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Separation and Detection of Quizalofop-Ethyl Herbicide by Thin-Layer Chromatography

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Abstract

Herbicides are frequently used in agriculture for control of weeds in crops. Quizalofop-ethyl is a postemergence herbicide widely used for control of grassy weeds in crops, intended for human consumption. The general population may be exposed to quizalofop-ethyl via ingestion of food or drinking water. Sometimes it is misused for suicidal poisoning. A systematic analysis of herbicides acting as poison in human body is carried out by forensic toxicologists. Their method involves screening of poison followed by its instrumental assay. Therefore a simple, rapid, sensitive and reliable thin- layer chromatographic method for detection of quizalofop-ethyl is presented. The quizalofop-ethyl contain quinoxaline ring in its structure having –N=C-CH=N --group. These react with Dragendorff`s reagent to give orange-red coloured spot in yellow background. The detection limit was found to be 10 µg per spot (20 µg/cm^2). The constituents of viscera (amino acids, peptides, proteins, etc.) do not interfere in the test.

Keywords: Herbicides; Quizalofop-ethyl; Thin-Layer Chromatography; Spray Reagent; Dragendorff`s.

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Introduction

Quizalofop-ethyl (2-[4-{6-chloro-2-quinoxalinyl} oxy] propionic acid ethyl ester) is a herbicide widely used to control grassy weeds in broad leaved crops.[1] But the World Health Organisation has classified it as moderately hazardous poison (Class II).[2] Owing to its ready availability; it is sometimes misused for acute intentional self poisoning. Such cases are referred to forensic science laboratories for detection of poison in biological materials.

Several instrumental methods[3-7] are reported in literature for isolation and quantitation of quizalofop-ethyl. Though the instrumental methods are sensitive they require elaborate instrumental assay. Therefore thin-layer chromatography (TLC) is preferred for screening the poisons, due to its simplicity and rapidity. We report Dragendorff`s reagent for detection of quizalofop-ethyl herbicide.

Materials and Methods

All chemicals used were of analytical reagent grade and quizalofop-ethyl was obtained from Dhanuka Pesticides, Gurgaon. Distilled water was used throughout. Standard solution of quizalofop-ethyl 2mg/ml was prepared in benzene.

Spray reagents: (i) Dragendorff`s reagent (a) Mix together 2 gm bismuth sub nitrate, 25 ml acetic acid and make to 100 ml with water. (b) Dissolve

40 gm potassium iodide in 100 ml water. Mix together 10 ml of (a) and 10 ml of (b) and use this as spray reagent.

(ii) Aqueous nitric acid 50% v/v.

Thin-layer Chromatography

Standard glass TLC plates (10 x 15 cm) were coated with slurry of silica gel G (Sisco Reasearch Laboratories, Mumbai) in water (1:2) to produce uniform 0.25 mm layers. These were left to dry at room temperature. Plates were activated by heating in oven at 100°C for ca. 1 hour. Before use the plates were stored in desiccators. Standard solutions of quizalofop-ethyl (1 µL, 5 µL and 10 µL) were spotted 1.5 cm from the bottom of the plate by means of a micropipette and spots were left to dry in air. Plates were then developed in a presaturated TLC chamber (development time 20 min) using two solvent systems, (I) hexane:acetone (8+2) and (II) chloroform:ether (7+3) at 25°C temperature, by ascending technique. After the mobile phase has migrated to ca. 10 cm, the plate was removed from the chamber and left to dry at room temperature. It was then sprayed uniformly with Dragendorff`s reagent followed by dil. nitric acid. Orange- red coloured spots for 5 µL and 10 µL were found in yellow background at R_F 0.55 in solvent system (I) and at R_F 0.92 in solvent system (II). The detection limit for quizalfop-ethyl was 10 µg per spot (20 µg/cm^2).

Recovery of quizalofop-ethyl from biological materials

For the semi-quantitative determination of quizalofop-ethyl, 2 mg of herbicide was added to ca. 50 gm of minced visceral tissue (stomach, intestine, liver, etc.) and kept for a day. The herbicide was then extracted with benzene as its recovery is more in benzene.[8] The solvent was evaporated at room temperature and the residue was dissolved in 1 ml ethanol. A 10 µl volume of this solution was spotted on an activated plate along with 10 µL each of standard solution containing 16.0 µg, 18.0 µg, 20.0 µg and 22.0 µg of quizalofop-ethyl. The plate was then developed as described above. The intensity of the orange- red spot produced by the visceral extract was comparable to that of the spot corresponding to 18 µg of quazalofop-ethyl (average of three experiments). Hence the recovery was ca. 90%.

Results and Discussion

The quizalofop-ethyl has a quinoxaline ring in its structure. It is heterocyclic in nature having two nitrogen at 1 and 4 positions in pyrazine ring. These are the reactive nitrogen which combines with heavy metal atom (Bi I_4) present in Dragendorff`s reagent to form ion pairs. This ion pair forms insoluble orange-red coloured complex. The colour of the spot on TLC remains stable for couple of days. The solvent system gives compact spots. The constituents of viscera (amino acids, peptides, proteins, etc.) generally co extracted with quizalofop-ethyl do not interfere with the test. Hence the proposed reagent, owing to its sensitivity can be useful for detection and semi-quantitative determination of quazalofop-ethyl in biological materials.

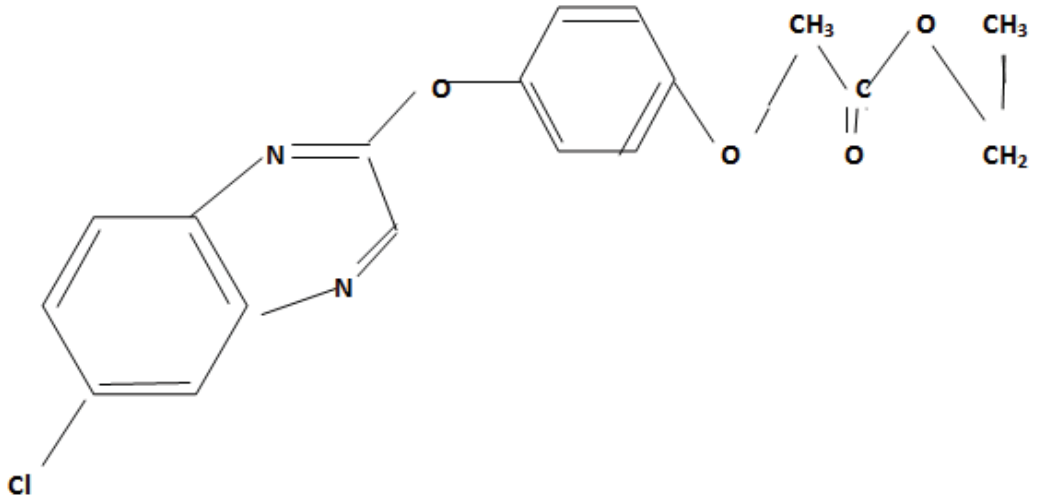

Fig. 1: Chemical structure of Quizalofop-ethyl

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