried out using novel benzil derivatives under UV light. The percentage recovery of chlorpyrifos showed a significant enhancement in its photostabilization by benzil derivatives as compared to 2,4-dihydroxybenzophenone taken as a reference. It is possible to minimize generation of toxic impurities resulting from photochemical decomposition of chlorpyrifos in the fields by employing suitable photostabilizers such as benzil derivatives presented in this communication.

Acknowledgements

The Authors thank Mr. Raju D. Patil, Transpek Industries Ltd., India for help in HPLC analyses and Dr. Piyush Upadhyay, United Phosphorous Limited, India for a gift sample of chlorpyrifos. GMP thanks UGC, New Delhi, India for the award of a Research Fellowship under RFSMS Scheme.

References

[1] Zepp R.G., Cline D.M. *Environ. Sci. Technol*., 1977, **11**:359

[2] Elliott M., Farnham A.W., Janes N.F., Needham P.H., Pulman D.A. *Nature*, 1974, **248**:710

[3] Kaushik B., Dureja P. *Pesticide Sci*., 1995, **43**:333

[4] Manzoor H., Perschke H., KutscherR. *Pesticide Sci*., 1990, **28**:345

[5] Gan J., Hussain M., Perschke H.,Rathor M.N. *Chemosphere*, 1990, **21**:589

[6] Sundaram K.M.S., Curry J. *J. Environ. Sci. Health Part B*, 1996, **31**:1041

[7] Sundaram K.M.S., Curry J. *Chemosphere*, 1996, **32**:649

[8] Bootharaju M.S., Pradeep T. *Langmuir*, 2012, **28**:2671

[9] Kamel A., Byrne C., Vigo C., Ferrario J., Stafford C., Verdin G., Siegelman F., Knizner S., Hetrick J. *Water Res*., 2009, **43**:522

[10] Atwood D., Paisley-Jones C., *Pesticides Industry: Sales and Usage 2008-2012, Market Estimates*. Office of Chemical Safety and Pollution Prevention, US Environmental Protection Agency, Washington, DC 20460, 2017

[11] Barceló D. *J. Chromatography A*, 1993, **643**:117

[12] Janice E. C.; Carr Russel L., *Toxicological Sciences*, 1993, **21**:111

[13] Allender W.J., Keegan J., *Bull. Environ.Contaminat. Toxicol.,* 1991, **46**:313

[14] Barcelo D., Durand G., De Bertrand N. *Toxicol. Environ. Chem*., 1993, **38**:183

[15] (a) Hussain, M., Perschke, H. and Kutscher, R., *Pest Manag. Sci.,* 1990, **28**:345; (b) Hussain, M.; Gan, J., Perschke, H. Rather, M. N., *Chemosphere,* 1990, **21**:589

[16] Dexter, D. L., *J. Chem. Phys.,* 1953, **21:**836

[17] Kavarnos G.J., Turro N.J. *Chem. Rev*., 1986, **86**:401

[18] Leppard, D.; Hayoz, P.; Vogel, T.; Wendeborn, F., *Chimia*, 2002, **56**:216

[19] Waiblinger F., Keck J., Stein M., Fluegge A.P., Kramer H.E.A., Leppard D. *J. Phys. Chem. A*, 2000, **104**:1100

[20] Paterson M.J., Robb M.A., Blancafort L., DeBellis A.D. *J. Phys. Chem. A*, 2005, **109**:7527

[21] Deota P.T., Upadhyay P.R., Patel K.B., Mehta K.J., Varshney A.K., Mehta M.H. *Natur. Product Lett*., 2002, **16**:329

[22] Deota P.T., Upadhyay P.R., Valodkar V.B. *Natur. Product Res*., 2003, **17**:21

[23] Mosquera M., Penedo J.C., Ríos Rodríguez M.C., Rodríguez-Prieto F. *J. Phys. Chem*., 1996, **100**:5398

[24] Woessner G., Goeller G., Kollat P., Stezowski J.J., Hauser M., Klein U.K.A., Kramer H.E.A. *J. Phys. Chem.,* 1984, **88**:5544

[25] Ghiggino K.P., Scully A.D., Leaver I.H. *J. Phys. Chem.*, 1986, **90**:5089

[26] Otterstedt J. A., *J. Chem. Phys.,* 1973, **58**:5716

How to cite this manuscript: Gautam M. Patel, Hemant S. Parmar, Pradeep T. Deota. Improved Photostabilization of Chlorpyrifos Insecticide with Novel Benzil Derivatives.ChemicalMethodologies 3(4), 2019, 481-493. DOI:10.22034/chemm.2018.151723.1101.