A rapid quantification method for simultaneous determination of pendimethalin and metribuzin contents in suspoemulsion formulation

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A B S T R A C T

Pendimethalin and metribuzin are combined to a suspoemulsion (SE) formulation that is treated as a pre-emergence and early post emergence herbicide. A simple reverse phase high performance liquid chromatography (RP-HPLC) method has been validated and applied for the simultaneous analysis of metribuzin and pendimethalin contents in suspoemulsion formulation. The mobile phase for the method was acetonitrile: water (65:35v/v) at a flow rate of 1.0 mL/min, and quantification was accomplished at 237 nm. Hypersil ODS column was used for the method's development and validation. Metribuzin's and pendimethalin's RTs were found to be 3.6 and 11.9 min, respectively. The limit of detection was 0.03 mg/l and 0.04 mg/l for Metribuzin and Pendimethalin respectively. The limit of quantification values was 0.09 mg/l for metribuzin and pendimethalin. The linearity of proposed method was investigated in the range of 2.51 to 100.54 mg/l (r^2 = 99997) and 0.25 to 9.80 mg/l (r^2 = 99997) for Pendimethalin and Metribuzin respectively. The percentage recovery found to be in range from 99.8 to 100.1 % and 99.8 to 100.3 for Pendimethalin and Metribuzin respectively. The percentage RSD values for intraday precision study and inter-day precision study were < 2.22 and < 1.57 for Metribuzin and Pendimethalin respectively as per modified Horwitz equation as requirements by SANCO. The method's performance was validated in terms of selectivity, specificity, precision, linearity, accuracy, LOD, LOQ, and robustness, according to SANCO guidelines. In this study, for the first time, an easy and speedy reverse phase high performance liquid chromatography approach for the simultaneous analysis of pendimethalin and metribuzin in SE formulation is presented.

Introduction

Insecticides, herbicides, rodenticides, and fungicides are one of the most applied pesticides. Around 860 active chemical constituents of pesticides have been formulated and are commercially sold [1–3].

Pendimethalin and Metribuzin are herbicides. both are commonly used to kill unwanted plants [4,5]. Selective herbicides are used to kill specific targets of unwanted plants, while leaving the desired crop relatively without harmed. Some pesticides work by inhibiting weed development, and they're frequently synthetic versions of natural plant hormones. Herbicides are categorised according to their mechanism of action, activity, and chemical family [6–7].

Metribuzin is a kind of herbicide that obstructs photosynthesis in vulnerable plants by binding to a protein in the photosystem II complex, which sets off a cascade of events in which highly reactive free radicals attack and oxidise the plant's lipids and proteins. Metribuzin used as a pre and post emergence in crops. It works by inhibiting photosynthesis

and widely used in agriculture. It is chemically known as 4-Amino-6-*tert*-butyl-3-methylthio-1,2,4-triazin-5(4H)-one [8–13]. (Fig. 1).

Pendimethalin is applied both pre and post emergence to suppress some broadleaf weeds and annual grasses. The roots and leaves absorb pendimethalin. Plants that have been affected die soon after germination or after emerging from the soil. It is chemically known as N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine, appears as orange – yellow crystals. Slightly soluble in water and freely soluble in acetone, acetonitrile, *n*-hexane methanol and xylene. Pendimethalin is utilized on fruits, vegetables and tobacco. [14–15].

The main objective of the current development is to make a reverse phase high performance liquid chromatography technique for the combination of pendimethalin & metribuzin in the suspoemulsion (SE). A review of the literature shows that many analytical techniques have been established for the detection of pendimethalin in soil, garlic samples, and rice samples using GC–MS, LC-MS, and HPLC [16–18]. Similar to this, numerous approaches, including spectrophotometric [19],
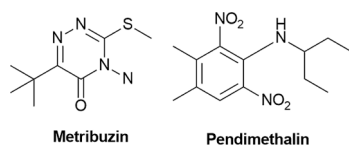
Fig. 1. Chemical structures of pendimethalin & metribuzin.

Chronopotentiometry using thin film mercury electrode [20], and HPLC [21–22], have been published for the quantification of metribuzin in both single and mixed formulations. There is no analytical technique is proposed that is premised on reserved-phase HPLC has been published for the combined analysis of both explored analytes (Pendimethalin and Metribuzin) in the suspoemulsion formulation, according to a review of the literature. However, the method discussed above has a number of drawbacks, including practical difficulties when analysing substances, the presence of intervention related with slushy samples, which might also contribute to the generation of bad results, becoming time-consuming and less responsive, lacking a bit of selectivity, and requiring the analysts to perform multiple sample analyses. The objective of creating a quick, easy, and repeatable analytical approach for the concurrently analysis of metribuzin and pendimethalin content in an agrochemical combination is therefore exceedingly difficult. The suggested method has higher selectivity, requires less time for analysis, and is more accurate and precise than the methods that have been described. Furthermore, it can be used to check the quality of metribuzin and pendimethalin when they are combined with suspoemulsion, emulsifiable concentrate, and zeon concentrate in a formulation (ZC).

Materials and methods

Reagents and chemicals

HPLC grade water and acetonitrile were purchased from Rankem. Pendimethalin and Metribuzin standard were obtained from UPL Limited. Pendimethalin Standard was used with purity of 97.36 % (Make: UPL, Lot No. 118). Metribuzin Standard was used with purity of 97.0 % (Make: UPL, Lot No.105). SE formulation of Metribuzin (3.5 %) and Pendimethalin (35 %) was obtained from BR Agrotech Limited, R&D, Panoli.

Instrument and chromatographic conditions

A calibrated HPLC system was used to determine the formulation's pendimethalin and metribuzin content. Shimadzu, Prominence-i LC-2030 at 237 nm with mobile phase Acetonitrile: Water (65:35 v/v) in isocratic mode. Hypersil ODS (250 × 4.6 mm, 5μ) column was used at 55 °C temperature with injection volume 10 μl. The run time was set to 15 min, and the flow rate was set to 1.0 mL/min.

Preparation of mobile phase and diluent

Acetonitrile of HPLC grade: Water (65:35 v/v); thoroughly mixed; sonicated to remove gas for 15 min. Acetonitrile was used as diluent for preparation of stock and sample.

Preparation of stock solutions

Pendimethalin standard stock solution

A volumetric flask of 250.0 mL was clean, dry, and correctly weighed to contain 125.67 mg of pendimethalin standard. After that, 100 mL of diluent was added, and the standard has been sonicated to dissolve. More dilution was added up to the mark with diluent and thoroughly mixed.

Metribuzin standard stock solution

A volumetric flask with a capacity of 250.0 mL was clean, dry, and correctly weighed to obtain 12.25 mg of metribuzin standard. Then, 100 mL of diluent was added, and the mixture was sonicated to dissolve it. Added more diluent until the desired level was reached, then mixed thoroughly.

Preparation of standard stock solution (Pendimethalin and Metribuzin)

Transferred 10.0 mL of pendimethalin standard stock solution and 10.0 mL of metribuzin standard stock solution in to a 100 mL of volumetric flask, brought the level up to the mark with diluent, and thoroughly mixed.

Preparation of sample solution

Approximately 270.10 mg of the SE sample, which contains pendimethalin (35 %), metribuzin (3.5 %), and sample, were carefully weighed before being placed into a dry, clean 100 mL volumetric flask. Sonicated to dissolve after adding around 70 mL of diluent. diluted and adjusted to the proper consistency. By adding diluent, further diluted this solution by 5 mL to 100 mL.

Methodology for evaluation (Validation)

System appropriateness

System appropriateness evaluations have become an important aspect of the chromatographic process, as well as they have been used to ensure the reproducibility of the chromatograms. The effectiveness of the standard solution was evaluated by repeatedly monitoring a set of system suitability measurement methods. A blank was injected initially, then six repetitions of a standard pendimethalin and metribuzin solution were added to assess the appropriateness of the system. The system's suitability for the suggested approach is assessed using the metrics retention time, theoretical plates, tailing factor, % RSD, resolution, and capacity factor.

Specificity. A specificity experiment was conducted to investigate the disruptions of excipients that are present in formulation. This study compared the chromatograms obtained from the analysis of the sample and standard as well as blank solution and the excipients to determine the specificity of the two combined pesticides (Pendimethalin and Metribuzin).

Linearity. The method's linearity was tested by testing of 10 various concentrations of Pendimethalin and Metribuzin in standard's solution. A calibration curve was plotted between the concentration and peak area, which ranged from 2.51 to 100.54 mg/l. for Pendimethalin and 0.25 to 9.80 mg/l. for Metribuzin.

Precision. Intra-day precision and Inter-day precision were measured in the precision study by comparing six solutions of one batch of a mixed pesticides formulation to every referencing standard solution on that day and on different day utilizing another instrument. The modified Horwitz equation was used to calculate the %RSD for the active component content in among the two sets of data.

Accuracy. The accuracy was determined by using the standard addition method by calculating the proportion of metribuzin and pendimethalin recovery values. The placebo of agrochemical formulation was analysed into the chromatographic system with known concentration of standard solutions of Metribuzin and Pendimethalin at 50 percent, 100 percent, and 150 percent. Each Standard Solution was made in triplicate and analysed.
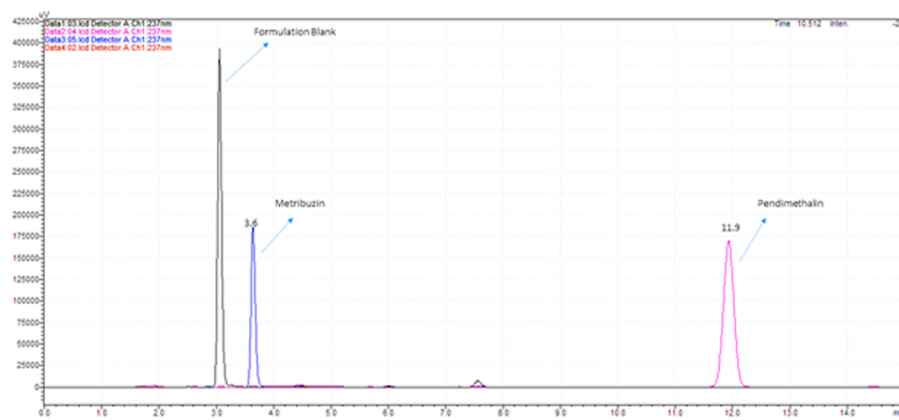
Fig. 2. Diluent, formulation blank, standard of Metribuzin and Pendimethalin.

Robustness. Various parameters of such recently developed method have been intentionally changed to establish robustness. The flow rate has been significant increase from 0.9 to 1.1 mL/min, the organic mobile phase (Acetonitrile) was changed from 63 to 67 percent, and the column oven's temperature had been modified. from 53 to 57 °C.

Limit of detection and quantification. Both the compound's (Pendimethalin and Metribuzin) limit of detection and limit of quantification results were analysed, when the signal to noise ratio were 3: 1 and 1: 10, respectively.

Solution stability. The sample and standard solutions were injected at regular intervals of 6 h to ensure solution stability.

RP-HPLC method's improvement and optimization of chromatographic conditions

During the optimization cycle, diverse analytical columns have been tested, including Inertsil C-8 (250 × 4.6 mm, 5μ), Inertsil C-18 (250 × 4.6 mm, 5μ), Inertsil pH-3 (250 × 4.6 mm, 5μ), Hypersil ODS (250 × 4.6 mm, 5μ) columns. Finally satisfactory separation was obtained on Hypersil ODS (250 × 4.6 mm, 5μ) column. When acetonitrile and methanol have been studied separately and concurrently as organic modifiers, acetonitrile was determined to be more appropriate since it improved the investigation's ability to separate pendimethalin and metribuzin. To accomplish a correct separation of the given analysis within a suitable run time, the isocratic technique of eluted using varying proportions of organic to aqueous phase have been Completed. The optimal flow rate was determined after examining several flow rates: 1.0 mL/min. At 237 nm, UV-Detection was used to quantify the sample. The column was set to a temperature of 55° C. Pendimethalin and metribuzin had great peak shapes and resolution due to the modified method. Metribuzin and pendimethalin retention times were observed at 3.6 and 11.9 min, respectively. All of the peaks were clearly defined and free of tailing, fronting, and widening at the experimental chromatographic conditions mentioned above.

Results

The goal of method validation would have been to ensure that how the methodology fulfilled the requirements of the SANCO [23] guidelines for its specified use. The described method has been thoroughly validated in condition of specificity, selectivity, precision, limit of detection, linearity, limit of quantification, accuracy, robustness, and solution stability.
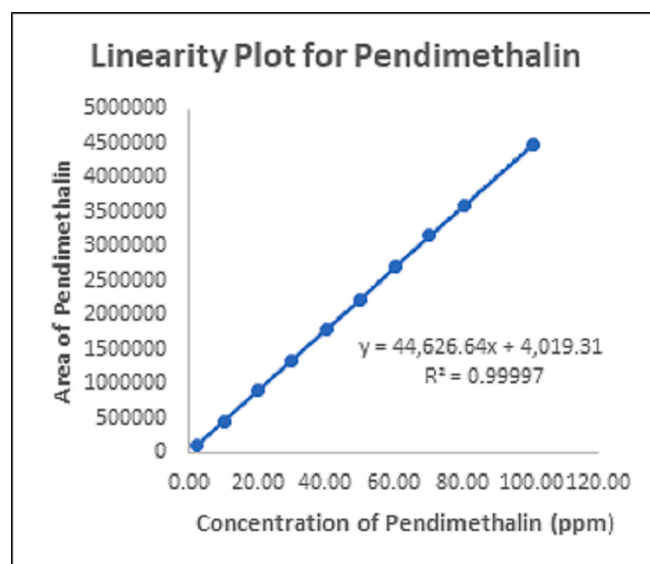

Fig. 3. Linearity curve for the Pendimethalin.

System appropriateness

The retention times for Metribuzin and Pendimethalin were observed on 3.6 and 11.9 min respectively; with tailing factors of 1.128 and 0.997 respectively; 9113 and 18,804 theoretical plates respectively; % RSD of peak areas of 0.48 and 0.16 respectively. While evaluating system appropriateness, resolution and capacity factor were found 32.97 and 2.27 respectively. The results meet the requirements for acceptance [23–25].

Specificity

The diluent blank and matrix (Placebo) had no significant interference at the retention time of metribuzin (3.6 min) and pendimethalin (11.9 min) standards, as shown in Fig. 2, showing the specificity of the proposed approach. (Fig. 2).

Linearity

The calibration curves' correlation coefficients were determined to be 0.99997 for Pendimethalin and 0.99997 for Metribuzin. The slopes of Metribuzin and Pendimethalin, with intercepts of 66.46 and 4019.31,
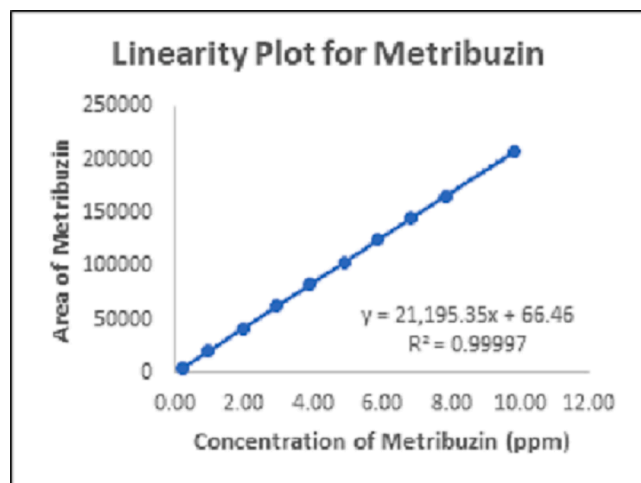
Fig. 4. Linearity curve for the Metribuzin.

were determined to be 2195.36 and 44626.4, respectively. Fig. 3., 4. and 5. show a summary of the findings. Correlation coefficients must be higher than or equivalent to 0.99 to meet the acceptance criteria. (Figs. 3-5).

Precision

Results of intra-day and inter-day precision studies are mentioned in Table 1. As per the determined results, Method was found precise for the combination of agrochemical formulation.

Accuracy

The % of recover amount at every stage was calculated using the peak area at every stage. Table 2 demonstrates the suggested methodology for accuracy data. (Table 2) For Metribuzin, the range of the acceptance criteria for recovery is 90 % to 110 %. For Pendimethalin, the acceptance percentage for recovery ranges from 97 % to 103 %.

Robustness

Table 3 summarizes the findings after intentionally changing the column flow rate from 0.9 to 1.1 mL/min, the organic mobile phase

(acetonitrile) from 63 to 67 percent, and the column oven's temperature from 53 to 57C.The percent Relative standard deviation for all tests performed and modified criteria were<2.0, implying the robustness of the proposed analytical technique. There is no significant difference noticed by intended variations, that confirmed the analytical method is robust. (Table 3).

Limit of detection and quantification

The limits of detection and limit of quantification indicate the quality of the method's sensitivity. Metribuzin's limit of detection and limit of quantification were determined 0.03 mg/l and 0.09 mg/l respectively. whereas Pendimethalin's limit of detection and limit of quantification were determined 0.04 mg/l and 0.09 mg/l respectively.

Solution stability

For solution stability, the sample and standard solutions were injected at regular time intervals. Metribuzin and Pendimethalin sample and standard solutions are stable at room temperature for up to 24 h. (Table 4).

Discussion

Additional benefits are provided by the proposed method such as single, rapid, and reproducible RP-HPLC method to determine of simultaneous analysis of metribuzin and pendimethalin content in formulation combination as well as individual technical product. There is no RP-HPLC method reported for simultaneous analysis of

Table 1
Results of precision studies of SE formulation.

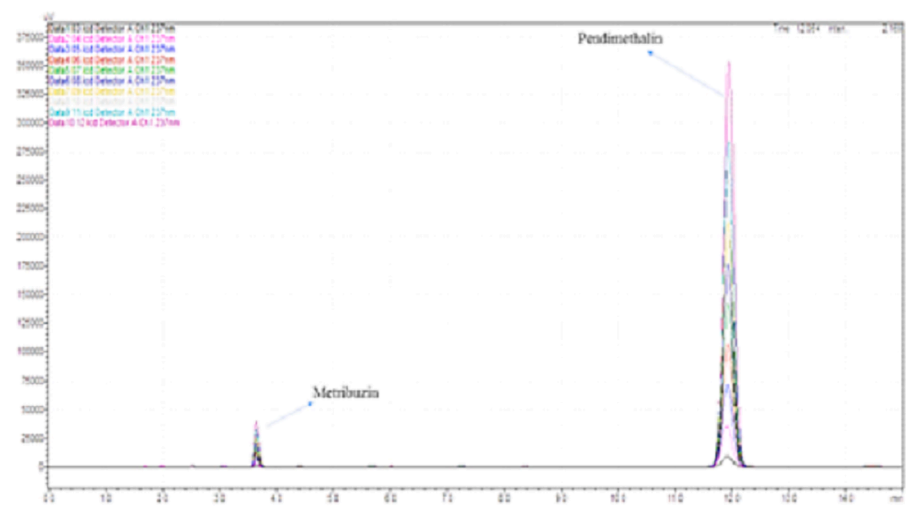| Level	Pendimethalin 35 %		Metribuzin 3.5 %	
Results	**Intra-day**	**Inter-day**	**Intra-day**	**Inter-day**
Average Active Ingredient (A.I.) Content (%, w/w)	35.10	35.11	3.58	3.60
%RSD	0.18	0.17	0.22	0.23
STD Dev	0.06	0.06	0.01	0.01
% Acceptance Criteria [23]	1.57		2.22	

Fig. 5. Linearity chromatograms of metribuzin and Pendimethalin.

Table 2
Result of accuracy studies of metribuzin and pendimethalin in SE formulation.

Recovery Level	Set No.	Recovery Result of Metribuzin					Recovery Result of Pendimethalin				
		Amount Added (mg)	Amount Recovered (mg)	% Recovery	% Average	% Acceptance Criteria [23]	Amount Added (mg)	Amount Recovered (mg)	% Recovery	% Average	%Acceptance Criteria [23]
50 %	1	4.78	4.71	98.6	99.3 ±	90 % to 110 %	44.12	43.58	98.8	100.1 ±	97 % to 103 %
50 %	2	4.70	4.68	99.6	0.6		43.23	43.31	100.2	1.2	
50 %	3	4.82	4.81	99.7			43.88	44.39	101.2		
100 %	1	9.90	9.89	99.9	99.8 ±		96.65	96.46	99.8	99.8 ±	
100 %	2	10.12	10.00	98.8	1.0		97.89	97.87	100.0	0.2	
100 %	3	9.95	10.03	100.8			98.42	97.98	99.6		
150 %	1	16.07	16.10	100.2	100.3 ±		169.00	168.80	99.9	100.1 ±	
150 %	2	15.98	16.09	100.7	0.3		168.88	168.66	99.9	0.4	
150 %	3	16.23	16.25	100.1			168.99	169.97	100.6		

Table 3
Result of the robustness studies of Metribuzin and Pendimethalin in SE formulation.

Set No.	Metribuzin Mean Area of Std.	Mean Area of Sample	A.I. Content of Metribuzin (%, w/w)	Pendimethalin Mean Area of Std.	Mean Area of Sample	A.I. Content of Metribuzin (%, w/w)
Set-1 (Method Precision)	102,232	104,168	3.59	2,204,302	2,138,060	35.15
Set-1 (0.9 mL/min Flow rate)	107,314	116,690	3.59	2,367,025	2,444,921	35.15
Set-2 (1.1 mL/min Flow rate)	107,079	115,870	3.58	2,362,184	2,431,612	35.03
Set-3 (63 % Organic in Mobile Phase)	108,060	118,118	3.61	2,380,828	2,474,257	35.36
Set-4 (67 % Organic in Mobile Phase)	107,540	117,365	3.61	2,371,230	2,459,303	35.29
Set-5 (53 °C Column Temperature)	109,178	119,538	3.62	2,395,712	2,512,920	35.69
Set-6 (57 °C Column Temperature)	108,890	118,608	3.6	2,391,868	2,488,836	35.41
		Average	3.6		Average	35.32
		STD Dev	0.02		STD Dev	0.23
		%RSD	0.42		% RSD	0.65

Table 4
Study of solution stability of Metribuzin and Pendimethalin.

Solution Stability				
Hrs	Standard Area			
	Metribuzin	%Area Variation of Metribuzin	Pendimethalin	%Area Variation of Pendimethalin
Initial	102,134	–	2,201,777	–
After 06 Hrs	103,025	0.87	2,214,396	0.57
After 12 Hrs	102,918	0.77	2,219,083	0.01
After 18 Hrs	103,841	1.67	2,246,416	2.03
After 24 Hrs	104,799	2.61	2,256,212	2.47
Average	103,343	1.48	2,227,577	1.27

pendimethalin and metribuzin content to determine with a single method. More selectivity, quicker analytical time, higher accuracy, and precision are all advantages over the reported methods. Furthermore, it can be used to determine the quality of Metribuzin and Pendimethalin in their formulation combination and individual technical product also. J. Shah et. al have reported partial validation in HPLC. The limit of detection and limit of quantification were reported 0.059 and 0.17 mg/l respectively [17], where in proposed method LOD and LOQ is 0.04 and 0.10 mg/l respectively for Pendimethalin. HPLC method was also reported with run time of 55.0 min and retention time of 29 min [18], where proposed method offers run time 15.0 min and retention time 11.9 min for pendimethalin. Similarly, M. Mehdizadeh has partial validation for metribuzin, with retention time of 9.5 min [21], where in

proposed method have 3.6 min. C. Swarna, K. Babau reported two methods for metribuzin with run time 8.0 min and 10 min. However, LOD and LOQ were reported 0.137 mg/l and 0.428 mg/l respectively whereas the proposed method LOD and LOQ for metribuzin are 0.03 and 0.09 mg/l. In Another method was also reported by Cwarna, comparison of both method, proposed method is highly suitable for analysis of individual and mixture [26–27]. The proposed analytical method is beneficial to previously reported method for single content also. Thus, Method will be highly utilized to industries for save time with extraordinary accuracy, precision, and recovery.

Conclusions

For the simultaneous analysis of Pendimethalin and Metribuzin in an agrochemical combination from SE formulation, a easy, accurate, and exact approach was developed. The developed and verified RP-HPLC method enabled for the easy and quick quantification of Pendimethalin and Metribuzin in a combination dose of agrochemical formulation. All validation parameters have been confirmed to be in the limits of the SANCO recommendations. The suggested method was proved to be simple, accurate, and specific for the agrochemical of concern, regardless of the presence of excipients, and the short retention durations allow the analyst to analyse a large number of samples in a less amount of time. The developed method was overserved to be simple, precise, and accurate. As a result, the developed method can be successfully used for routine analysis of combined dosage from a variety of sources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Contributions of authors

Mr. Rakesh Singh carried out laboratory experiments and wrote the manuscript. Dr. Bhavin Dhaduk evaluated all of the experiment's data for agreement with the guidelines. Dr. Jayesh Dhalani planned the studies, interpreted the chromatograms, created figures and tables, and supervised the entire process. The manuscript was reviewed by all of the writers.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rechem.2023.100779.

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