Investigation of Heat-Induced Chemical Changes in Black-Eyed Beans (*Phaseolus vulgaris*) with and without Dichlorvos (Sniper) Treatment Using Gas Chromatography-Mass Spectrometry (GC-MS

Original Research Article

Abstract

Aim: This research is to investigate the effect of heat on the chemical profile of black-eyed beans (*Phaseolus vulgaris*) treated under different conditions. Sample A (used as received from the farmer without further treatment) served as a control to compare with Samples B and C, which were treated with Dichlorvos (Sniper) using Gas Chromatography-Mass Spectrometry (GC-MS).

Study Design: This study prepared three black-eyed bean samples: untreated (Sample A), Dichlorvos-treated with black water discarded (Sample B), and Dichlorvos-treated without black water discarded (Sample C). Each sample was air-dried, washed, and cooked. Hexane extracts were analyzed using GC-MS to investigate the effect of heat on the chemical profile of the samples and the risks associated with the consumption of Dichlorvos (Sniper)-treated beans.

Place and duration of study: The study was conducted at University of Africa, Toru-Orua, Nigeria, from February to August, 2024.

Method: Three black-eyed bean samples were prepared for analysis. Sample A (Untreated)**:** 1000 g of raw beans were air-dried for 14 days, washed twice with 100 ml distilled water and cooked to dryness at 100°C for 60 minutes. The samples were air-dried again, pulverized, and stored for analysis. Sample B (Dichlorvos-treated, black water discarded)**:** 1000 g of raw beans were treated with 5 ml Dichlorvos (Sniper), shaken gently for even distribution, air-dried for 14 days, washed twice with 100 ml distilled water, parboiled for 10 minutes and the black water discarded. The samples were cooked to dryness at 100°C for 50 minutes, air-dried, pulverized, and stored for analysis. Sample C (Dichlorvos-Treated)**:** 1000 g of raw beans were treated with 5 ml Dichlorvos, agitated and air-dried for 14 days. The samples were washed twice with 100 ml distilled water and cooked to dryness at 100 °C for 60 minutes. The samples were air-dried, pulverized, and stored for analysis.

Results: GC-MS analysis identified 43, 51, and 31 compounds in Samples A, B, and C, respectively. Natural compounds included Prenol, Benzaldehyde, 2-methyl, Benzeneacetaldehyde, and o-Cymene, which contribute to beans' metabolism, aroma, and defense. Sample A (untreated) contained harmful contaminants such as 2-Propenoic acid, 2-propenyl ester (92.6%), a skin and respiratory irritant; 1,3-Butadiene, 2-fluoro (97.0%), a carcinogen; Benzene (81.9%), a known carcinogen; and Toluene

(80.5%), which poses neurological and respiratory risks. Sample B (Dichlorvos-treated, black water discarded) had contaminants like Isobutane (92.9%), an asphyxiant; Cycloheptane (76.8%), which affects the central nervous system; and Benzaldehyde, 2-methyl (70.5%), a skin irritant. Sample C (Dichlorvos-treated, black water retained) showed lower contaminant levels, indicating reduced absorption or degradation of certain toxic chemicals during processing. The detection of harmful chemicals in Sample A highlights potential contamination from pesticides, poor agricultural practices, or environmental pollutants. The persistence of toxic chemicals in all samples suggests that heat treatment causes thermal decomposition of pesticides into stable, harmful byproducts, which are absorbed into the bean matrix.

These findings emphasize the health risks associated with pesticide residues and the need for stringent monitoring, regulation, and control at every stage of bean production, handling, and storage.

Keywords: *GC-MS, Beans, dichlorvos, natural components, contaminants, health implication*

1. INTRODUCTION

Legumes, members of the *Leguminosae* family, are classified into three subfamilies: *Papilionoideae*, *Caesalpinioideae*, and *Mimosoideae*. Among these, the subfamily *Papilionoideae* predominantly encompasses edible legume crops such as soybean, chickpea, bean, and pea [1, 2]. Historically, legumes have served as vital sources of nutritional security, particularly during periods of food scarcity, owing to their remarkable durability when properly dried and stored [3, 4]. Black-eyed beans (*Phaseolus vulgaris*), illustrated in Figure 1, are widely recognized for their ease of cultivation and resilience. Furthermore, they are esteemed as an excellent dietary source of protein, contributing significantly to food systems and nutritional health [5-7].

Fig. 1: Freshly harvested black eyed beans

Common beans, often referred to as the "poor man's meat" in Eastern Africa, serve as a critical source of protein for the majority of households. They play a significant role in human nutrition, food security, and income generation for small-scale farmers [8-9]. In many regions, beans are grown seasonally, and after harvesting, they are stored under safe conditions to maintain their quality throughout the season. Proper storage ensures a consistent food supply, availability of seeds for subsequent planting seasons, and surplus produce for income generation [10-11].

The quality of stored beans is influenced by several factors, including initial grain condition, storage conditions, moisture content, and susceptibility to insect pests, bacterial, and fungal infestations. Among these, insect pests pose the most significant threat to stored beans, impacting both their quality and quantity [12-13]. Among the various bruchid species, the common bean weevil (Acanthoscelides obtectus Say) and Zabrotes subfasciatus Boh. are particularly notorious for causing substantial post-harvest damage. Their presence in stored beans results in a considerable reduction in both the quality and quantity of the produce [14-15].

Chemical control methods, including the use of pesticides, are a key component of Integrated Pest Management (IPM) programs. These methods aim to reduce pest populations (insects, pathogens, rodents, etc.) to levels that do not adversely affect crop yield and quality [16]. The modern era of pesticide usage began with the discovery of highly effective compounds such as dichlorodiphenyltrichloroethylene (DDT) and organophosphate (OP) insecticides [17].

Dichlorvos (2,2-dichlorovinyldimethylphosphate), an organophosphate pesticide was first introduced in 1961 [18]. It has the molecular formula, $C_4H_7Cl_2O_4P$ and molecular weight, 220.98 g/mol. Dichlorvos has a boiling point of 140 °C and a vapor pressure of 1.6 Pa at 20°C [19].

Dichlorvos is categorized as a highly hazardous (Class Ib) chemical [20]. It is a volatile compound, and exposure to it can result in acute or chronic toxicity. Inhalation is the most common route of acute toxicity, with symptoms primarily linked to cholinesterase inhibition [21]. Prolonged exposure to dichlorvos may lead to fatal outcomes. Organophosphates, including dichlorvos, act by inhibiting acetylcholinesterase – an enzyme essential for breaking down acetylcholine. In mammals, dichlorvos is primarily metabolized by esterases into dimethyl phosphate and dichloroacetaldehyde [19].

Although no human deaths have been directly attributed to inhalation of dichlorvos, Okoroiwu and Iwara [21] documented the case of a woman who died a day after ingesting dichlorvos. Another reported case involved a 19-month-old girl who succumbed after consuming a cake-like bait containing dichlorvos. In addition, two pesticide workers in Costa Rica reportedly died after spilling a dichlorvos-containing insecticide on their skin and failing to wash it off adequately [21].

In a study involving rats exposed to air containing high concentrations of dichlorvos (up to 34 ppm), all the animals died within three days [22]. Zhang and colleagues [23] reported that acute dichlorvos poisoning induces hemorheological abnormalities in rabbits through oxidative stress mechanisms. Aquatic studies have shown LC50 values ranging from 0.2 – 12 mg/L for freshwater and estuarine fish, indicating significant toxicity to aquatic life [24].

Respiratory irritation following dichlorvos exposure was reported in a study involving children [25]. This study highlighted a strong correlation between acute respiratory symptoms and dichlorvos exposure; however, the authors could not entirely rule out the potential irritant effects of the solvents used to disperse dichlorvos. An animal study investigating the acute toxic effects of inhaled dichlorvos vapor on respiratory mechanisms in guinea pigs revealed a significant decrease in respiratory frequency and a significant increase in tidal volume in animals treated with 35 mg/mL and 75 mg/mL concentrations [26]. A histological study on the lungs of rats exposed to dichlorvos demonstrated an extension of basal-associated lymphoid tissue (BALT) in rats exposed for one, four, and five weeks [27]. A study examining the effects of dichlorvos treatment on butyrylcholinesterase (BuChE) activity and lipid metabolism in rats reported a significant decrease in BuChE activity in both sexes of the rats. Furthermore, the study observed a significant increase in triglyceride levels (60–600 %) and total cholesterol (35–75%) [28].

Certainly, there is a plethora of reports on the toxic effects of dichlorvos on living organisms, but there is a limited knowledge on the effect of heat on the chemical profile of dichlorvos pesticide preserved crops. Therefore, this research aims to investigate the effect of heat on the chemical profile of black-eyed beans (*Phaseolus vulgaris*) treated under different conditions. Sample A (used as received from the farmer without further treatment) served as a control to compare with Samples B and C, which were treated with Dichlorvos (Sniper) using Gas Chromatography-Mass Spectrometry (GC-MS). This study aims to provide a comprehensive understanding of the public health and food safety risks associated with the consumption of Dichlorvos (Sniper)-treated beans. The findings will offer critical insights to stakeholders, including consumers and agricultural producers, helping to enhance the safety and quality of bean production and consumption.

2. MATERIALS AND METHODS

2.1 Chemicals and Reagents

Analytical grade chemicals, sourced from BDH and Labtech Chemicals, were utilized in this study without further purification.

2.2 Plant Collection and Identification

Freshly harvested raw black-eyed beans (*Phaseolus vulgaris*) were procured from Kogi, located in the Middle Belt of Nigeria. The plant samples were properly identified and confirmed at the Biological Sciences Department of the University of Africa, Toru-Orua, Nigeria.

2.3 Samples Preparations

2.3.1 Untreated (As Received From the Farm) Black-Eyed Beans Samples

1000 g of raw black-eyed bean seeds (as received from the farm) were weighed and air-dried for 14 days. The air-dried beans were washed twice with 100 ml distilled water, and cooked to dryness for 60 minutes at 100 °C. The beans were allowed to cool and air-dried for another 14 days, and pulverized with an electric blender, and stored in a 1.5 Kg reagent bottle, labeled Sample A.

2.3.2 Dichlovos (Sniper Pesticide)-Treated Black Water Discarded Beans Samples

1000 g of raw black-eyed bean seeds were weighed and transferred into a 1.5 Kg reagent bottle. 5 ml of Dichlorvos (Sniper insecticide) was sprinkled on the beans and manually agitated for 5 minutes and air-dried for 14 days. The beans were washed twice with 100 ml distilled water and parboiled for 10 minutes. The black water was discarded and 300 ml hot distilled water was added and further cooked to dryness for 50 minutes at 100 ^{o}C. The beans were allowed to cool and air-dried for 14 days, and pulverized with an electric blender and stored in a clean 1.5 Kg reagent bottle, labeled Sample B.

2.3.3 Dichlovos-Treated Beans Samples

1000 g of raw black-eyed bean seeds were weighed and transferred into a 1.5 Kg reagent bottle. 5 ml of Dichlorvos (Sniper insecticide) was sprinkled on the beans and manually agitated for 5 minutes and air-dried for 14 days. The Sniper-treated air-dried beans were washed twice with 100 ml distilled water and cooked to dryness for 60 minutes at 100 ^{o}C. The beans were allowed to cool and air-dried for 14 days, and pulverized with an electric blender and stored in a clean 1.5 Kg reagent bottle, labeled Sample C.

2.4 Gas Chromatography-Mass Spectroscopy (GC-MS) Analysis

GC-MS analyses of hexane extracts of the three samples (A, B, C) were performed using an Agilent 6890 gas chromatograph (GC) coupled with an Agilent 5973N mass spectrometer (MS). The system was equipped with an Agilent 7683 Series Automatic liquid sampler for automated sample introduction. Chromatographic separation was achieved using a META X5 fused silica capillary column (30 m × 0.25 mm internal diameter, 0.25 µm film thickness) with a maximum temperature of 325 °C.

The GC oven temperature program started at 70 °C, held for 2 minutes, and increased to 300 °C at a rate of 20 °C/min. Ultra-high-purity helium (99.99 %) was used as the carrier gas at a flow rate of 1.0 mL/min. A 1 µL sample volume was injected in split mode with a split ratio of 20:1. The injection port, transfer line, and ion source were maintained at 280 °C, while the source and quadrupole temperatures were set at 230 °C and 150 °C, respectively. Mass spectra were acquired over a scan range of 50 to 550 amu with electron ionization energy of 70 eV, and the electron multiplier voltage was autotuned.

2.5 Chemical Compounds Identification

Chemical compounds in the extracts were identified based on their retention times and by comparing the corresponding mass spectra against the NIST library (version 2014), which includes over 590,000 spectral patterns. Advanced computer algorithms facilitated the identification of molecular weights, molecular formulas, chemical structures, and fragmentation patterns. This method ensured precise characterization of the chemical constituents in the palm oil samples.

2.5 Statistical Analysis

The data obtained from Gas Chromatography-Mass Spectrometry (GC-MS) analyses were analyzed using one-way analysis of variance (ANOVA), SPSS version 21.0. All analyses were conducted in triplicate, and results are presented as mean values ± standard deviation.

3. RESULTS

The results of the study are presented in Tables 1–3, which detail the findings from the GC-MS analyses. Visual representations of the results are provided in Figures 2–7. These analyses offer comprehensive insights into the chemical profile of the three *Phaseolus vulgaris* (bean) samples A, B, and C.

Table 1: GC-MS analysis of chemical profile of unadulterated cooked black-eyed beans powder (sample A)

S/N	Retention Time (min)	Bioactive compound	Probability percentage (%)	Molecular formula (MF)	Molecular weight (MW)
1.	1.270	2-Propenoic acid, 2-propenyl ester	92.6	$C_6H_8O_2$	112
2.	1.333	1,3-Butadiene, 2-fluoro	97.0	C_4H_5F	72
3.	1.409	Oxirane, propyl	96.8	$C_5H_{10}O$	86
4.	1.429	3-Penten-2-ol	92.2	$C_5H_{10}O$	86
5.	1.468	Prenol	90.0	$C_5H_{10}O$	86
6.	1.577	2-Pentyn-1-ol	87.5	C_5H_8O	84
7.	1.774	Benzene	81.9	C_6H_6	78
8.	1.947	1,5-Hexadiyne	89.2	C_6H_6	78
9.	2.126	4-Pentynoic acid	97.7	$C_5H_6O_2$	98
10.	2.334	1-Pentene, 3,3-dimethyl	49.5	C_7H_{14}	98
11.	2.395	Cycloheptane	76.8	C_7H_{14}	98
12.	3.466	Cyclooctane	63.7	C_8H_{16}	112
13.	3.611	1,3-Cyclopentadiene, 5-(1-methylethylidene)-	82.8	C_8H_{10}	106

14.	3.702	Bicyclo[2.1.1]hex-2-ene, 2-ethenyl	83.1	C_8H_{10}	106
15.	3.748	Toluene	80.5	C_7H_8	92
16.	3.779	Cyclopropane, 1-methyl-2-pentyl	52.0	C_9H_{18}	126
17.	3.874	o-Xylene	65.8	C_8H_{10}	106
18.	3.897	Bicyclo[2.1.1]hex-2-ene, 2-ethenyl	83.1	C_8H_{10}	106
19.	3.990	Cyclohexane, 1,2,3-trimethyl	77.8	C_9H_{18}	126
20.	4.067	Pentalene, octahydro-1-methyl	77.1	C_9H_{16}	124
21.	4.121	Cyclohexanone, 2-ethyl	90.1	$C_8H_{14}O$	126
22.	4.183	4-Methyl-1,3-heptadiene	56.8	C_8H_{14}	110
23.	4.248	(Z)-4-Decen-1-ol, trifluoroacetate	67.4	$C_{12}H_{19}F_3O_2$	252
24.	4.275	Benzeneacetaldehyde	88.9	C_8H_8O	120
25.	4.334	Benzene, 1-ethyl-2-methyl	63.3	C_9H_{12}	120
26.	4.400	2-Nitro-1-phenyl-ethano	91.3	$C_8H_9NO_3$	167
27.	4.451	2,3-Heptadien-5-yne, 2,4-dimethy	76.0	C_9H_{12}	120
28.	4.471	3-Hexene, 3-ethyl-2,5-dimethyl	91.2	$C_{10}H_{20}$	140
29.	4.554	Benzaldehyde, 2-methyl	70.5	C_8H_8O	120
30.	4.639	2-Piperidinone, N-[4-bromo-N-butyl]	82.0	$C_9H_{16}BrNO$	233
31.	4.666	Decane, 4-methyl	62.3	$C_{11}H_{24}$	156
32.	4.697	o-Cymene	61.8	$C_{10}H_{14}$	134

33.	4.724	Benzene, 1,2,4-trimethyl	65.7	C_9H_{12}	120
34.	4.763	Cyclohexane, butyl	82.7	$C_{10}H_{20}$	140
35.	4.853	Decane, 5-methyl	85.2	$C_{11}H_{24}$	156
36.	4.874	Benzene, 1-methyl-3-propy	70.4	$C_{10}H_{14}$	134
37.	4.904	Benzene, 1-ethyl-3,5-dimethyl	50.1	$C_{10}H_{14}$	134
38.	4.943	Naphthalene, decahydro	66.8	$C_{10}H_{18}$	138
39.	5.068	Benzene, 1-ethyl-2,3-dimethyl	53.7	$C_{10}H_{14}$	134
40.	5.097	Undecane	55.0	$C_{11}H_{24}$	156
41.	5.219	9-Iodotricyclo[4.2.1.1(2,5)]decane	81.5	$C_{10}H_{15}I$	262
42.	5.325	trans-Decalin, 2-methyl	82.0	$C_{11}H_{20}$	152
43.	5.581	Dodecane	62.2	$C_{12}H_{26}$	170

Table 2: GC-MS analysis of the chemical profile of Dichlorvos-treated, black water discarded beans powder (sample B)

S/N	Retention Time (min)	Bioactive compound	Probability percentage (%)	Molecular formula (MF)	Molecular weight (MW)

1.	1.241	Isobutane	92.9	C_4H_{10}	58
2.	1.270	2-Propenoic acid, 2-propenyl ester	92.6	$C_6H_8O_2$	112
3.	1.329	1,3-Butadiene, 2-fluoro	97.0	C_4H_5F	72
4.	1.403	Oxirane, propyl	96.8	$C_5H_{10}O$	86
5.	1.443	Prenol	90.0	$C_5H_{10}O$	86
6.	1.570	2-Pentyn-1-ol	87.5	C_5H_8O	84
7.	1.884	Benzene	81.9	C_6H_6	78
8.	1.938	4-Pentynoic acid	97.7	$C_5H_6O_2$	98
9.	2.094	Hexane, 3-methy	83.5	C_7H_{16}	100
10.	2.396	Cycloheptane	76.8	C_7H_{14}	98
11.	2.434	1-Pentene, 3,3-dimethy	49.5	C_7H_{14}	98
12.	2.556	1-Nonanol	61.4	$C_9H_{20}O$	144
13.	2.582	2-Heptyn-1-ol	87.5	$C_7H_{12}O$	112
14.	2.622	1,5-Hexadien-3-yne, 2-methyl	91.5	C_7H_8	92
15.	3.278	Acetic acid, trichloro-, nonyl ester	76.1	$C_{11}H_{19}Cl_3O_2$	288
16.	3.453	Cyclooctane	63.7	C_8H_{16}	112
17.	3.586	Benzenepropanamine	92.0	$C_9H_{13}N$	135
18.	3.615	1,3-Cyclopentadiene, 5-(1-methylethylidene)	82.8	C_8H_{10}	
19.	3.733	Toluene	80.5	C_7H_8	92
20.	3.764	3,5-Octadiyne	86.2	C_8H_{10}	106
21.	3.800	1-Dodecanol	55.4	$C_{12}H_{26}O$	186
22.	3.857	Bicyclo[2.1.1]hex-2-	83.1	C_8H_{10}	106

		ene, 2-ethenyl			
23.	3.884	3,5-Octadiyne	86.2	C_8H_{10}	106
24.	3.976	Cyclohexanone, 4-ethyl	89.0	$C_8H_{14}O$	126
25.	4.052	Pentalene, octahydro-2-methyl	68.0	C_9H_{16}	124
26.	4.108	Cyclohexanone, 2-ethyl	90.1	$C_8H_{14}O$	126
27.	4.169	Cyclohexane, (1,2-dimethylbutyl	92.4	$C_{12}H_{24}$	168
28.	4.236	(Z)-4-Decen-1-ol, trifluoroacetate	67.4	$C_{12}H_{19}F_3O_2$	252
29.	4.262	Benzene, propyl	89.4	C_9H_{12}	120
30.	4.321	2,3-Heptadien-5-yne, 2,4-dimethyl	76.0	C_9H_{12}	120
31.	4.362	Benzene, 1-ethyl-3-methy	61.7	C_9H_{12}	120
32.	4.543	Benzaldehyde, 2-methyl	70.5	C_8H_8O	120
33.	4.459	3-Hexene, 3-ethyl-2,5-dimethyl	91.2	$C_{10}H_{20}$	140
34.	4.585	Benzene, 1,2,3-trimethy	61.4	C_9H_{12}	120
35.	4.627	Benzeneacetaldehyde, α-methyl	78.7	$C_9H_{10}O$	134
36.	4.654	Decane, 4-methy	62.3	$C_{11}H_{24}$	156
37.	4.685	p-Cymene	70.4	$C_{10}H_{14}$	134
38.	4.711	Benzene, 1,2,4-trimethyl	65.7	C_9H_{12}	120
39.	4.752	Cyclohexane, (2-	93.6	$C_{10}H_{20}$	140

		methylpropyl			
40.	4.843	Decane, 5-methyl	85.2	$C_{11}H_{24}$	156
41.	4.864	Benzene, 1-methyl-3-propyl	70.4	$C_{10}H_{14}$	134
42.	4.894	Benzene, 1,4-diethyl	71.4	$C_{10}H_{14}$	134
43.	4.932	Naphthalene, decahydro	66.8	$C_{10}H_{18}$	138
44.	5.023	o-Cymene	61.8	$C_{10}H_{14}$	134
45.	5.057	Benzene, 4-ethyl-1,2-dimethyl	51.0	$C_{10}H_{14}$	134
46.	5.087	Undecane	55.0	$C_{11}H_{24}$	156
47.	5.209	Adamantane-2-thiol	88.7	$C_{10}H_{16}S$	168
48.	5.233	trans-Decalin, 2-methyl	82.0	$C_{11}H_{20}$	152
49.	5.316	Naphthalene, decahydro-2-methyl	74.9	$C_{11}H_{20}$	152
50.	5.572	Dodecane	62.2	$C_{12}H_{26}$	170
51.	6.016	Tridecane	61.2	$C_{13}H_{28}$	184

Table 3: GC-MS analysis of the chemical profile of Dichlorvos-treated, black water not discarded beans powder (sample C)

S/N	Retention Time (min)	Bioactive compound	Probability percentage (%)	Molecular formula (MF)	Molecular weight (MW)

1.	1.273	2-Propenoic acid, 2-propenyl ester	92.6	$C_6H_8O_2$	112
2.	1.332	1,3-Butadiene, 2-fluoro	97.0	C_4H_5F	72
3.	1.411	Aziridine, 2,2-dimethyl	95.5	C_4H_9N	71
4.	1.453	1,2,3-Trimethyldiaziridine	94.7	$C_4H_{10}N_2$	86
5.	1.501	Prenol	90.0	$C_5H_{10}O$	86
6.	1.573	Oxirane, (1-methylbutyl)	93.8	$C_7H_{14}O$	114
7.	1.924	Benzene	81.9	C_6H_6	78
8.	2.090	2-Hexyn-1-ol	86.3	$C_6H_{10}O$	98
9.	2.363	1-Pentene, 3,3-dimethyl	49.5	C_7H_{14}	98
10.	2.422	Cycloheptane	76.8	C_7H_{14}	98
11.	2.666	Toluene	80.5	C_7H_8	92
12.	3.466	Cyclooctane	63.7	C_8H_{16}	112
13.	3.618	1,3-Cyclopentadiene, 5-(1-methylethylidene)	82.8	C_8H_{10}	106
14.	3.779	2-Methylenecyclohexanol	85.3	$C_7H_{12}O$	112
15.	3.872	Bicyclo[2.1.1]hex-2-ene, 2-etheny	83.1	C_8H_{10}	106
16.	3.990	Dichloroacetic acid, nonyl ester	79.3	$C_{11}H_{20}Cl_2O_2$	254
17.	4.067	Cyclohexane, 1-propenyl	68.3	C_9H_{16}	124
18.	4.122	Cyclohexanone, 2-ethyl	90.1	$C_8H_{14}O$	126
19.	4.249	(Z)-4-Decen-1-ol, trifluoroacetate	67.4	$C_{12}H_{19}F_3O_2$	252
20.	4.276	Benzene, propyl	89.4	C_9H_{12}	120
21.	4.637	Benzene, 1,2,4-trimethyl	65.7	C_9H_{12}	120
22.	4.664	Decane, 4-methyl	62.3	$C_{11}H_{24}$	156
23.	4.761	Cyclohexane, butyl	82.7	$C_{10}H_{20}$	140
24.	4.872	Benzene, 1-methyl-3-propyl	70.4	$C_{10}H_{14}$	134

25.	4.902	1,3,8-p-Menthatriene	67.6	$C_{10}H_{14}$	134
26.	4.940	Naphthalene, decahydro-, trans	66.9	$C_{10}H_{18}$	138
27.	5.029	o-Cymene	61.8	$C_{10}H_{14}$	134
28.	5.094	Undecane	55.0	$C_{11}H_{24}$	156
29.	5.240	trans-Decalin, 2-methyl	82.0	$C_{11}H_{20}$	152
30.	5.322	Naphthalene, decahydro-2-methyl	74.9	$C_{11}H_{20}$	152
31.	5.579	Dodecane	62.2	$C_{12}H_{26}$	170

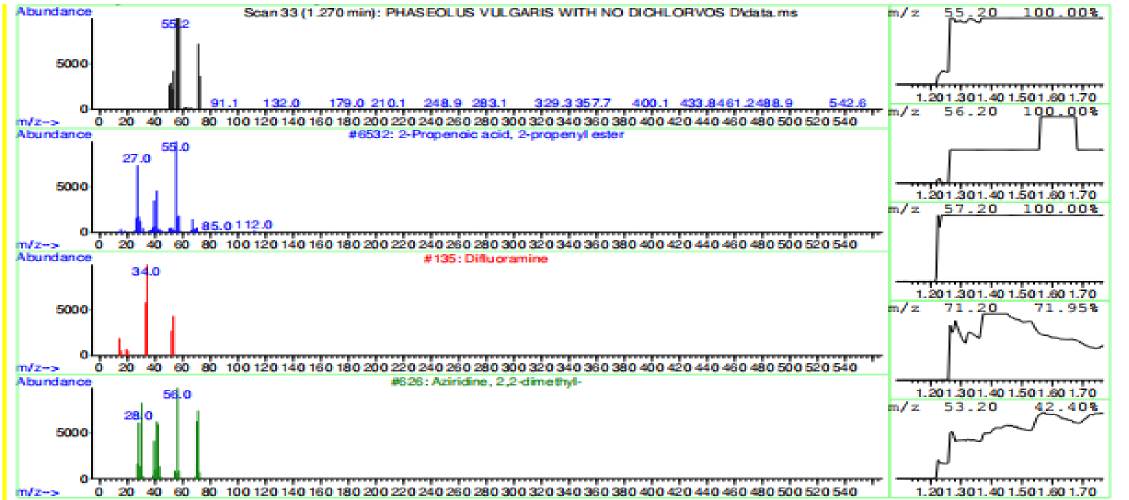
4. DISCUSSION

Table 1 presents the results of the GC-MS analysis of hexane extract of Sample A, identifying 43 compounds. The most abundant compound was 4-Pentynoic acid, with a peak area of 97.7%, while Benzene, 1-ethyl-3,5-dimethyl showed the lowest peak area at 50.1% (Fig. 2). Peak area percentages below 5% were considered negligible.

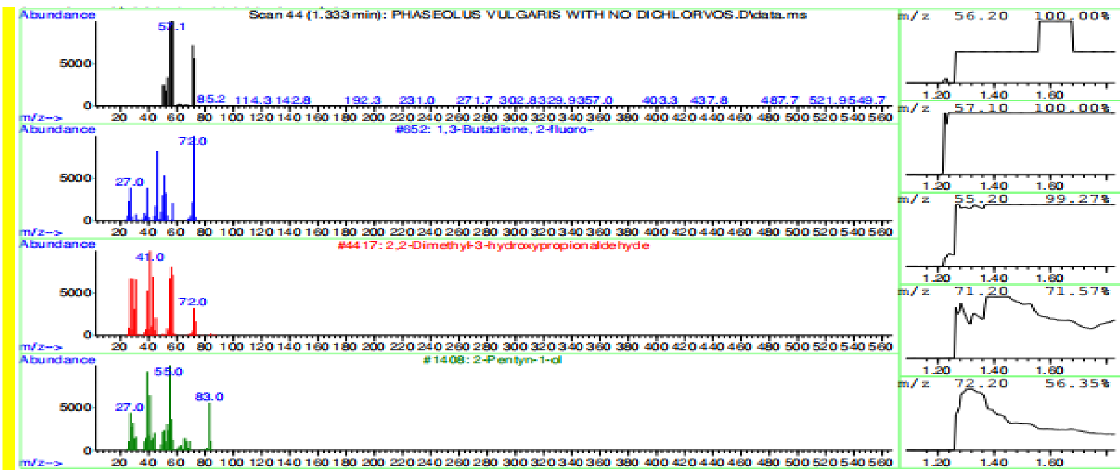
Fig. 2: GC-MS chromatogram of untreated cooked black-eyed beans powder (sample A)

Natural chemicals in Sample A include: Prenol (90.0%), also known as 3-methyl-2-buten-1-ol is a simple terpenoid alcohol involved in biosynthetic pathways and serves as a precursor for isoprenoids vital for plant growth and metabolism [29]; Benzaldehyde, 2-methyl (70.5%), commonly referred to as o-tolualdehyde, is a secondary metabolite that contributes to flavor, defense mechanisms, and metabolic processes in plants [30]; Benzeneacetaldehyde (88.9%) is part of the aromatic compound mixture responsible for the characteristic flavor and fragrance of beans [31]; o-Cymene (61.8%), a monoterpene, is known for its pleasant citrus and sweet aroma [32].

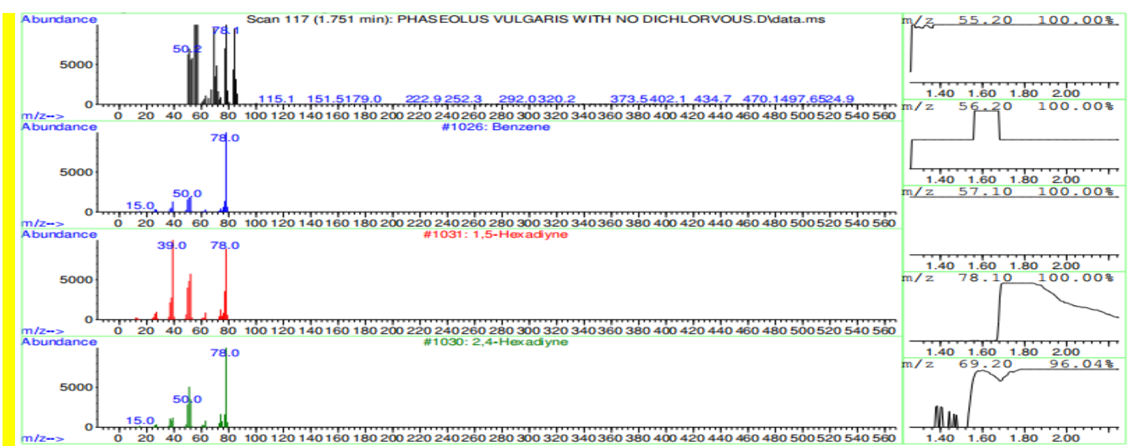
Lectins identified include: 2-Propenoic acid, 2-propenyl ester (92.6%); 1,3-Butadiene, 2-fluoro (97.0%); and Decane, 5-methyl (85.2%) [33]. 2-Propenoic acid, 2-propenyl ester (allyl acrylate) (Fig. 3a) is a skin and eye irritant and may cause respiratory issues [34]. 1,3-Butadiene, 2-fluoro (Fig. 3b) is harmful; 1,3-butadiene is a known carcinogen associated with respiratory problems [35]. Benzene (Fig. 3c) is highly toxic and a known carcinogen linked to leukemia and other blood disorders [36]. Toluene (Fig. 3d) is neurotoxic, capable of causing respiratory issues and damage to the nervous system, and harmful if ingested [37].


Scan 33 (1.270 min): PHASEOLUS VULGARIS WITH NO DICHLORVOS D\data.ms
#6532: 2-Propenoic acid, 2-propenyl ester
#135: Difluoramine
#626: Aziridine, 2,2-dimethyl-
Abundance
m/z-->

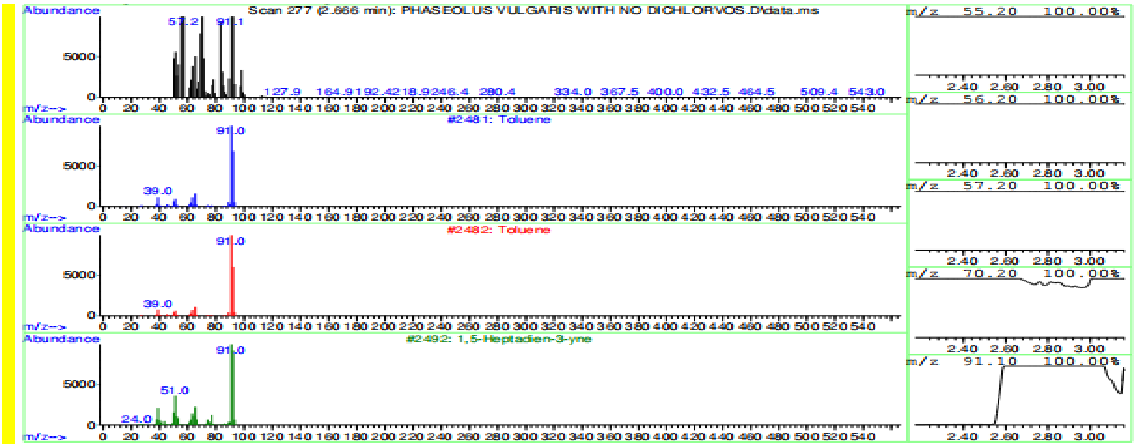
(a)


Scan 44 (1.333 min): PHASEOLUS VULGARIS WITH NO DICHLORVOS.D\data.ms
#652: 1,3-Butadiene, 2-fluoro-
#4417: 2,2-Dimethyl-3-hydroxypropionaldehyde
#1408: 2-Pentyn-1-ol
Abundance
m/z-->

(b)


Scan 117 (1.751 min): PHASEOLUS VULGARIS WITH NO DICHLORVOUS.D\data.ms
#1026: Benzene
#1031: 1,5-Hexadiyne
#1030: 2,4-Hexadiyne
Abundance
m/z-->

(c)



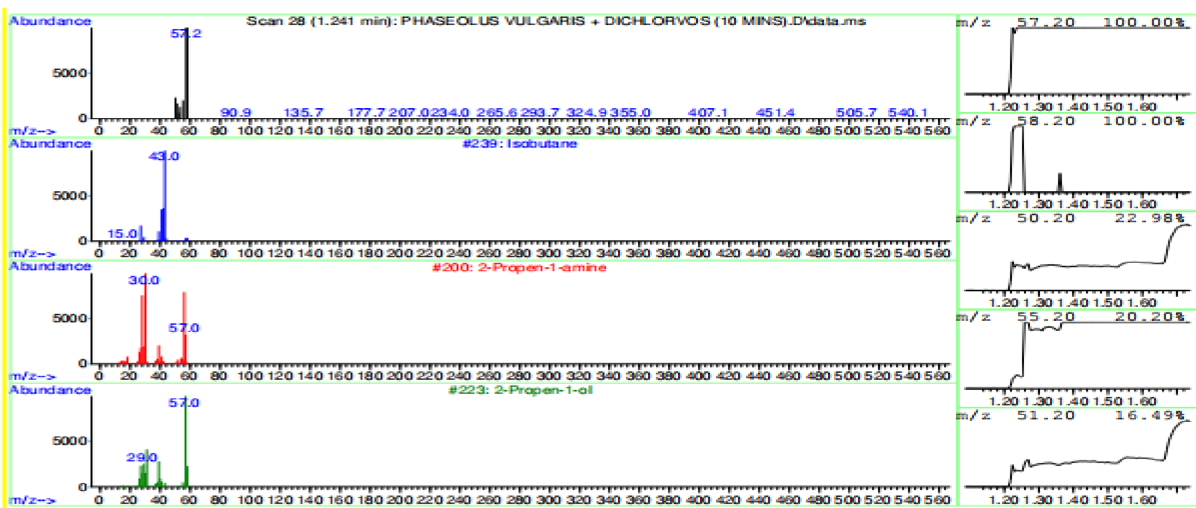
(d)

Fig. 3: Chromatograms of major chemical compounds analysed from Sample A: 2-Propenoic acid, 2-propenyl ester (a), 1,3-Butadiene, 2-fluoro (b), Benzene (c), Toluene (d)

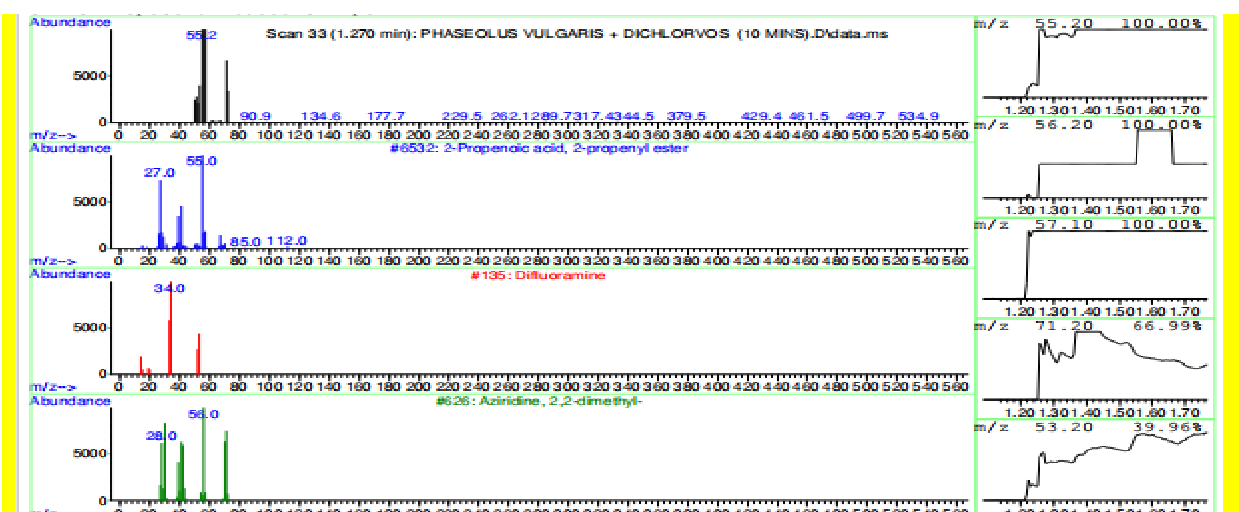
Fifty one (51) compounds were identified from Sample B, as presented in Table 2. The highest peak area (97.7%) was recorded for 4-Pentynoic acid, while 1-Pentene, 3,3-dimethyl had the lowest peak area (49.5%) (Fig.4).

Fig. 4: GC-MS chromatogram of Dichlorvos-treated, black water discarded beans powder (Sample B)

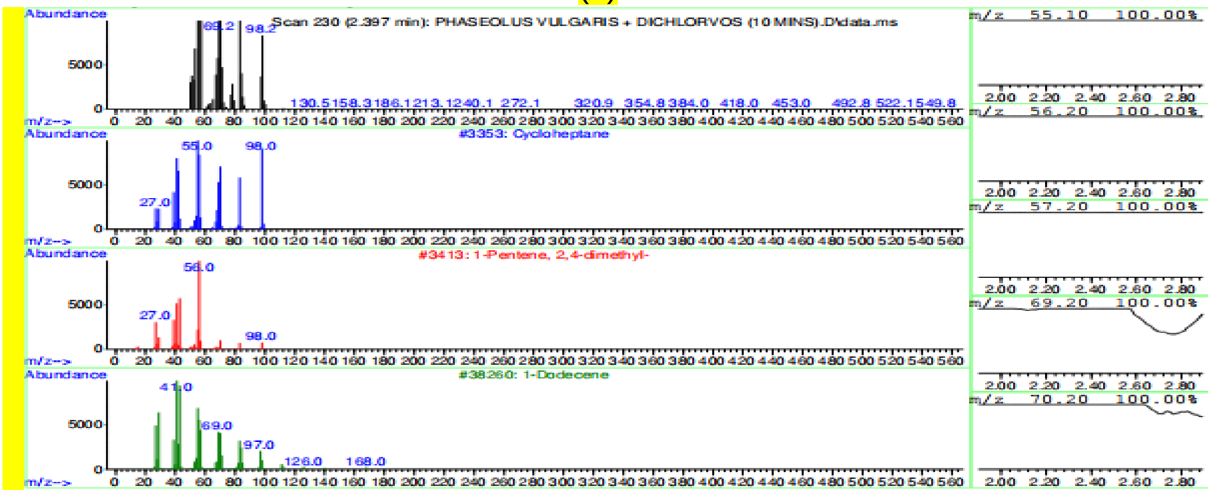
Natural components include: Prenol (90.0%) and o-Cymene (61.8%). Non-natural components identified in Sample B include: Pentyn-1-ol (87.5%), Cyclohexanone, 4-ethyl (89.0%), and Acetic acid, trichloro-, nonyl ester (76.1%) [33]. Isobutane (Fig. 5a) is a flammable solvent with a low toxicity, but can be an asphyxiant in high concentrations [38]. 2-Propenoic acid, 2-propenyl ester (Fig. 5b) is an irritant. Cycloheptane (Fig. 5c) is low to moderate toxic but can cause central nervous system effects [39]. Benzaldehyde, 2-methyl (Fig. 5d) can cause irritation [40]. Kang and colleaques [41] reported similar findings in spiked grains, beans, fruits and vegetables.

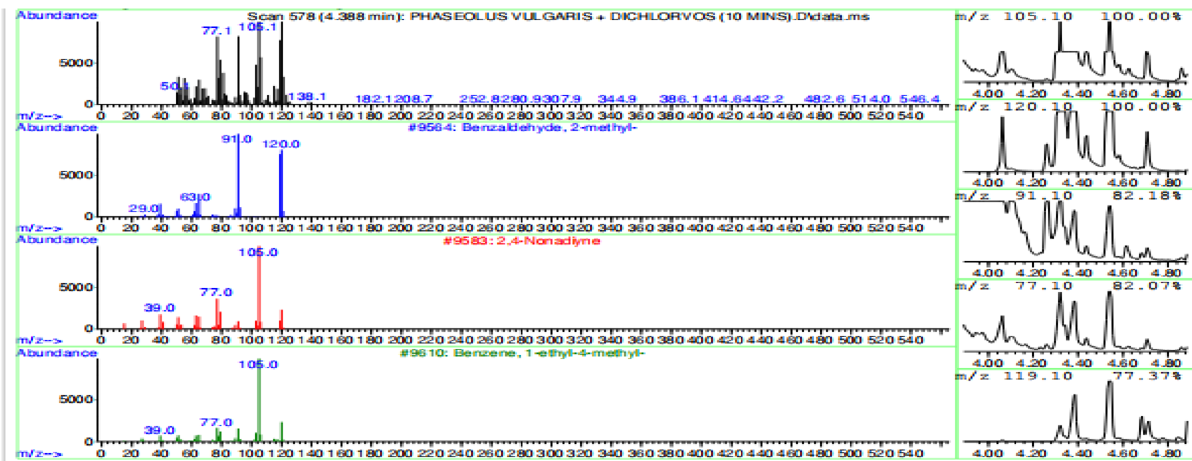


(a)



(b)





(c)

(d)

Fig. 5: Chromatograms of major chemical compounds analysed from Sample B: Isobutane (a), 2-Propenoic acid, 2-propenyl ester (b), Cycloheptane (c), Benzaldehyde, 2-methyl (d)

Table 3 presents thirty one (31) compounds identified from the hexane extract of Sample C. The highest peak area (97.7%) was recorded for 4-Pentynoic acid, while 1-Pentene, 3,3-dimethyl had the lowest peak area (49.5%) (Fig. 6).

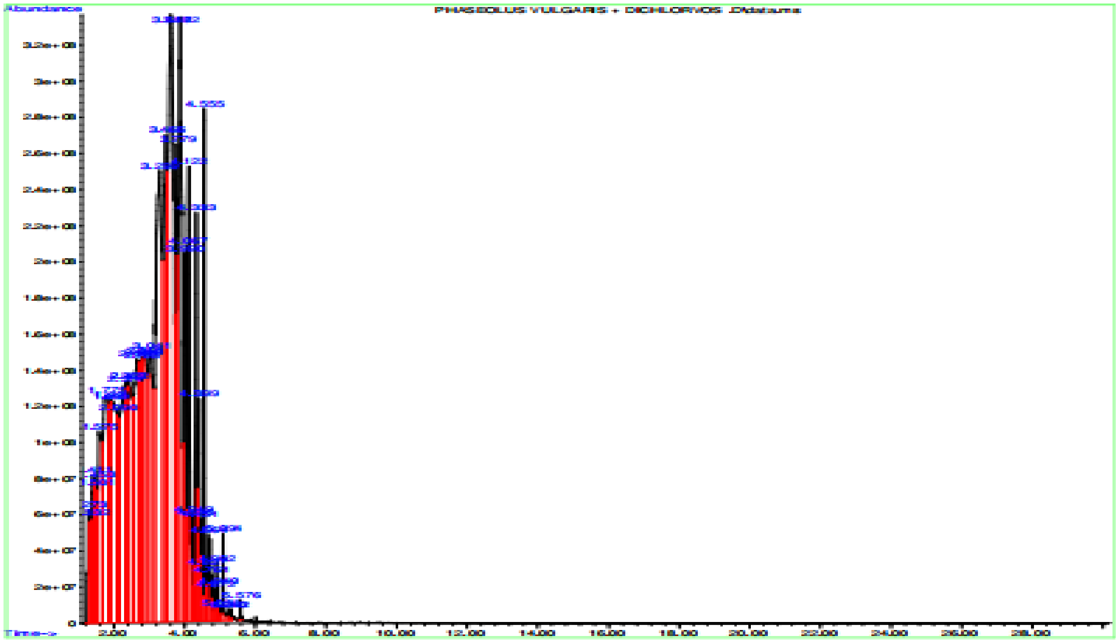


Fig. 6: GC-MS chromatogram of Dichlorvos-treated, black water retained black-eyed beans powder (Sample c)

Notable natural components include: Prenol (90.0%); and 1,3,8-p-Menthatriene (66.9%) which is associated with the sweet aroma of beans [42]. Non-natural components detected include: 2-Methylenecyclohexanol (85.3%); Naphthalene, decahydro-, trans (66.9%); 1-Pentene, 3,3-dimethyl (49.5%); Aziridine, 2,2-dimethyl (95.5%), a known irritant; Benzene, 1-methyl-3-propyl (70.4%), a toxicant to aquatic life with lasting effects [43-46].

Propylene oxide (Oxirane, propyl (Fig. 7a) is a toxic compound that can cause irritation, respiratory issues, and a potential human carcinogen [47]. Toluene (Fig. 7b) is neurotoxic while dodecane (Fig. 7c) is a solvent and a distillation chaser [48].

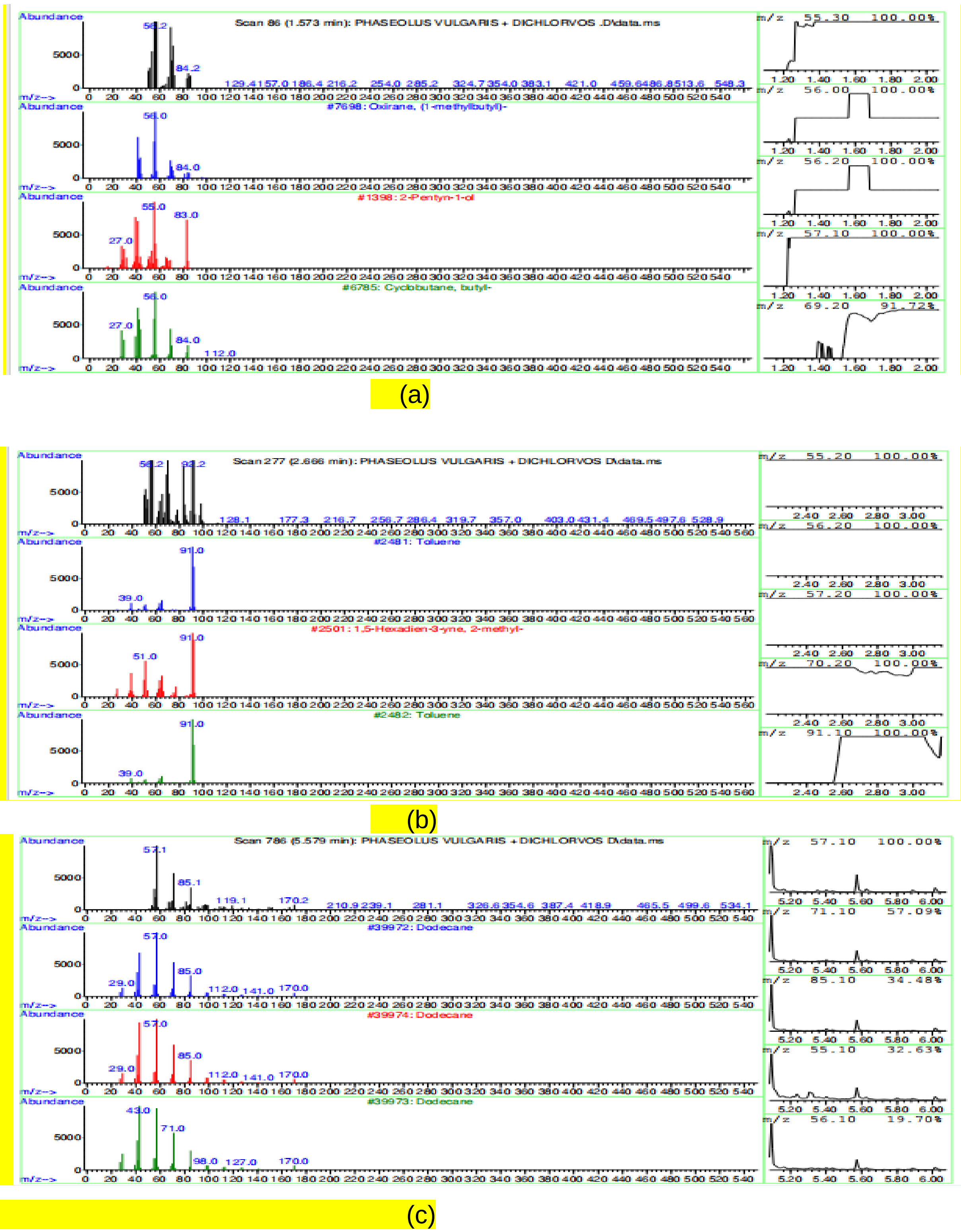


Fig. 7: Chromatograms of some chemical compounds analysed from sample C: Oxirane, (1-methylbutyl) (a), Toluene (b), Dodecane (c)

The detection of harmful chemicals in Sample A highlights potential contamination from pesticides, poor agricultural practices, or environmental pollutants. The persistence of toxic chemicals in all samples suggests that heat treatment causes thermal decomposition of pesticides into stable, harmful byproducts, which are absorbed into the bean matrix [49-50].

These findings emphasize the health risks associated with pesticide residues and the need for stringent monitoring, regulation, and control at every stage of bean production, handling, and storage.

5. CONCLUSION

The GC-MS analysis of black eyed beans subjected to different treatments (sample A, B, and C) revealed the presence of beneficial phytochemicals and substantial levels of volatile toxic compounds in all the samples. While the identified phytochemicals may offer some health benefits, the detection of toxic substances raises significant health concerns. Many of the compounds found are associated with adverse effects on human health.

Dichlorvos is highly toxic to the nervous system, and its degradation or reaction with other substances can form harmful byproducts linked to acute symptoms like respiratory and skin irritation, headaches, and dizziness. In more severe cases, they may cause damage to the liver, kidneys, and thyroid, or lead to long-term effects such as carcinogenicity and mutagenicity.

Benzene and its derivatives, such as toluene are often byproducts of pesticide degradation or contamination during storage and handling. Benzene is a known carcinogen, and toluene can cause neurological symptoms and other toxicological effects upon exposure. Additionally, cycloalkanes like cyclohexane and cyclooctane were present, potentially originating from solvents or byproducts in pesticide formulations. These volatile compounds may contribute to respiratory irritation and other health risks. Toxic hydrocarbons such as naphthalene and decane, likely resulting from the breakdown of complex organic molecules in pesticides, pose further risks. Naphthalene is associated with hemolytic anemia and is classified as a possible human carcinogen.

Dichlorvos is moderately water-soluble, but washing or discarding the black water after parboiling does not guarantee complete removal. Heat from cooking may not effectively degrade dichlorvos into safe byproducts, and some degradation products remain harmful. Thus, any residual pesticide, even in small amounts, poses a significant hazard. The persistence of these toxic compounds makes it clear that conventional cooking methods are insufficient to mitigate the risks associated with pesticide contamination.The findings underscore the urgent need for improved handling, storage, and monitoring of pesticide use in agricultural produce to minimize contamination.

Our next project will focus on developing effective strategies for decontaminating contaminated beans to enhance food safety and safeguard consumers from the adverse health effects of these harmful substances.

RECOMMENDATION

Diclovos (Sniper) is an organophosphate, hence, beans should not be preserved with Dichlorvos, and beans contaminated with Dichlorvos should not be consumed under any circumstances, even after cooking. The health risks posed by organophosphates are too significant to ignore.

Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of this manuscript.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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