SHAFIU MUSTAPHA

IN VITRO ASSESSMENT OF THE HERBICIDAL ACTIVITY OF SOME POLYFUNCTIONAL COMPOUNDS

Dissertation presented to the Federal University of Viçosa, as part of the requirements of the Minas Gerais Multi Center for Chemistry, to obtain the title of *Magister Scientiae.*

Adviser: Elson Santiago de Alvarenga

Co-adviser: Diego Pereira Sangí

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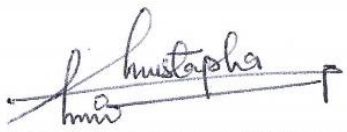

Shafiu Mustapha
Author

Elson Santiago de Alvarenga
Advisor

I dedicate this work to God Almighty, the giver and sustainer of life. And to my late parents.

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All thanks and glorifications are due to God almighty, the giver and sustainer of everything. May His peace and blessings be upon His noble apostle Muhammad, his household, and companions.

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ABSTRACT

MUSTAPHA, Shafiu, M.Sc., Universidade Federal de Viçosa, July, 2023. ***In vitro* assessment of the herbicidal activity of some polyfunctional compounds.** Adviser: Elson Santiago de Alvarenga.

For everyone to live an active and healthy life, they must always have physical and financial access to enough food that is safe, satisfies their nutritional needs, and suits their tastes, and only then we can have food security. As such, it is inconceivable to exaggerate the significance of herbicides in decreasing or eradicating weed-related losses given the size of the world's population and the need for a sustainable supply of food. This research study aimed to assess the herbicidal selectivity potential of twenty different polyfunctional compounds on the seeds of lettuce (*Lactuca sativa* L.), ryegrass (*Lolium multiflorum*), brachiaria (*Brachiaria* spp), cucumber (*Cucumis sativus* L.), and sorghum (*Sorghum bicolor* L.). The evaluation was conducted by performing in vitro germination of the seeds, capturing digital images, measuring the cumulative impact of these compounds on the stem and root lengths, and subsequently comparing the results with those obtained from the control group using DMSO. The results showed that some of the tested polyfunctional compounds exhibited good herbicidal potential on the seeds, some excellently inhibiting germination completely (up to 100%) in some of the tested plant seeds at high concentrations, yet some demonstrated stimulation (acting like hormones) on different plant seeds, in varying concentrations. In conclusion, all synthesized compounds exhibited activity in seed germination. However, compounds GSCB 01, 54, 56, and 58 showed superior activity to the commercial herbicide S-metolachlor

Keywords: Herbicidal potential. Polyfunctional compounds. Benzoxazole derivatives. *In-vitro* germination.

RESUMO

MUSTAPHA, Shafiu, M.Sc**.,** Universidade Federal de Viçosa, julho de 2023. **Avaliação *in vitro* da atividade herbicida de alguns compostos poli-funcionais**. Orientador: Elson Santiago de Alvarenga.

Para que todos vivam uma vida ativa e saudável, eles devem sempre ter acesso físico e financeiro a alimentos suficientes que são seguros, satisfazem suas necessidades nutricionais e atendem aos seus gostos, e somente então podemos ter segurança alimentar. Como tal, é inconcebível exagerar o significado dos herbicidas na diminuição ou erradicação de perdas relacionadas a ervas daninhas, dado o tamanho da população mundial e a necessidade de um suprimento sustentável de alimentos. Este estudo de pesquisa teve como objetivo avaliar o potencial de seletividade herbicida de vinte compostos poli -funcionais diferentes nas sementes da alface (Lactuca sativa L.), azevém (lolium multiflorum), braquiaria (Brachiaria spp), pepino (cucumis sativus l.) e sorgo (Sorgo bicolor L.). A avaliação foi realizada realizando a germinação in vitro das sementes, capturando imagens digitais, medindo o impacto cumulativo desses compostos nos comprimentos do caule e das raízes e subsequentemente comparando os resultados com os obtidos do grupo controle usando DMSO. Os resultados mostraram que alguns dos compostos poli-funcionais testados exibiram um bom potencial herbicida nas sementes, algumas inibindo completamente a germinação (até 100%) em algumas das sementes de plantas testadas em altas concentrações, mas algumas estimulações demonstradas (agindo como hormônios) em Diferentes sementes de plantas, em concentrações variadas. Em conclusão, todos os compostos sintetizados exibiram atividade na germinação de sementes. No entanto, os compostos GSCB 01, 54, 56 e 58 mostraram atividade superior ao herbicida comercial S-metolaclor.

Palavras-chave: potencial herbicida. Compostos poli-funcionais. Derivados de benzoxazol. Germinação in vitro.

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LIST OF SYMBOLS AND ABBREVIATIONS

δ	Chemical shift
$\overline{v}$	Wavenumber
Λ	Wavelength
B.O.D.	*Biological oxygen demand*
GC	Gas chromatography
μM	Micro moles
D	Duplet
dd	duplet of duplet
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
MS	Mass spectrometry
$CDCl_3$	Deutrated Chloroform
Hz	Hertz, frequency unit
IR	Infrared
J	Coupling constant
m	Multiplet
m/v	Mass/volume ratio
m/z	Mass/charge ratio
ppm	Chemical shift unit in NMR spectra
q	Quintet
R_f	Retention factor
^{13}C NMR	Carbon 13 Nuclear Magnetic Resonance
^{1}H NMR	Hydrogen Nuclear Magnetic Resonance
S	Singlet
r.t.	*Room temperature*
T_f	Melting temperature
T	Triplet
UV	Ultraviolet

SUMMARY

CHAPTER 1

GENERAL BACKGROUND ON THE NEED FOR HERBICIDE SELECTIVITY

1.0 INTRODUCTION

For everyone to live an active and healthy life, they must always have physical and financial access to enough food that is safe, satisfies their nutritional needs, and suits their tastes, and only then we can have food security (EREZ-ESCAMILLA, 2017). Given the magnitude of the world's population and the requirement for a sufficient supply of food, it is impossible to overstate the importance of herbicides in reducing or eliminating weed-related losses (CHAUHAN, 2020). In agricultural settings, herbicides are used to lessen dangerous weeds. Herbicides may kill some weeds and retard the growth of others. From the mid-20th century, pesticide use has greatly increased. If herbicides are not employed, agricultural produce will suffer considerable losses, both quantitative and qualitative (T et al., 2020).

In chemical weed control tactics, herbicide selectivity is a farming technology that is heavily used. The combined activity of numerous defence mechanisms prevents phytotoxicity from herbicide treatment, lowering or even eliminating the threshold of agronomically acceptable damage (PINTO DE CARVALHO et al., 2009). Herbicide selectivity is primarily caused by differences in metabolism between crop and weed plant species, with weeds having a restricted capacity to carry out this metabolism under agronomically advised conditions (OWEN, 1991). When metabolism is the primary issue, phytotoxicity can be seen as the overriding of a plant's innate power to detoxify a specific molecule or as a bypassing of the highest level of protection offered by the systems of selectivity (RANA, 2019).

The symptoms of phytotoxicity represent an additional energy waste that should not be recognized as a normal physiological reaction and may thus lead to yield losses when herbicide metabolism involves energy disposal (PURCELL, 2009). Herbicide application guidelines must be based on findings from meticulously conducted selectivity studies to prevent or minimize crop losses or damages. Growers must also be made more aware of how to use each product effectively (PINTO DE CARVALHO *et al.*, 2009)
.

1.1 Objectives

In broad terms, this study aims to analyze the herbicidal selectivity potential of twenty different polyfunctional compounds on five distinct seed types, namely: lettuce, ryegrass, brachiaria, cucumber, and sorghum. In specific terms, we are going to:

- Collect seed samples from agrochemical vendors and local farmers (as the case may be) within the state of Minas Gerais, Brazil;
- The samples collected will be prepared, those collected from local farmers will have to undergo a screening process, to remove dirt and bad seeds among them
- *In vitro* germination of the samples will be carried out using 5ml of water, DMSO and five different concentrations of the benzoxazole stocks (500, 300, 150, 75 and 50 micromoles), for five days in the case lettuce (*Lactuca sativa* L.), brachiaria (*Brachiaria* ssp), cucumber (*Cucumis sativus* L.), and sorghum (*Sorghum bicolor* L.), while ryegrass (*Lolium multiflorum*) will take fourteen days;
- Freezing the germinated seeds for 24 hours in order to stop their growth;
- Measuring the stem and root lengths of the germinated seeds;
- Comparing the measured lengths with that of the control (DMSO) to determine the percentage effect of the compounds on the samples.

1.2 JUSTIFICATION

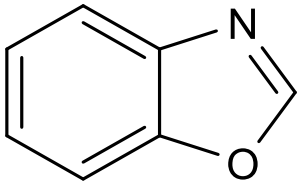
A more specific weed management method that can completely eradicate weeds even at the post-emergent stage is required due to some plants' resistance to non-selective herbicides used at the pre-emergent stage. This can ensure that the desired crops are protected from weeds, and adequate food supply is maximised.

CHAPTER 2
REVIEW OF RELATED LITERATURE ON BENZOXAZOLE DERIVATIVES FOR THEIR NOVEL HERBICIDAL POTENTIAL

2.0 Benzoxazoles

Benzoxazole is a type of heterocycle that has a bicyclic structure with an aryl ring bonded to the "d" site of an oxazole molecule.

Figure 1- Structure of benzoxazole.



Source: the author.

The parent benzoxazole structure is found to be a component of several biologically occurring compounds and has a planar architecture. As both oxygen and nitrogen atoms can serve as nucleophiles, the molecule frequently demonstrates affinity and selectivity toward a variety of biological targets and displays several noncovalent interactions (WONG & YEONG, 2021).

Benzoxazole also enables π-π stacking, π-cation, and hydrophobic interactions with bio-macromolecules due to the presence of a planar benzene ring. As a result, this scaffold is frequently referred to as the building blocks for the synthesis of different compounds with pharmacological relevance (JI RAM & PRATAP, 2019).

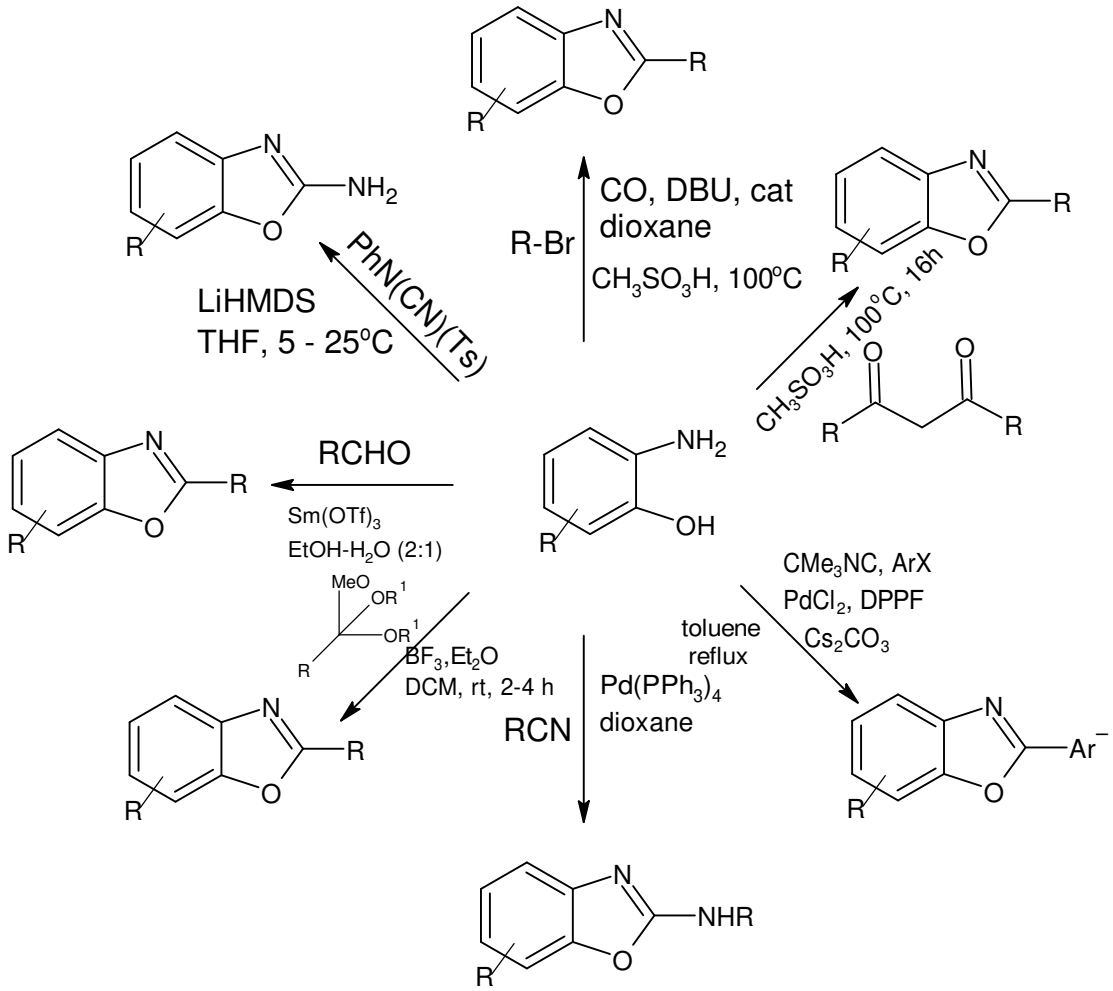
2.1 Generalized Synthesis of Benzoxazoles

Several methods for the synthesis of benzoxazoles have been established in the past by considering the biological importance of these compounds (SONG et al., 2020).

Using *o*-aminophenol as one of the primary starting materials, produces a number of one-pot synthesis processes, which follows environmentally sustainable processes. Samarium triflate is used as a reusable acid catalyst during the condensation of o-aminophenol with aldehydes to produce the corresponding benzoxazoles in an aqueous environment (SARTORI et al., 2018).

In the same manner, these precursors were created by reacting o-aminophenol with a variety of substrates, including aldehydes, alcohols, aryl halides, benzoic acids, benzoyl chlorides, diketones, *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide halogenated nitriles, and isocyanides under various conditions, as shown in the following scheme (JI RAM & PRATAP, 2019).

Figure 2 **-** One-Pot Synthesis of Benzoxazoles.



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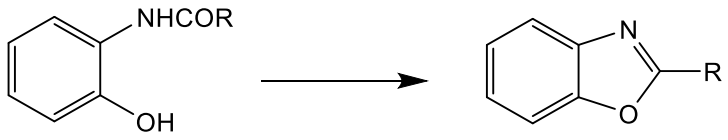
Moreover, the most popular method for creating these chemicals is thermal dehydration of o-(acylamino) phenols.

Figure 3 - Dehydration of o-acylamino-phenol.



Source: the author.

Shainda Laeeq, used a mixture of KS_2COEt (17.6 g, 0.11 mol) and 2-amino-4-methylphenol (12.3 g, 0.10 mol) in 100 mL of pyridine, stirred, and refluxed for two hours. It was brought to room temperature before being added to 400 mL of ice water and concentrated HCl (40 mL). The material was collected, washed with water, and dried overnight in the hood and for several hours in an oven at 45 °C to produce a yellowish-grey solid; yield: 16.0 g (97%); mp 220-2238 °C (Laeeq et al., 2013).

Figure 4 - Benzothiozole moiety.

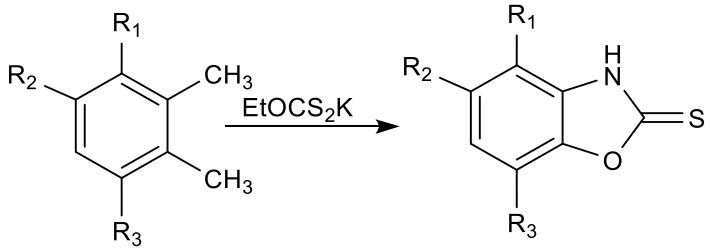


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Table 1 **-** Benzothiozole substitutes.

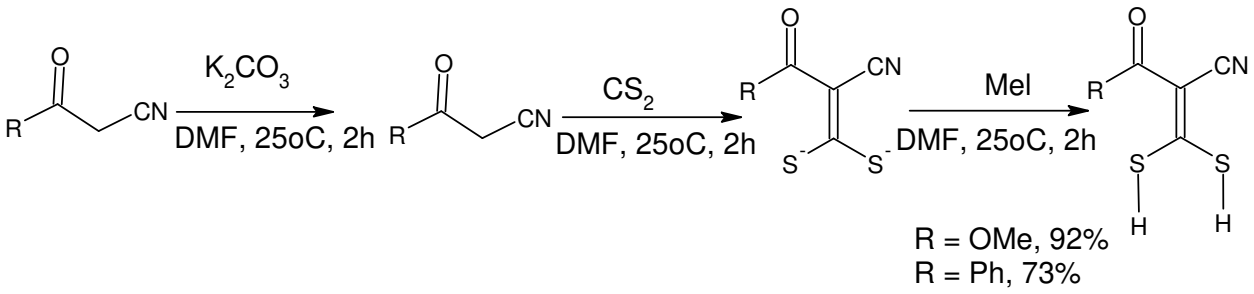
R1	**R2**	**R3**	**Conditions**	**Yield (%)**
H	Me	H	KS_2COEt, pyridine, reflux	97
H	Ms	H	KS KS_2COEt, pyridine, reflux	57
H	Cl	H	KS_2COEt, pyridine, reflux	94
H	CO_2, Me	H	KS_2COEt, pyridine, reflux	96
H	NO_2	H	KOH, CS_2, EtOH	66
H	H	H	KOH, CS_2, EtOH	61
Me	Cl	iPr	KOH, CS_2, MeOH	87
H	OMe	H	KOH, CS_2, EtOH	90

Source: the author.

In this study, we applied the method of annulation by nucleophilic double substitution of polarized kethenedithioacetals on vinylic carbon, with 2-aminophenols serving as the nucleophiles.

A three-step one-pot synthesis was previously used to create the methyl 3,3-*bis*(methylsulfanyl)-2-cyanoacrylate and 2-benzoyl-3,3-*bis*(methylsulfanyl)-acrylonitrile ethenedithioacetals, the deprotonation of substances with active hydrogens, the addition of carbon disulfide, and the alkylation of methyl iodide (Scheme 1).

Scheme 1 Alkylation of methyl iodide



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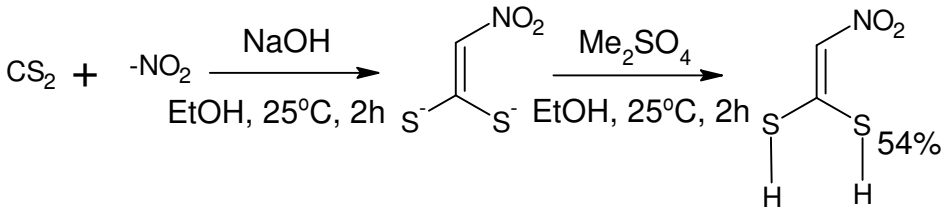
By deprotonating nitromethane and mixing it with carbon disulfide, 1,1-*bis*-methylsulfanyl-2-nitroethylene was created, in order to create a salt that was later separated and dissolved in aqueous methanol solution for dimethylation with dimethyl sulfate (Scheme 2).

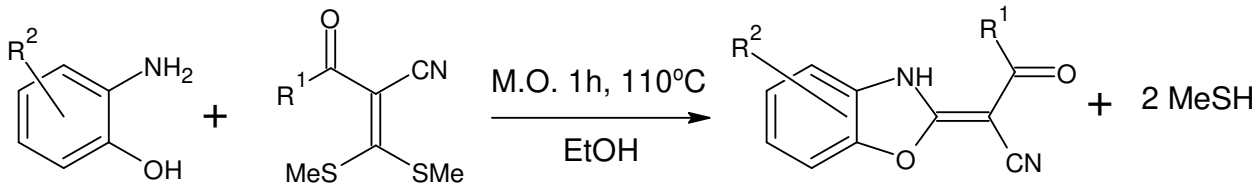
Scheme 2 Formation of 1,1-*bis*-methylsulfanyl-2-nitroethylene



Source: the author.

Then, with the aid of microwave irradiation, the kethenodithioacetals were subjected to vinylic double substitution processes. We exploited the amino and hydroxy groups of 2-aminophenols as nucleophiles in these reactions, facilitating the substitution of methylsulfanyl groups, which serve as leaving groups in the form of molecules of methanethiol (Scheme 3).

Scheme 3 Microwave assisted cyclization



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2.2 Characterization of Benzoxazoles

Spectrometric analysis is employed to physically identify an organic molecule. Although, specific spectra are expected for different derivatives of Benzoxazoles, there are however, a general perspective that can be employed to identify the presence of Benzoxazoles and their derivatives.

2.2.1 UV-Visible: The electronic transitions of a molecule are examined using UV-vis spectroscopy. Due to the existence of conjugated systems, benzoxazole derivatives often exhibit absorption bands in the UV-vis region. Information on the electronic structure and the existence of particular functional groups can be found in the absorption peaks (SANTOS et al., 2011; DA SILVA et al., 2022).

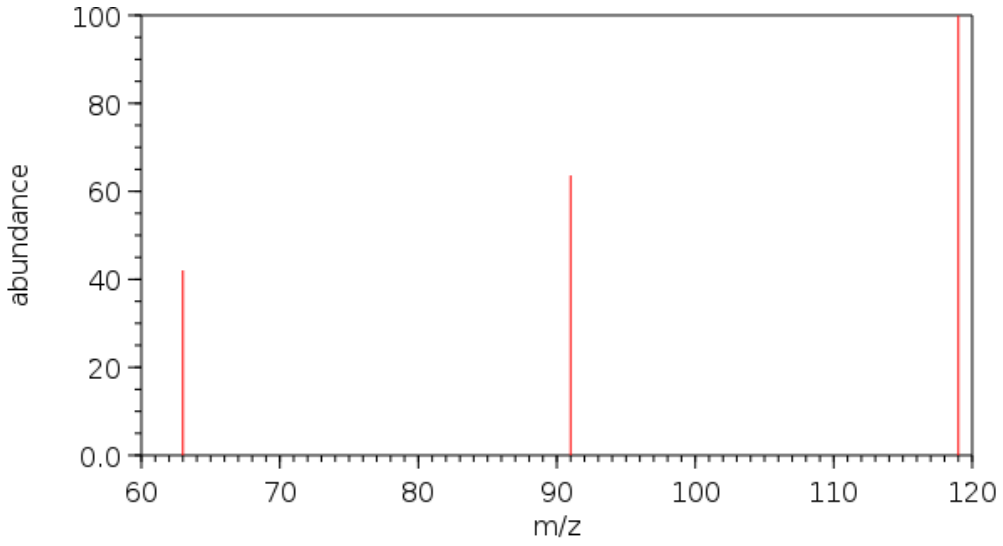
2.2.2 Infrared (IR) Spectroscopy: IR spectroscopy is useful for determining the functional groups that exist in a molecule. In a benzoxazole derivative, it can reveal the presence of particular bonds and functional groups. The IR spectrum may contain important absorption bands linked to the stretching vibrations of C-H, C=O, C-N, and C=C (SYETOV & VDOVIN, 2010).

2.2.3 Nuclear Magnetic Resonance (NMR) Spectroscopy: NMR spectroscopy gives details about the connectivity and surroundings of the various atoms in a molecule. For benzoxazole derivatives, proton NMR (^{1}H NMR) and carbon-13 NMR (^{13}C NMR) are

frequently utilized. The structure of the compound, particularly the locations and kinds of substituents attached, can be identified through the NMR spectra (KAKKAR et al., 2018).

2.2.4 Mass Spectrometry (MS): Mass spectrometry is used for estimating a compound's molecular weight and fragmentation pattern. It offers details on the molecular make-up and the existence of particular functional groups. For the investigation of benzoxazole derivatives, methods like matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI) can be used (OSMANIYE et al., 2021).

Figure 5 - A spectrum showing the molecular weight of Benzoxazole.



Source: the author.

Benzoxazole has a molecular weight of 119 g mol^{-1}, which can be seen in the spectrum above, appearing as the base peak.

2.2.5 X-ray Crystallography: X-ray crystallography is an effective method utilized for identifying the three-dimensional structure of a molecule. If a benzoxazole derivative can form crystals, X-ray crystallography can reveal precise details on the angles and distances between bonds in the molecule (LAYEK et al., 2020).

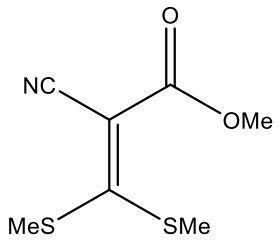
2.2.6 Thermal Analysis: To investigate the thermal stability and phase transitions of benzoxazole derivatives, methods like differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) can be employed. Such studies can reveal details regarding the melting point, decomposition temperature, and other thermal properties (DEV et al., 2016).

2.3 Synthesis of polarized Ethenedithioacetals 54 and 76

A solution was prepared using dimethylformamide (140 mL) and methyl or benzoylacetonitrile cyanoacetate (0.12 mol). Then 0.12 mol of potassium carbonate was added to the mixture. For two hours, the reaction mixture was continuously stirred at ambient temperature (25°C). Then, carbon disulfide (0.12 mol) was added, the stirring continuous for the next two hours, as the color change is being observed.

Finally, 0.24 mol of methyl iodide was added to the mixture, and the reaction was continuously stirred for 24 hours. 250 mL of water were added to finish the reaction, which resulted in the precipitation of either 2-benzoyl-3,3-*bis*(methylsulfanyl)-acrylonitrile or methyl 3,3-*bis*(methylsulfanyl)-2-cyanoacrylate, which can then be purified using vacuum filtration and washing with ethanol (SANGI et al., 2014).

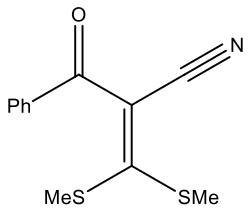
Methyl 3,3-*bis*(methylsulfanyl)-2-cyanoacrylate (GSCB 54): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 3H), 2.68 (s, 3H), 2.53 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 181.61, 162.97, 116.29, 98.34, 52.78, 21.15, 19.13.



GSCB54

2-benzoyl-3,3-*bis*(methylsulfanyl)-acrylonitrile (GSCB 76): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91-7.87 (m, 2H); 7.57 (tt, J = 7.2 and 1.5 Hz, 1H); 7.49-7.44 (m, 2H); 2.77 (s,

3H); 2.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.27; 179.46; 136.57; 133.29; 129.14; 128.52; 117.55; 105.96; 20.21; 19.56.



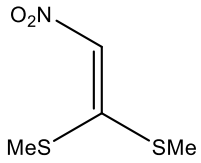
GSCB76

2.4 Preparation of 1,1-dimethylsulfanyl-2-nitroethene

To a 250 mL flask containing 25mL ethanol, nitromethane (0.163 mol, 9.95 g), carbon disulfide (0.250 mol, 19.00 g), with magnetic stirring at a temperature of 25 ˚C. A solution of potassium hydroxide (0.350 mol, 19.6 g) in ethanol (100 mL) was added dropwise after the mixture had been stirred for 15 minutes. The stirring was continued for 30 more minutes, while maintaining the same temperature.

Without first purifying it, the red precipitate was collected, washed with ethanol (30 mL) and diethyl ether (20 mL), and then solubilized in 40% aqueous methanol (200 mL). Dropwise additions of dimethyl sulfate (0.224 mol, 28.22 g) were made after the solution had been cooled to 0 °C. At room temperature, the reaction mixture was agitated for two hours. Water (200 mL) was added to stop the reaction, and the precipitate that resulted was filtered before being washed with water and dried under reduced pressure. Yellow solid (14.59) g of 1,1-dimethylsulfanyl-2-nitroethene was produced with a 54% yield (SANGI et al., 2019).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 1H); 2.54 (s, 3H); 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.65; 125.11; 17.55; 15.09.



GSCB58

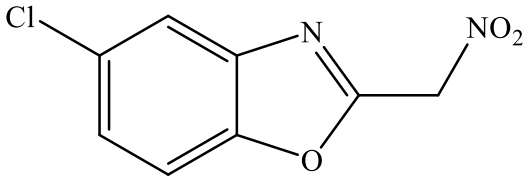
2.5 Synthesis of Benzoxazole Nuclei through Nucleophilic Double Substitution

The development of the reaction was monitored by CCD throughout the hour-long microwave treatment of a suspension of polarized ethenodithioacetal (1 mmol) and 2-aminophenols (1 mmol) in ethanol (3 mL).

At the end of the reaction, the precipitates containing the benzoxazoles were created. If necessary, these precipitates may be removed by conventional filtration and subsequently purified using column chromatography.

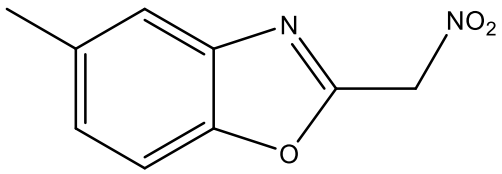
Following irradiation, the solvent was evaporated in the case of benzoxazoles GSCB 01 and 02, and the product was subsequently purified using column chromatography on silica gel with dichloromethane as the eluent (SANGI et al., 2014).

5-chloro-2-(nitromethyl) benzoxazole (GSCB 01): 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 1H, J = 2.12); 7.54 (dd, 1H, J = 8.49); 7.44 (dd, 1H, J = 8.49 and 2.12); 5.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.26; 149.90; 141.67; 130.97; 127.34; 121.04; 112.07; 71.48.



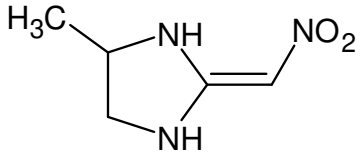
GSCB01

5-methyl-2-(nitromethyl) benzo-[d]-oxazole (GSCB 02): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.50 (s, 3H), 5.78 (s, 2H), 7.25-7.29 (m, 1H), 7.47 (d, 1H, J = 8.37 Hz), 7.57-7.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.48, 71.70, 110.58, 120.82, 128.06, 135.32, 140.84, 153.97.



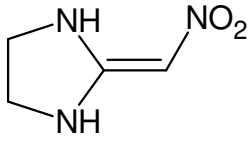
GSCB02

4-methyl-2-(nitromethylene) imidazolidine (GSCB 03): Yield 95%. ^{1}H NMR (500 MHz,dmso) δ 8.25 (m, 2H), 6.31 (s, 1H), 4.03 (m, 1H), 3.72 (t, *J* = 9.8 Hz, 1H), 3.16 (dd, *J* = 9.8, 7.3 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H).



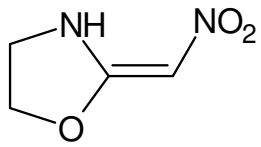
GSCB03

2-(nitrometilene)imidazolidine (GSCB 05):Yield 98%. RMN ^{1}H (400 MHz, MeOD): *δ* 6,57 (s, 1H); 3,75 (s, 4H). ^{13}C NMR (100 MHz, MeOD): *δ* 162,53; 98,13; 44,63.



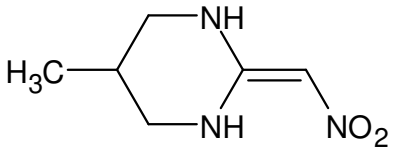
GSCB05

2-(nitrometilene)oxazolidine (GSCB 06): Yield 95%. RMN ^{1}H (400 MHz, DMSO-d^{6}): δ6,53 (s, 1H); 3,56-3,14 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d^{6}): δ 156,75; 97,69; 59,92; 44,71.



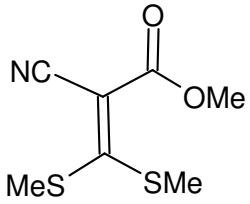
GSCB06

2-(nitrometilene) hexahydropirimidin-5-ol (GSCB 15): Yield 76%. RMN ^{1}H (500 MHz,DMSO-d^{6}) δ 8,80 (s, 2H); 6,28 (s, 1H); 5,27 (d, *J* = 3,5 Hz, 1H); 4,04 - 4,00 (m, 1H); 3,36 - 3,31 (m, 2H), 3,17 - 3,13 (m, 2H).^{13}C NMR (101 MHz, DMSO) δ 154.23, 98.47, 58.38, 44.57.



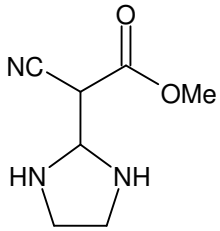
GSCB15

Methyl-2-cyano-3,3-*bis*(methylthio)acrylate (GSCB 54): Yield 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 3H), 2.68 (s, 3H), 2.53 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 181.61, 162.97, 116.29, 98.34, 52.78, 21.15, 19.13.



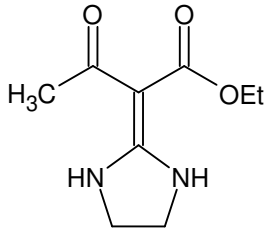
GSCB54

Methyl-2-cyano-2-(imidazolidin-2-ylidene) acetate (GSCB 55): Yield 80%. RMN ^{1}H (300 MHz, DMSO-d^{6}) δ 3,53 (s, 4H); 3,42 (s, 3H). RMN ^{13}C (75 MHz, DMSO-d^{6}) δ 167,98; 165,59; 119,84; 51,87; 50,75; 43,65.



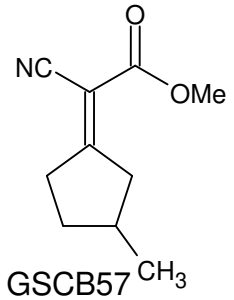
GSCB55

Ethyl-2-(imidazolidin-2-ylidene)-3-oxobutanoate (GSCB 56): Yield 83%. ^{1}H NMR (500MHz, cdcl$_3$) δ 9.13 (s, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.63 (s, 3H), 2.35 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 196.17, 170.12, 167.34, 87.77, 59.48, 42.90, 31.83, 14.67.



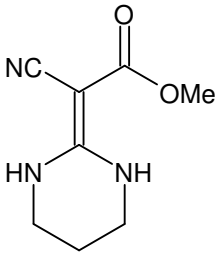
GSCB56

Methyl-2-cyano-2-(4-methylimidazolidin-2-ylidene) acetate (GSCB 57): Yield 93%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 5.84 (s, 1H), 4.17 – 4.01 (m, 1H), 3.76 (t, J = 9.3 Hz, 1H), 3.63 (s, 3H), 3.22 (d, J = 9.3, 7.4 Hz, 1H), 1.26 (d, J = 6.3 Hz, 3H).



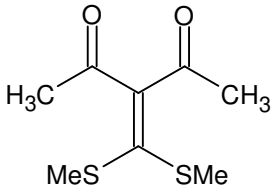
GSCB57

Methyl 2-cyano-2-(tetrahydropirimidin-2(1H)-ylidene)acetate (GSCB 59): Yield 77%. RMN ^{1}H (500 MHz, $CDCl_3$) δ 9,02 (s, 1H); 5,85 (s, 1H); 3,60 (s, 3H); 3,33-3,30 (m, 4H); 1,90 (q, J 6,0 Hz, 2H).



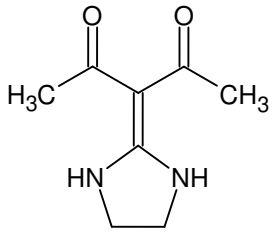
GSCB59

3-(*bis*(methylthio)methylene) pentane-2,4-dione (GSCB 60): Yield 59%. ^{1}H NMR (500 MHz, $cdcl_3$) δ 2.39, 2.36.



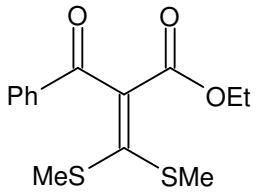
GSCB60

3-(imidazolidin-2-ylidene) pentane-2,4-dione (GSCB 61): Rendimento de 89%. RMN ^{1}H (300 MHz, $CDCl_3$) δ 9,65 (s, 2H); 3,67 (s, 4H); 2,39 (s, 6H). RMN ^{13}C (75 MHz, $CDCl_3$) δ 196,25; 166,92; 102,06; 42,71; 32,04.



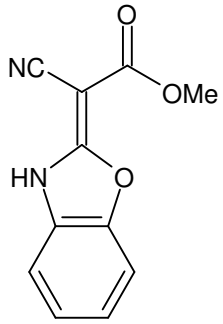
GSCB61

Ethyl-2-benzoyl-3,3-bis(methylthio)acrylate (GSCB 62): Yield 74%. ^{1}H NMR (300 MHz, $cdcl_3$) δ 7.93 – 7.86 (m, 2H), 7.61 – 7.53 (m, 1H), 7.50 – 7.42 (m, 2H), 4.18 – 4.09 (q, J = 7.1 Hz, 2H), 2.52 (s, 3H), 2.23 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.58, 163.28, 157.06, 137.05, 133.26, 132.48, 129.08, 128.60, 61.17, 19.43, 17.26, 13.94.



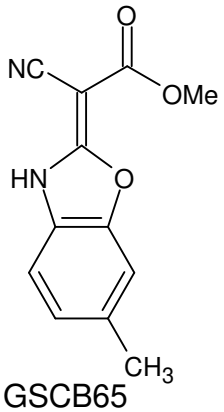
GSCB62

Methyl-2-(benzo[d]oxazol-2(3H)-ylidene)-2-cyanoacetate (GSCB 64): Yield 85%. NMR ^{1}H (300 MHz, DMSO-d6) δ 12,95 (s, 1H); 7,66 – 7,63 (m, 1H); 7,46 – 7,42 (m, 1H); 7,34 (dt, J 7.5 e 1.5 Hz, 1H); 7,30 – 7,24 (dt, J 7.5 e 1.5 Hz, 1H); 3,72 (s, 3H). NMR ^{13}C (75 MHz, DMSO-d6) δ 166,30; 165,68; 146,13; 130,63; 126,08; 124,46; 116,73; 112,96; 111,07; 56,28; 51,72.



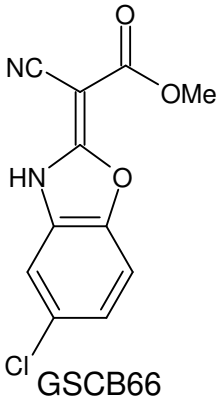
GSCB64

2-cyano-2-(6-methylbenzo[d]oxazol-2(3H)-ylidene)acetate (GSCD 65): Yield 65%.RMN 1H (300 MHz, DMSO-d6) δ 12,71 (s, 1H); 7,46 (s, 1H); 7,29 (d, J 8,0 Hz, 1H); 7,13 (d, J 8,0 Hz, 1H); 3,71 (s, 3H); 2,36 (s, 3H). RMN 13C (75 MHz, DMSO-d6) δ 166,35; 165,48; 146,34; 134,48; 128,35; 126,62; 116,83; 112,44; 111,24; 55,98; 51,65; 21,36.



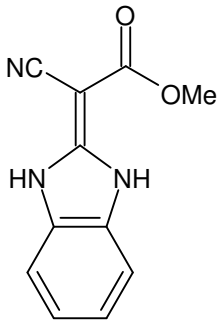
GSCB65

Methyl 2-(5-clorobenzo[d]oxazol-2(3H)-ilideno)-2-cyanoacetate (GSCB 66): Yield28%. ^{1}H NMR (300 MHz, DMSO) δ 7.67 (d, J = 8.7 Hz, 1H), 7.37 (d, J = 1.8 Hz, 1H), 7.30 (dd, J 8.7, 2.1 Hz, 1H), 3.72 (s, 3H).13C NMR (75 MHz, DMSO) δ 166.42, 166.14, 145.17, 132.27, 129.97, 124.10, 116.38, 112.62, 112.40, 56.94, 51.83.



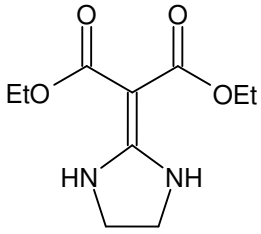
GSCB66

Methyl 2-cyano-2-(1,3-dihydro-2H-benzo[d]imidazol-2-ylidene) acetate (GSCB 69):Yield 77%. RMN ^{1}H (300 MHz, DMSO-d^{6}) δ 12,34 (s, 2H); 7,40 (dd, *J* 5.5 and 3.2 Hz, 2H); 7,22 – 7,12 (m, 2H); 3,66 (s, 3H). RMN ^{13}C (75 MHz, DMSO-d^{6}) δ 167,66; 152,91; 131,37; 123,28; 119,75; 111,89; 51,47; 50,95.



GSCB69

Diethyl 2-(imidazolidin-2-ylidene) malonate (GSCB 83): Yield 96%. ^{1}H NMR (300 MHz, DMSO-d^{6}) δ 8.38 (s, 2H), 3.99 (q, *J* = 7.1 Hz, 4H), 3.52 (s, 4H), 1.16 (t, *J* = 7.1Hz, 6H). ^{13}C NMR (75 MHz, dmso) δ 168.90, 166.50, 73.45, 58.73, 43.31, 14.80.



GSCB83

2.6 Application of Benzoxazoles

Due to their structural resemblance to the bases adenine and guanine, benzoxazoles can react with biomolecules found in living systems. These substances have antibacterial, anti-inflammatory, analgesic, and anti-hyperglycaemic effects. They also have central nervous system and anti-hyperglycaemic effects (KAKKAR *et al*., 2018). Moreover, it can serve as a building block for other bioactive compounds (Osmaniye et al., 2021). New generations of benzoxazoles were found to have altered biological

profiles and structural changes that made them more powerful and had higher biological activity (LAEEQ et al., 2013).

These substances haven't gotten much attention in terms of their prospective utility in agrochemical research as a result of their widespread use in pharmacological chemistry, minimal cytotoxicity, and the ease with which they can be made into benzoxazole derivatives which are capable of being used as herbicides with selective potential (JYOTHI & MERUGU, 2017).

2.7 Benzoxazole Herbicides

Herbicides are substances that are applied to undesired plants, such as weeds, to control or destroy them. Depending on the type of herbicide applied as well as the species and growth stage of the weed, different herbicides have different effects on different types of weeds.

Herbicides typically function by obstructing a plant's regular growth and development. Some herbicides can cause plants to produce less energy and eventually perish by interfering with the process of photosynthesis in plants. Other herbicides prevent the synthesis of specific hormones or enzymes in plants, which can likewise impair the growth and development of plants (CHRISTINE LEHMAN, 2019).

Herbicides can be used in a variety of methods to treat weeds, including spraying, sprinkling, and injection. Herbicides' effects on weeds might also vary depending on how they are applied. For instance, some herbicides are meant to get through the weed's leaves, while some are intended to pass through its roots (VATS, 2015).

Herbicides are often used to specifically target and eliminate weeds while causing the least amount of harm to beneficial plants and the environment.

Herbicides that are related to benzoxazoles are a type of herbicide used to manage weeds in a variety of crops. Herbicides derived from benzoxazole include clomazone, oxadiazon, and dichlormid, to name a few (KOOKANA et al., 2011).

2.8 Mode of Action

In addition, herbicides can be divided into groups according to whether they affect plants before or after germination.

Pre-germination herbicides are applied on plant bed or soil before weed seeds have a chance to sprout. They are made to build a wall or zone of inhibition that keeps weed

seeds from sprouting. Pre-germination herbicides may function by preventing the germination of the seedling from dividing cells, synthesizing proteins, or engaging in other metabolic activities (OLIVEIRA et al., 2020).

Post-germination contact herbicides: These are herbicides that are sprayed on leaves or other above-ground plant components after they have emerged from the soil. Contact herbicides can operate swiftly and kill or harm the target plant's foliage, but they might not have an impact on the plant's roots or other sections. Contact herbicides may function by interfering with the plant's cell membranes, photosynthesis, or other biological functions (TRIGUEIRO et al., 2007).

Post-germination systemic herbicides: After germination, these herbicides are likewise applied to the leaves or other above-ground plant components, but they are made to be absorbed and distributed throughout the entire plant. Systemic herbicides, which are particularly powerful against persistent weeds, can attack the entire plant, including the roots. Systemic herbicides may function by disrupting the plant's ability to synthesize amino acids, maintain hormone balance, or carry out other metabolic processes (TRIGUEIRO *et al*., 2007).

Burndown herbicides: In order to rid the field of weeds or other vegetation, these herbicides are administered to vegetation before planting or before a crop emerges. Burndown herbicides, which are frequently used in no-till or minimal tillage systems, may work by desiccating or drying out the vegetation or by interfering with cellular functions in the plant (QI et al., 2020).

2.8.1 Herbicide Selectivity and Type of Leaf (cotyledon)

A plant's sensitivity to or resistance to particular herbicides can depend on the sort of cotyledon (seed leaf) that it has. Monocotyledons (monocots) and dicotyledons (dicots) are the two primary categories of cotyledons.

Plants like grasses, corn, and wheat are examples of monocots, which have only one seed leaf. Plants like beans, peas, and the majority of broadleaf weeds are dicots, which contain two seed leaves (ABDELGAWAD et al., 2021).

Selective or non-selective herbicides are both possible. While selective herbicides are made to solely kill specific kinds of plants, non-selective herbicides will destroy any plant they come into contact with.

While certain herbicides are more effective against monocots than they are against dicots, some are the opposite. For example, the herbicide glyphosate (Roundup) is a non-selective herbicide that targets both monocots and dicots. Yet, it works better on dicots than on monocots (Fogliatto et al., 2020).

The herbicide sethoxydim, on the other hand, is a selective herbicide which primarily affects monocot grassland weeds. Dicots, which have a different kind of cell membrane that is resistant to sethoxydim, are not susceptible to this herbicide (Belkebir et al., 2006). Therefore, since herbicides may be made to target particular kinds of plants based on their cotyledon type, the type of cotyledon a plant has can have an impact on herbicide selectivity.

2.8.2 Herbicide Selectivity and Structure

It was discovered that new generations of benzoxazoles have different biological features and structural alterations that increased their potency and biological action. For instance, dicamba, a benzoxazole herbicide prefers broadleaf weeds to grasses when used as a weed killer. Due to the existence of a carboxylic acid functional group, which enables it to be translocated throughout plants and aggregate in the meristematic tissue of dicots, killing them, dicamba has a selectivity (PAL et al., 2018).

Although benzobicyclon, a separate benzoxazole herbicide, is also selective for broadleaf weeds, its selectivity is caused by a distinct structural characteristic. Due to benzobicyclon's bicyclic ring structure, which makes it easier for dicots to absorb than monocots, it prefers broadleaf weeds over grasses (HU et al., 2022).

Therefore, a benzoxazole herbicide's structure can influence its selectivity by affecting its mode of action and absorption inside the plant, enabling it to specifically target particular weed species yet mostly sparing the intended crop.

CHAPTER 3

BIOANALYSIS OF SOME POLYFUNCTIONAL COMPOUNDS FOR THEIR SELECTIVE HERBICIDAL POTENTIAL ON FIVE DIFFERENT PLANTS: LETTUCE (*Lactuca sativa* L.), RYEGRASS (*Lolium multiflorum*), BRACHIARIA (*Brachiaria* ssp), CUCUMBER (*Cucumis sativus* L.), AND SORGHUM (*Sorghum bicolor* L.)

3.0 METHODOLOGY

3.1 Materials:

Pipettes (5 mL, 10 mL, and 20 mL);

Volumetric flasks (1000 mL, 200 mL, and 100 mL);

Petri dishes (3-inch diameter);

Germination papers;

Stretching boards (14 cm X 20 cm);

Incubator (BOD);

Freezer;

DMSO (Sigma Aldrich).

3.2 Methods

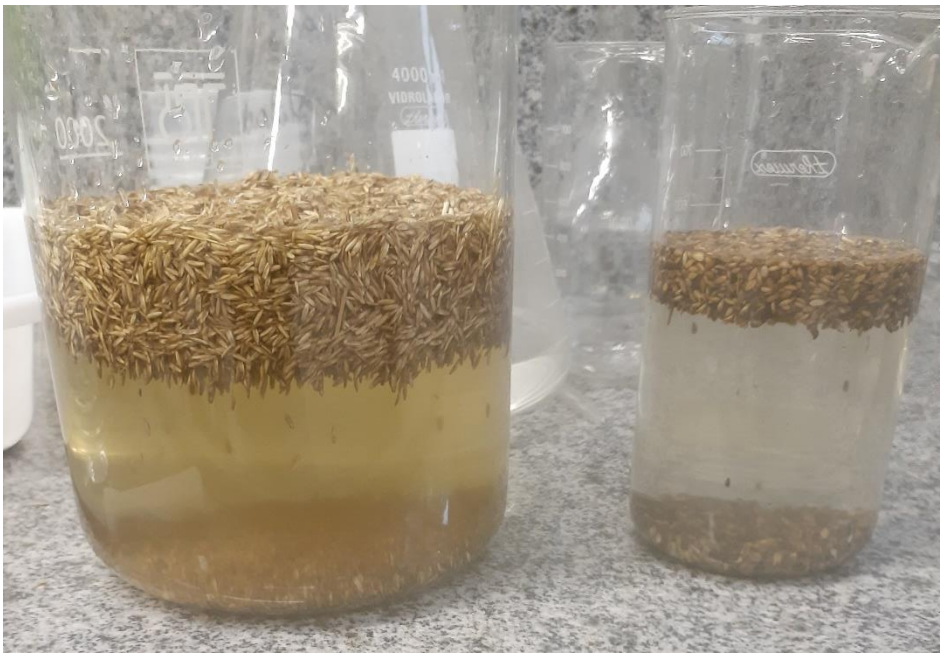
3.2.1 Sample collection

Samples of lettuce and cucumber were purchased from agrochemical vendors, while ryegrass, brachiaria, and sorghum were purchased from local farmers within the state of Minas Gerais, Brazil.

3.2.2 Sample Preparation

Samples of lettuce and cucumber are well preserved in airtight packages, while that of brachiaria and ryegrass were washed with water to remove excess dirt, then immersed in water for 24 hours.

Figure 6 - Seed screening process.



Source: the author.

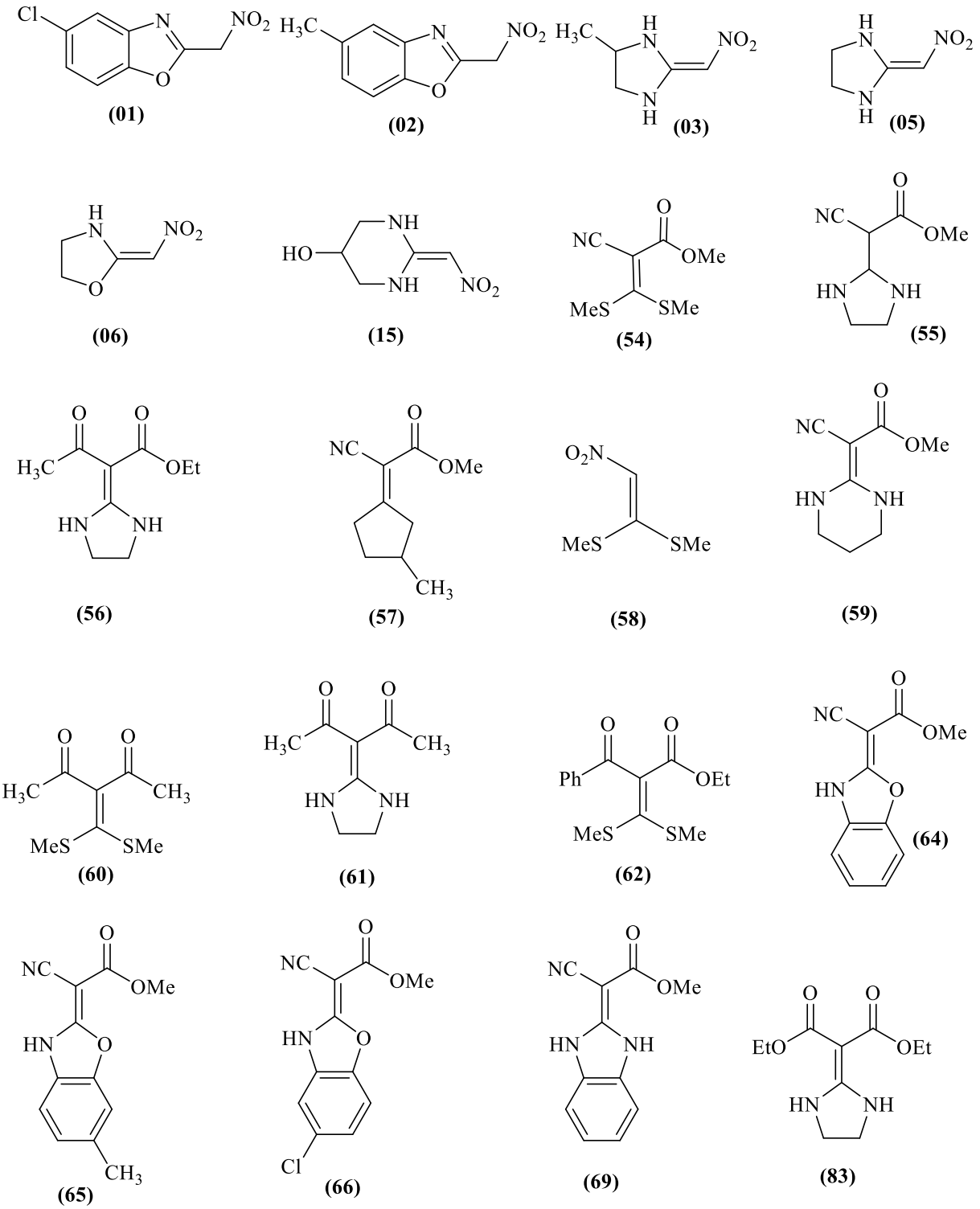
Good seeds settled at the bottom, while bad ones floated and were removed. Excess water was removed from the good seeds using paper towel and then allowed to air dried completely to prevent undesired germination.

Solution Preparation

DMSO: 0.3% DMSO was prepared by pipetting 3 mL of DMSO into a 1000 mL volumetric flask, it was the filled with distilled water up to the mark

Stock: For each compound, the highest concentration was set at 500 micromoles (µM). From this concentration, solutions of 300 µM, 150 µM, 75 µM, and 50 µM were prepared. To create a 500 µM solution in a 200 mL volumetric flask, the required amount was determined based on the molar mass of the compound. The compound was weighed and transferred into the 200 mL flask, which was then filled to the mark with distilled water. Once the 500 µM solution was prepared in the 200 mL flask, 60 mL, 30 mL, 15 mL, and 10 mL aliquots were pipetted into separate 100 mL flasks to obtain concentrations of 300 µM, 150 µM, 75 µM, and 50 µM, respectively. Distilled water was added to each flask to reach the mark.

Figure 7 - The Structures of the Polyfunctional compounds.



Source: the author.

3.2.3 Bioassay

Alcohol was passed through the petri dishes and their lids in order to sterilize them from any contaminant. The germination paper, that was cut to fit the petri dish, were then be put into the dishes. Twenty number seeds were counted into 21 dishes for each of *Lettuce, Ryegrass, Brachiaria, Cucumber* and *Sorghum*; 3 dishes were labelled for each of DMSO, water, 500 μM, 300 μM, 150 μM, 75 μM and 50 μM.

Figure 8 - Seeds being prepared for germination

Source: the author.

5 mL of each of the above-mentioned solutions were added into the dishes. The dishes were sealed with cling film and kept in an incubator (BOD) for five days in the case of lettuce, brachiaria, cucumber, and sorghum; and fourteen days in the case of ryegrass.

After the germination, the seeds were frozen in a freezer for a period of 24 hours to stop their growth. They were then stretched on a 14 cm by 20 cm boards and their digital image captured.

Figure 9 - The researcher stretching the germinated seed for subsequent measurements.

Source: the author.

Figure 10 - Cucumber seeds stretched on the board at 500, 300 and 150 μM concentration.

Source: the author.

A digital measurer was used to measure the stem and root lengths of the seeds. Using aqueous DMSO (0.3 v/v) as the control, the percentage difference in length can be computed to determine the impact of benzoxazole derivatives on the seeds.

CHAPTER 4

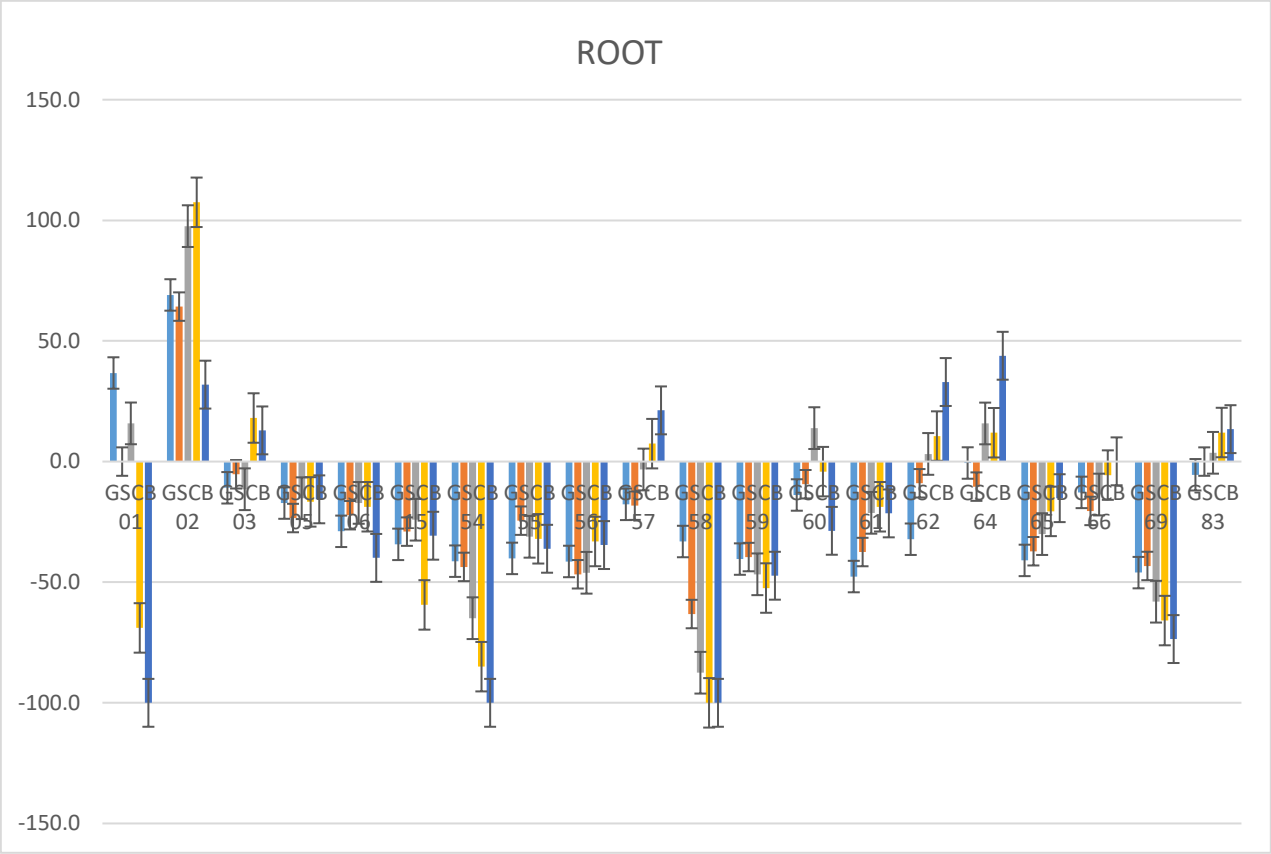
RESULTS AND DISCUSSION

Table 2 - Percentage root elongation in lettuce with respect to the control.

INHIBITION: LETTUCE ROOT					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	36.7	0.00	15.8	-68.9	-100.0
GSCB 02	69.1	64.2	97.6	107.5	31.9
GSCB 03	-10.9	-5.3	-11.5	18.1	12.9
GSCB 05	-17.2	-23.4	-15.2	-16.7	-15.7
GSCB 06	-28.9	-22.2	-17.1	-18.7	-39.9
GSCB 15	-34.3	-29.0	-24.1	-59.4	-30.7
GSCB 54	-41.3	-43.7	-64.9	-85.0	-100.0
GSCB 55	-40.1	-24.5	-31.2	-32.0	-36.1
GSCB 56	-41.4	-46.7	-46.1	-33.1	-34.6
GSCB 57	-17.7	-18.3	-3.3	7.4	21.2
GSCB 58	-33.1	-63.2	-87.5	-100.0	-100.0
GSCB 59	-40.4	-39.6	-46.7	-52.4	-47.3
GSCB 60	-13.9	-9.4	13.9	-4.2	-28.7
GSCB 61	-47.7	-39.6	-21.2	-18.7	-21.5
GSCB 62	-32.2	-9.0	3.2	10.6	33.0
GSCB 64	-0.6	-10.4	15.8	12.0	43.9
GSCB 65	-41.0	-37.2	-30.1	-20.6	-15.2
GSCB 66	-12.8	-20.5	-13.7	-5.6	0.1
GSCB 69	-46.0	-43.3	-58.1	-65.9	-73.6
GSCB 83	-5.5	0.00	3.6	12.1	13.4

Source: the author

Figure 11 – A graph showing the root elongation in lettuce.



Source: the author.

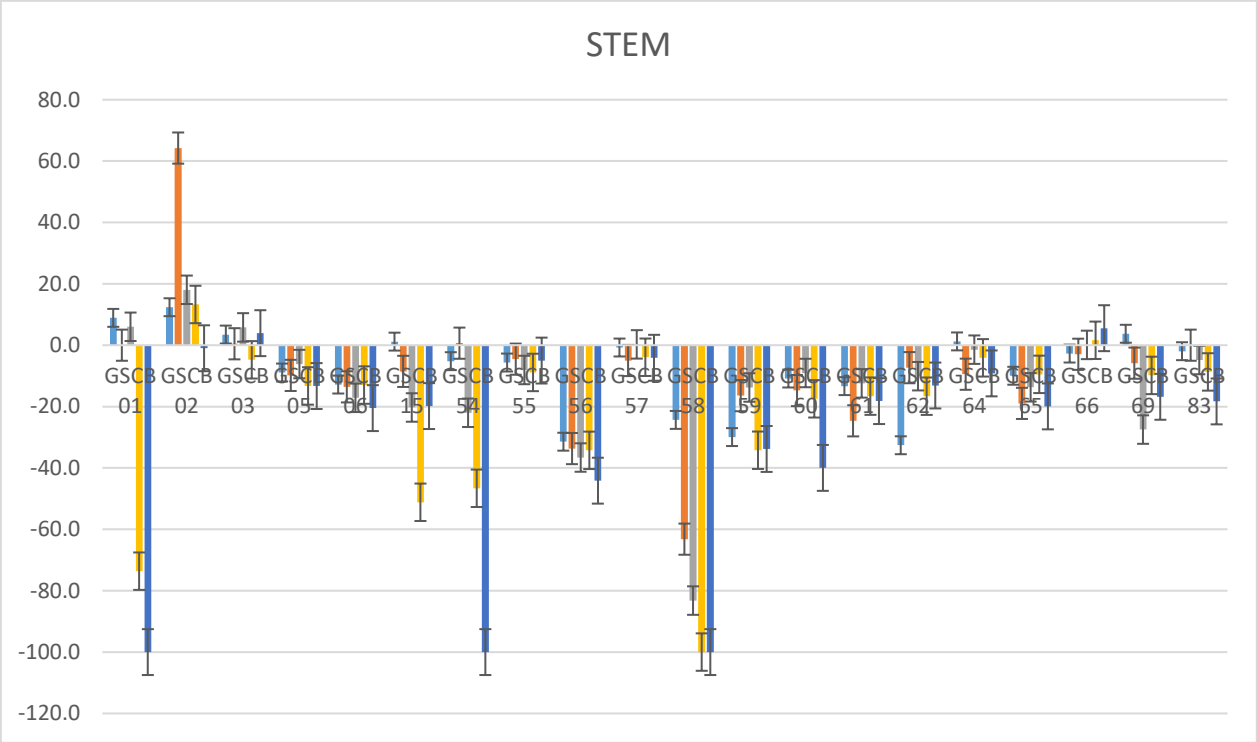
The result above demonstrate the impact of Benzoxazole derivatives on the root elongation of Lettuce seeds. While most of the compounds show significant inhibition with GSCB 01, 54, and 58 having up to 100% at high concentrations, GSCB 02 shows more than 100% stimulation at high concentration. The rest of the compounds showed an average inhibition of about 50%, with GSCB 03, 04, and 57 having much insignificant inhibitions, almost resulting in poor stimulation in GSCB 57 at higher concentrations. In GSCB 54, a successive inhibition was observed as the concentration of the compound decreases, yet GSCB 58 has the highest inhibition observed among all the test compounds.

Table 3 – Percentage stem elongation in lettuce with respect to the control.

INHIBITION: LETTUCE STEM					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	8.9	0.00	6.0	-73.6	-100.0
GSCB 02	12.4	64.2	18.1	13.3	-1.0
GSCB 03	3.5	0.5	5.8	-4.8	3.9
GSCB 05	-8.9	-9.8	-6.1	-13.3	-13.3
GSCB 06	-12.8	-13.6	-17.1	-13.0	-20.5
GSCB 15	1.2	-8.5	-20.3	-51.2	-19.8
GSCB 54	-5.2	0.7	-22.0	-46.6	-100.0
GSCB 55	-5.6	-4.5	-8.1	-8.9	-5.0
GSCB 56	-31.4	-33.7	-36.6	-34.3	-44.1
GSCB 57	-0.8	-5.0	0.3	-3.9	-4.1
GSCB 58	-24.3	-63.2	-83.2	-100.0	-100.0
GSCB 59	-29.9	-16.4	-13.8	-34.2	-33.8
GSCB 60	-10.9	-14.8	-9.1	-17.5	-40.0
GSCB 61	-13.3	-24.6	-12.4	-16.6	-18.2
GSCB 62	-32.6	-7.3	-10.1	-16.6	-13.1
GSCB 64	1.2	-9.5	-1.5	-4.1	-9.2
GSCB 65	-10.0	-19.0	-13.7	-9.5	-19.9
GSCB 66	-2.7	-3.0	0.1	1.6	5.5
GSCB 69	3.7	-5.8	-27.5	-9.8	-16.8
GSCB 83	-2.0	0.00	-4.8	-8.7	-18.3

Source: the author.

Figure 12 - A graph showing the stem elongation in lettuce.



Source: the author.

When take a look at the grapha above, we can see that the stem elongation also agrees with that of the root. Compound GSCB 01, 54, and 58 have shown great inhibition of up to 100% at 500 µM concentrations, with GSCB 58 maintaining that percentage up to 300 µM. GSCB 02 shows stimulation of 64.2% at 75 µM concentration, with GSCB 03 showing much less stimulation on stem elongation. GSCB 15, 56, and 59 presented an average inhibition, while GSCB 05, 06, 55, and 57 showed much less inhibition.

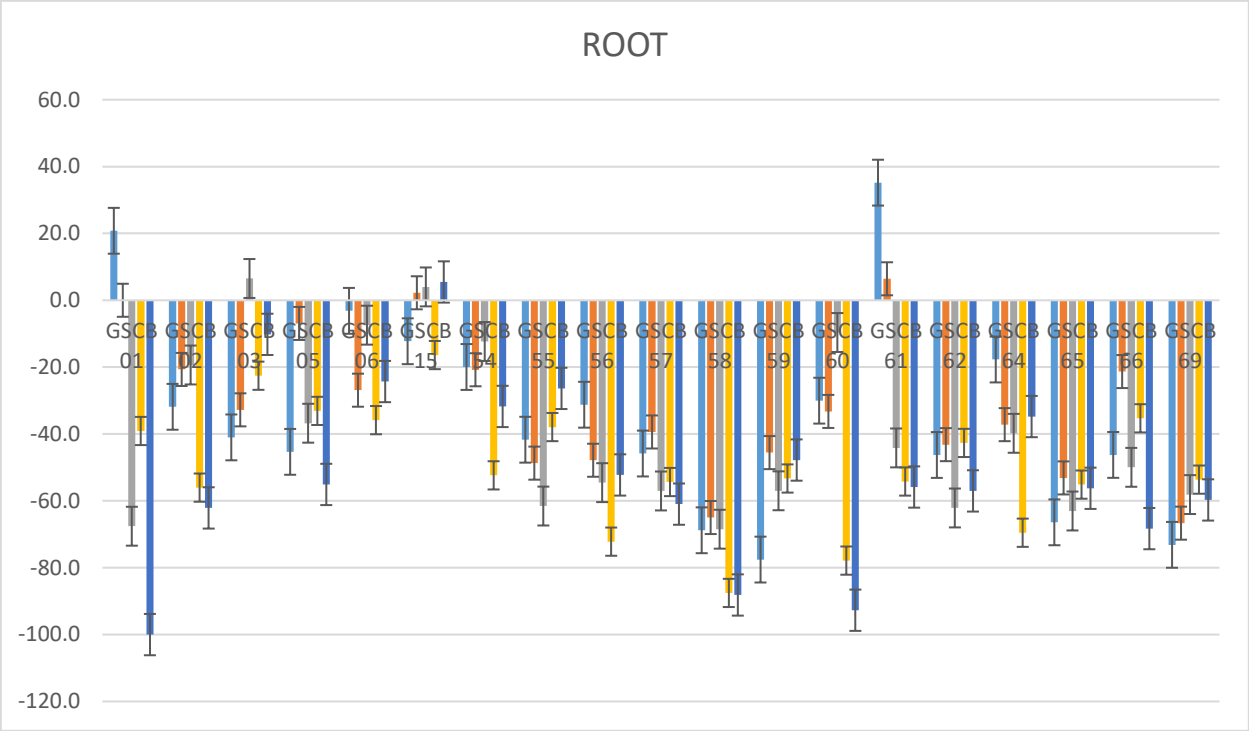
From the two graphs above we can deduce that compounds GSCB 01, 54, and 58 have good haerbicidal potential on lettuce seeds at 500 µM concentrations, whith GSCB 58 extending up 100%, >80%, and >60% at 300, 150, and 75 micro moles concentration respectively, in both root and stem elongation of lettuce seed.

Table 4 - Percentage root elongation in ryegrass with respect to the control.

INHIBITION: RYEGRASS ROOT					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	20.8	0.00	-67.6	-39.1	-100.0
GSCB 02	-31.9	-20.7	-19.4	-56.0	-62.1
GSCB 03	-41.0	-32.8	6.5	-22.6	-10.2
GSCB 05	-45.3	-6.9	-36.8	-33.1	-55.1
GSCB 06	-3.2	-26.9	-7.4	-35.9	-24.3
GSCB 15	-12.2	2.2	4.0	-16.4	5.5
GSCB 54	-20.0	-20.8	-12.3	-52.4	-31.8
GSCB 55	-41.7	-48.7	-61.5	-37.9	-26.4
GSCB 56	-31.2	-47.8	-54.6	-72.2	-52.2
GSCB 57	-45.8	-39.4	-57.0	-54.4	-61.0
GSCB 58	-68.8	-65.0	-68.5	-87.5	-88.1
GSCB 59	-77.6	-45.6	-57.0	-53.3	-47.8
GSCB 60	-30.0	-33.2	-9.6	-77.9	-92.7
GSCB 61	35.2	6.4	-44.2	-54.2	-55.9
GSCB 62	-46.3	-43.2	-62.1	-42.7	-57.0
GSCB 64	-17.7	-37.2	-39.8	-69.5	-34.8
GSCB 65	-66.4	-53.1	-63.0	-55.1	-56.2
GSCB 66	-46.3	-21.3	-50.0	-35.3	-68.3
GSCB 69	-73.2	-66.7	-58.1	-53.6	-59.7

Source: the author.

Figure 13 - A graph showing the root elongation in ryegrass.



Source: the author.

The graph above shows the percentage inhibition in root elongation of GSCB compounds at different concentrations in a ryegrass seed, with respect to the control. Looking at the results, we can see that all the compounds showed considerable inhibition and that none have stimulation. GSCB 01 has the highest percentage inhibition (100%) at 500µM followed by GSCB 58 with more than 80% at concentrations of 300 and 500 micro moles. GSCB 02, 05, 54, 55, 56, 57, and 59 have at least 50% inhibition at higher concentrations. The least among the compounds is GSCB 15 with less than 20% inhibition, seconded by GSCB 03 with percentage inhibition slightly above 40%.

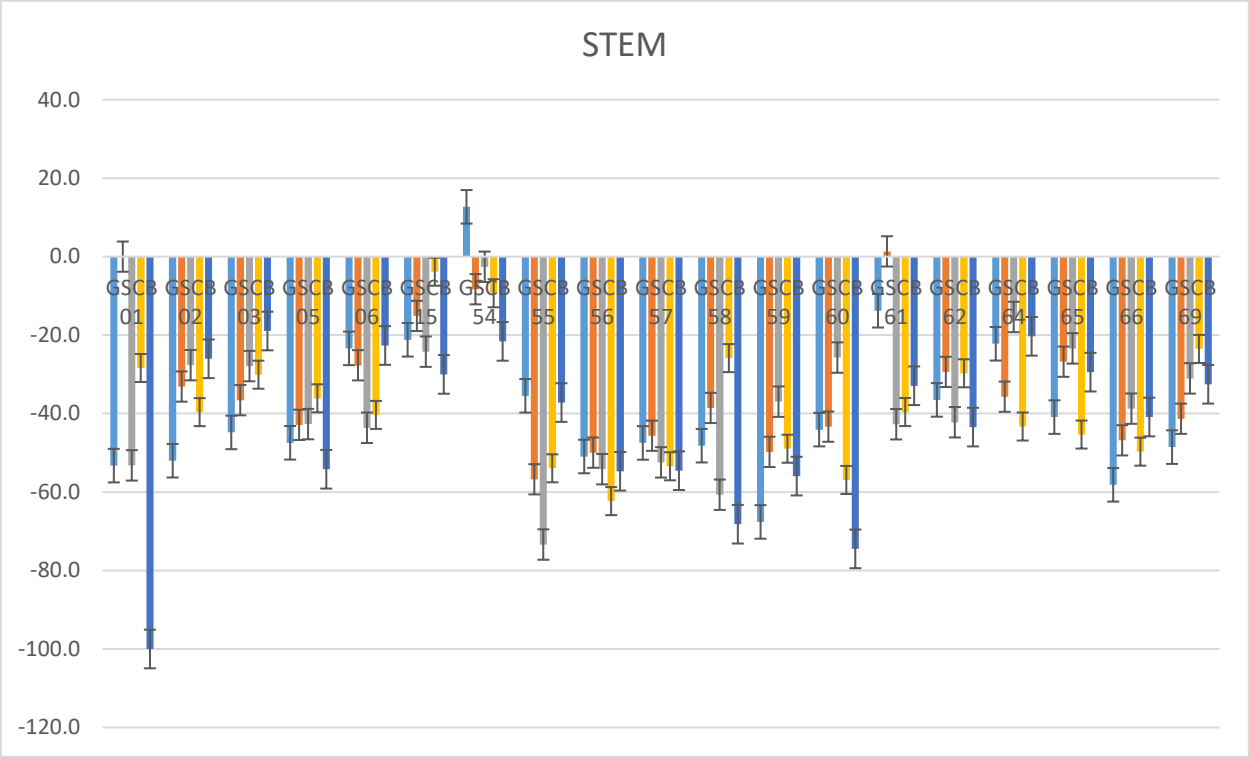
In general, the compounds under study have presented a very good herbicidal potential on root elongation of ryegrass.

Table 5 - Percentage stem elongation in ryegrass with respect to the control.

INHIBITION: RYEGRASS STEM					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	-53.3	0.00	-53.2	-28.4	-100.0
GSCB 02	-52.0	-33.1	-27.7	-39.6	-26.0
GSCB 03	-44.8	-36.6	-27.9	-30.1	-19.0
GSCB 05	-47.4	-42.9	-42.7	-36.1	-54.2
GSCB 06	-23.4	-27.7	-43.6	-40.3	-22.7
GSCB 15	-21.2	-15.1	-24.2	-3.8	-30.0
GSCB 54	12.7	-8.3	-2.6	-9.3	-21.6
GSCB 55	-35.5	-56.8	-73.4	-53.9	-37.2
GSCB 56	-50.9	-50.0	-54.2	-62.3	-54.7
GSCB 57	-47.5	-45.6	-52.4	-53.4	-54.6
GSCB 58	-48.2	-38.6	-60.7	-25.9	-68.2
GSCB 59	-67.6	-49.8	-37.0	-49.0	-55.9
GSCB 60	-44.1	-43.3	-25.7	-56.9	-74.5
GSCB 61	-13.8	1.3	-42.7	-39.6	-32.9
GSCB 62	-36.5	-29.4	-42.2	-29.7	-43.4
GSCB 64	-22.2	-35.7	-15.4	-43.3	-20.3
GSCB 65	-40.9	-26.8	-23.4	-45.3	-29.4
GSCB 66	-58.2	-46.8	-38.7	-49.7	-40.9
GSCB 69	-48.5	-41.3	-31.0	-23.5	-32.5

Source: the author.

Figure 14 - A graph showing the stem elongation in ryegrass.



Source: the author.

The above graph indicates the stem growth percentages of the compounds under test in five different concentrations, with respect to the control. In the same manner, GSCB 01 has the highest percentage inhibition of 100 at 500 micro moles, while GSCB 58 has almost 70 at the same concentration. Note that GSCB 55 and 59 have high percentage inhibition of 73.4 and 67.6 at 150 and 50 micro mole concentrations, respectively. The compounds with average percentage inhibition are GSCB 02, 05, 56 and 57 with at least 50% in one of their concentrations. The least percentage inhibition is observed in GSCB 54 with slightly above 20% at 500 micro moles concentration, which is seconded by GSCB 15 with 30% at the same concentration. The compound GSCB 06 has 43% inhibition as its highest at 150 μM concentration.

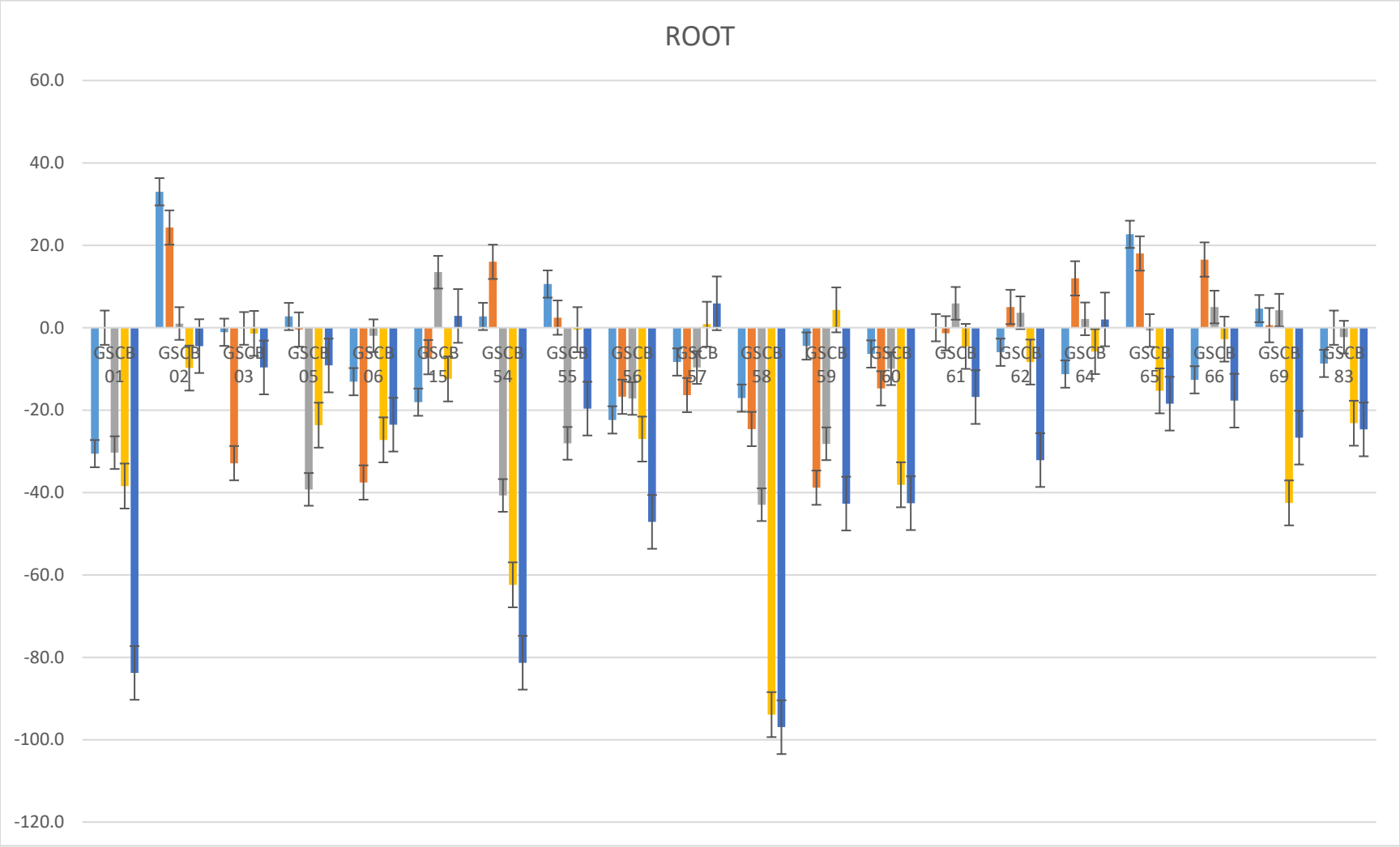
As reported earlier, ryegrass was collected from local farmers, which undergone screening process before tested for its inhibition. This might explain the little anomalies observed in the way it reacted to the compounds**.**

Table 6 - Percentage root elongation in brachiaria with respect to the control.

INHIBITION: BRACHIARIA ROOT					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	-30.6	0.00	-30.3	-38.4	-83.8
GSCB 02	33.0	24.3	1.0	-9.8	-4.5
GSCB 03	-1.1	-32.9	-0.2	-1.4	-9.7
GSCB 05	2.7	-0.4	-39.2	-23.7	-9.2
GSCB 06	-13.1	-37.6	-2.0	-27.2	-23.5
GSCB 15	-18.1	-7.2	13.5	-12.4	2.9
GSCB 54	2.7	16.0	-40.7	-62.4	-81.3
GSCB 55	10.6	2.4	-28.1	-0.5	-19.6
GSCB 56	-22.4	-16.8	-17.2	-27.0	-47.1
GSCB 57	-8.3	-16.4	-9.7	0.8	5.9
GSCB 58	-17.1	-24.6	-43.0	-93.9	-97.0
GSCB 59	-4.4	-38.8	-28.2	4.3	-42.7
GSCB 60	-6.4	-14.7	-10.0	-38.1	-42.6
GSCB 61	0.0	-1.4	5.9	-4.5	-16.8
GSCB 62	-6.0	5.0	3.6	-8.3	-32.1
GSCB 64	-11.3	12.0	2.1	-5.8	2.0
GSCB 65	22.7	18.0	-0.7	-15.3	-18.4
GSCB 66	-12.6	16.5	5.0	-2.8	-17.7
GSCB 69	4.6	0.6	4.3	-42.5	-26.7
GSCB 83	-8.7	0.00	-2.3	-23.2	-24.7

Source: the author.

Figure 15 A graph showing the root elongation in brachiaria.



Source: the author.

If we look at the above graph, we will notice high degree of inhibition in compounds GSCB 01, 54, and 58, as observed in the periously discussed seeds (lettuce and ryegrass) and on the root elonhgation of brachiaria. This further strengthen the fact that these threee compounds above, possess the requesite herbicidal potential, on the root elongation of the three different seeds/plants. And as always, higher percentage inhibition is experienced at higere concentrations; indicating direct proportionality. In GSCB 02, 65, and 66, stimulation was observed at lower concentrations, with poor inhibition at high concentrations. In the compounds GSCB 05, 06, 56, 69, and 83, mild inhibitions were observed at high concentrations, while in GSCB 03, 15, 55, and 57, it is between insignificant inhibition and poor stimulation projections.

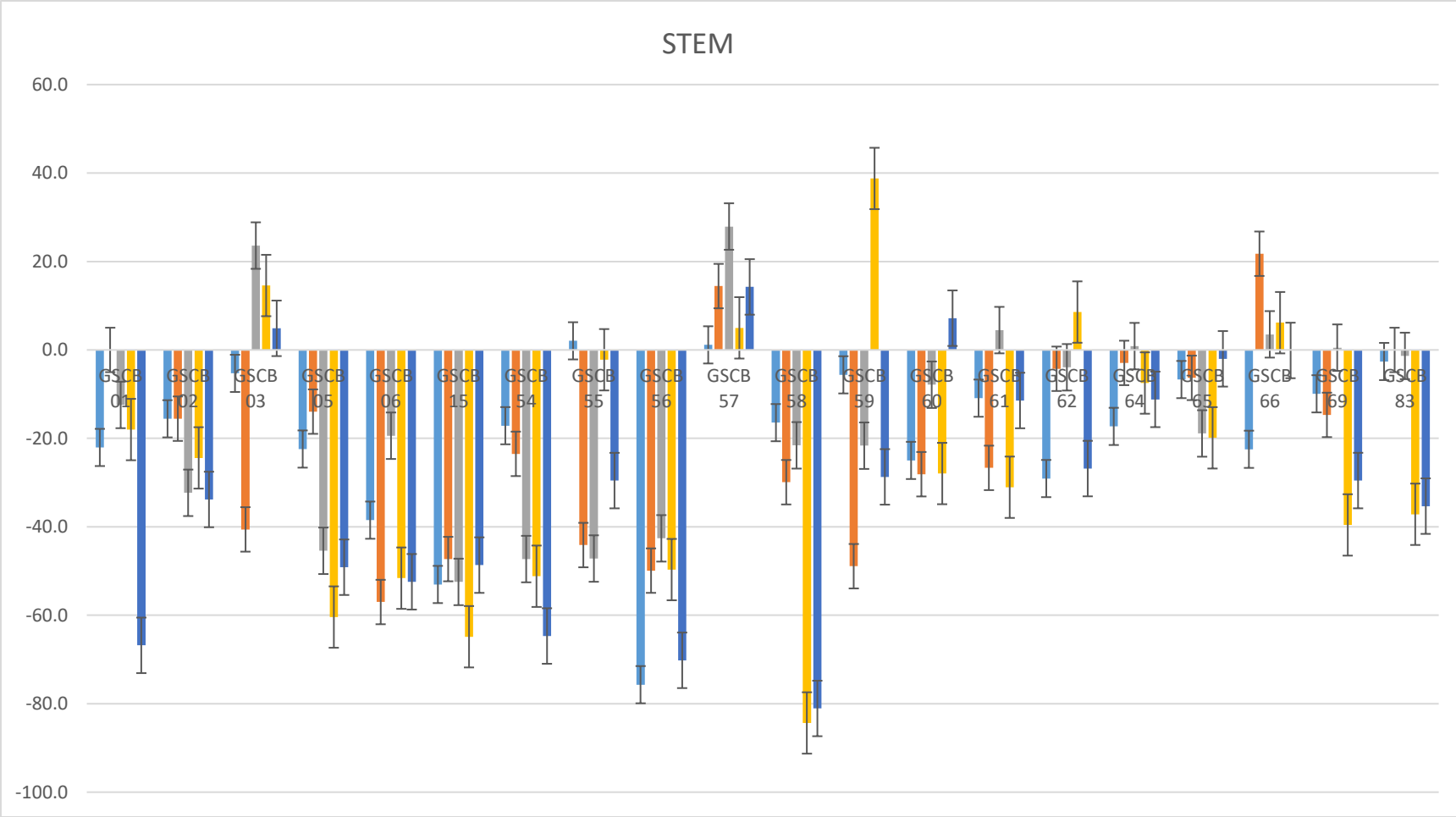
Brachiaria is a weed plant and a monocot, the general biological activity of the compounds tested showed inhibition on its root elongation.

Table 7 - Percentage stem elongation in brachiaria with respect to the control.

INHIBITION: BRACHIARIA STEM					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	-22.1	0.00	-12.4	-18.0	-66.8
GSCB 02	-15.6	-15.5	-32.3	-24.4	-33.8
GSCB 03	-5.3	-40.6	23.6	14.6	4.9
GSCB 05	-22.4	-14.0	-45.4	-60.4	-49.1
GSCB 06	-38.5	-57.0	-19.4	-51.6	-52.4
GSCB 15	-53.0	-47.3	-52.5	-64.9	-48.7
GSCB 54	-17.1	-23.5	-47.3	-51.2	-64.7
GSCB 55	2.1	-44.1	-47.2	-2.2	-29.5
GSCB 56	-75.7	-49.9	-42.6	-49.7	-70.2
GSCB 57	1.1	14.4	27.9	5.0	14.2
GSCB 58	-16.4	-29.9	-21.6	-84.4	-81.1
GSCB 59	-5.6	-48.9	-21.7	38.8	-28.7
GSCB 60	-25.0	-28.1	-7.9	-28.0	7.2
GSCB 61	-10.9	-26.7	4.5	-31.1	-11.4
GSCB 62	-29.1	-4.3	-3.9	8.6	-26.8
GSCB 64	-17.3	-2.9	0.9	-7.5	-11.2
GSCB 65	-6.7	-6.3	-18.9	-19.9	-2.0
GSCB 66	-22.5	21.8	3.5	6.2	-0.1
GSCB 69	-9.9	-14.7	0.5	-39.6	-29.5
GSCB 83	-2.6	0.00	-1.4	-37.2	-35.3

Source: the author

Figure 16 - A graph showing the stem elongation in brachiaria.



Source: the author.

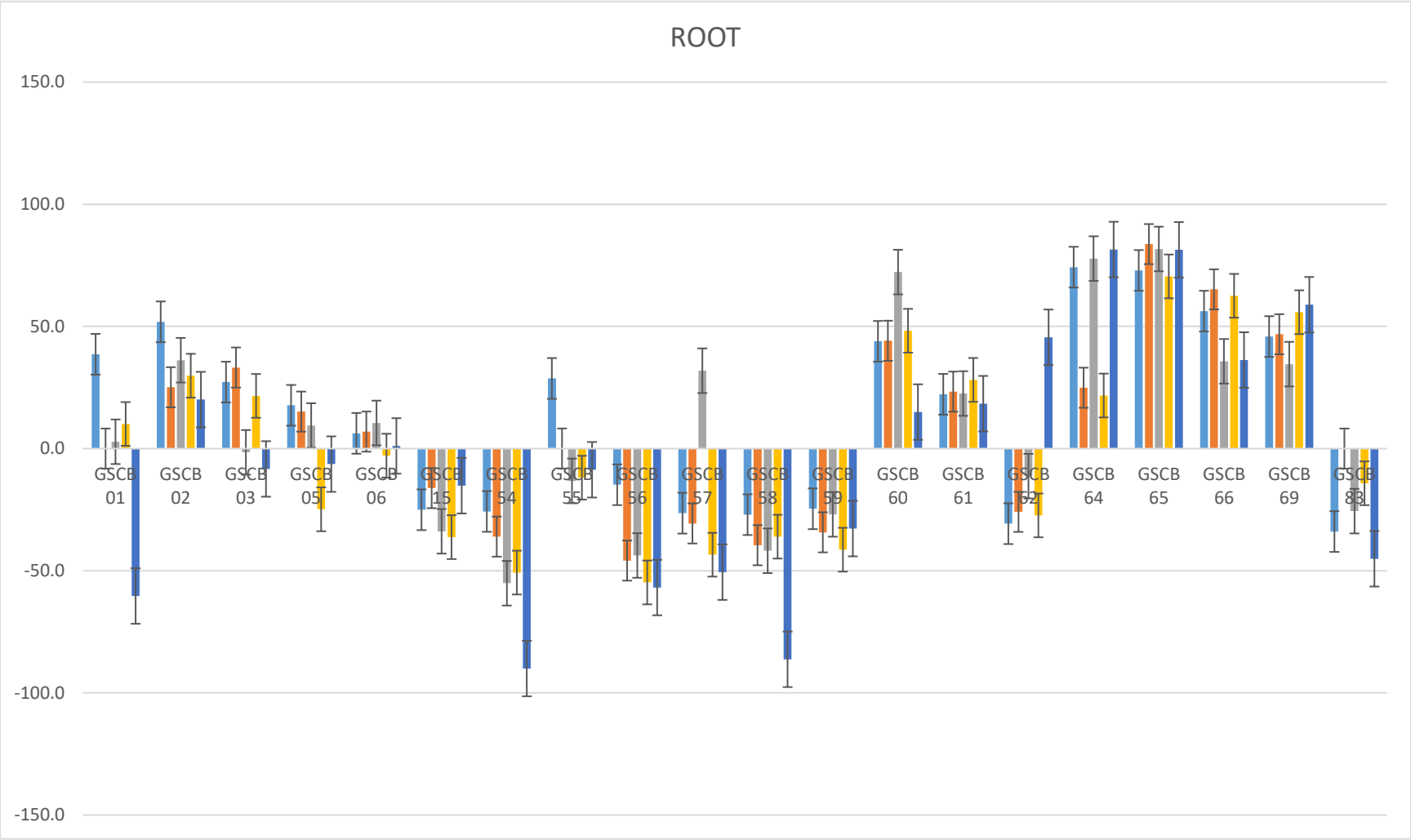
Looking at the graph above, we can observe that almost all the compounds exhibit between average and high inhibitions, except GSCB 57 which depicts stimulation in almost all of its concentrations. GSCB 01, 05, 06, 15, 54, 56 and 58 showed greater than or equal to 50% inhibition on the stem elongation of brachiaria seed. GSCB 02, 03, 55, 59, 60, 61, 62, 69, and 83, have percentage inhibitions between 02 and 49 in at least one of their concentrations. GSCB 59 and 66 showed some percentage stimulation at 300 μM and 75 μM concentrations respectively.

Table 8 - Percentage root elongation in cucumber with respect to the control.

INHIBITION: CUCUMBER ROOT					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	38.6	0.00	2.8	10.1	-60.4
GSCB 02	51.9	25.1	36.2	29.8	20.1
GSCB 03	27.2	33.2	-1.5	21.6	-8.3
GSCB 05	17.7	15.1	9.4	-24.9	-6.4
GSCB 06	6.2	6.9	10.5	-2.9	1.1
GSCB 15	-25.0	-16.2	-33.9	-36.3	-15.2
GSCB 54	-25.7	-36.0	-55.1	-50.8	-90.0
GSCB 55	28.7	0.0	-13.2	-11.9	-8.7
GSCB 56	-14.8	-45.8	-43.8	-54.8	-56.9
GSCB 57	-26.4	-30.6	31.9	-43.4	-50.6
GSCB 58	-27.0	-39.6	-41.8	-36.1	-86.3
GSCB 59	-24.6	-34.3	-26.9	-41.4	-32.8
GSCB 60	43.9	44.1	72.3	48.2	15.0
GSCB 61	22.2	23.3	22.5	28.1	18.4
GSCB 62	-30.7	-25.9	-11.3	-27.4	45.6
GSCB 64	74.3	24.9	77.8	21.7	81.5
GSCB 65	72.9	83.7	81.7	70.5	81.4
GSCB 66	56.3	65.2	35.7	62.5	36.3
GSCB 69	45.9	46.8	34.6	55.8	58.9
GSCB 83	-34.0	0.00	-25.6	-14.2	-45.1

Source: the author.

Figure 17 A - graph showing the percentage root elongation in cucumber.



Source: the author.

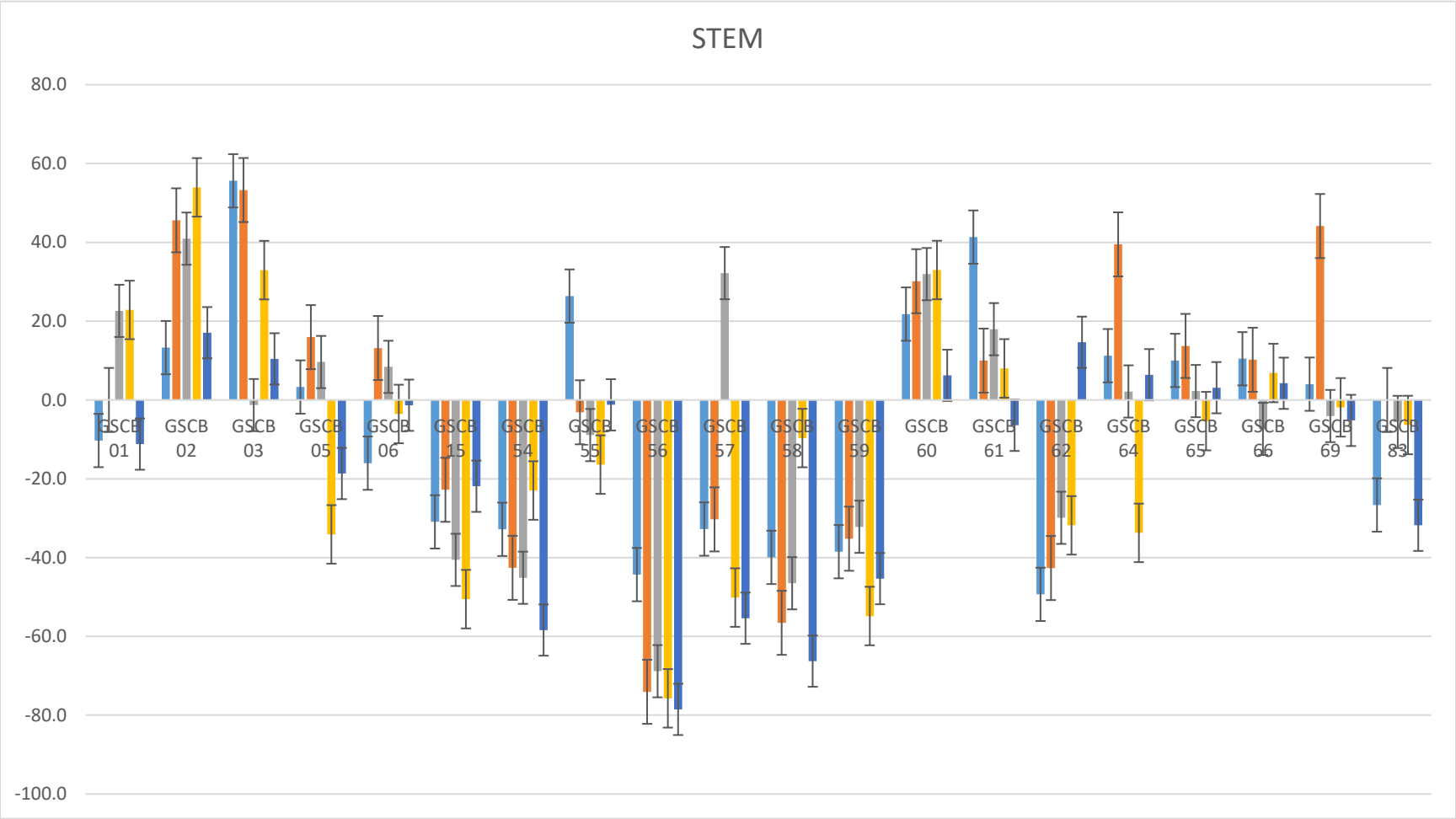
The graph above shows the impact of the test compounds on the root elongation of the seeds of cucumber with respect to the control, and as previously observed, we have GSCB 01, 54, and 58 having above average inhibitions at high concentrations; even though GSCB 01 shows stimulation at lower concentration. GSCB 15, 57, 59, and 83 have average range of inhibition, in at least one of their concentrations. In GSCB 02, 03, 06, 60, 61, 64, 65, 66, and 69, it was stimulation that was observed, with more than 50% in GSCB 60, 64, 65, 66, and 69. Compounds GSCB 05, 55, and 69 displayed low inhibitions at the majority of their tested concentrations. However, GSCB 55 and 62 showed a slight stimulation of 28.7% and 45.6% at concentrations of 50 μM and 500 μM, respectively. In GSCB 15, a percentage inhibition of less than 40% was observed with no stimulation in any of its concentrations.

Table 9 - Percentage stem elongation in cucumber with respect to the control.

INHIBITION: CUCUMBER STEM					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	-10.3	0.00	22.6	22.8	-11.2
GSCB 02	13.3	45.6	40.9	54.0	17.1
GSCB 03	55.6	53.3	-1.3	33.0	10.4
GSCB 05	3.3	15.9	9.6	-34.1	-18.7
GSCB 06	-16.0	13.2	8.4	-3.6	-1.3
GSCB 15	-30.9	-22.8	-40.6	-50.6	-21.9
GSCB 54	-32.8	-42.6	-45.1	-23.0	-58.4
GSCB 55	26.4	-3.1	-8.9	-16.4	-1.2
GSCB 56	-44.3	-74.1	-68.8	-75.7	-78.5
GSCB 57	-32.8	-30.3	32.2	-50.1	-55.4
GSCB 58	-39.9	-56.6	-46.5	-9.7	-66.3
GSCB 59	-38.5	-35.2	-32.2	-54.8	-45.3
GSCB 60	21.8	30.1	31.9	33.0	6.3
GSCB 61	41.3	10.0	18.0	8.0	-6.4
GSCB 62	-49.3	-42.7	-29.9	-31.8	14.6
GSCB 64	11.2	39.5	2.2	-33.7	6.4
GSCB 65	10.0	13.7	2.3	-5.4	3.1
GSCB 66	10.5	10.2	-7.4	6.8	4.2
GSCB 69	4.0	44.1	-4.1	-1.9	-5.2
GSCB 83	-26.7	0.00	-5.6	-6.4	-31.8

Source: the author.

Figure 18 - A graph showing the percentage stem elongation in cucumber.



Source: the author.

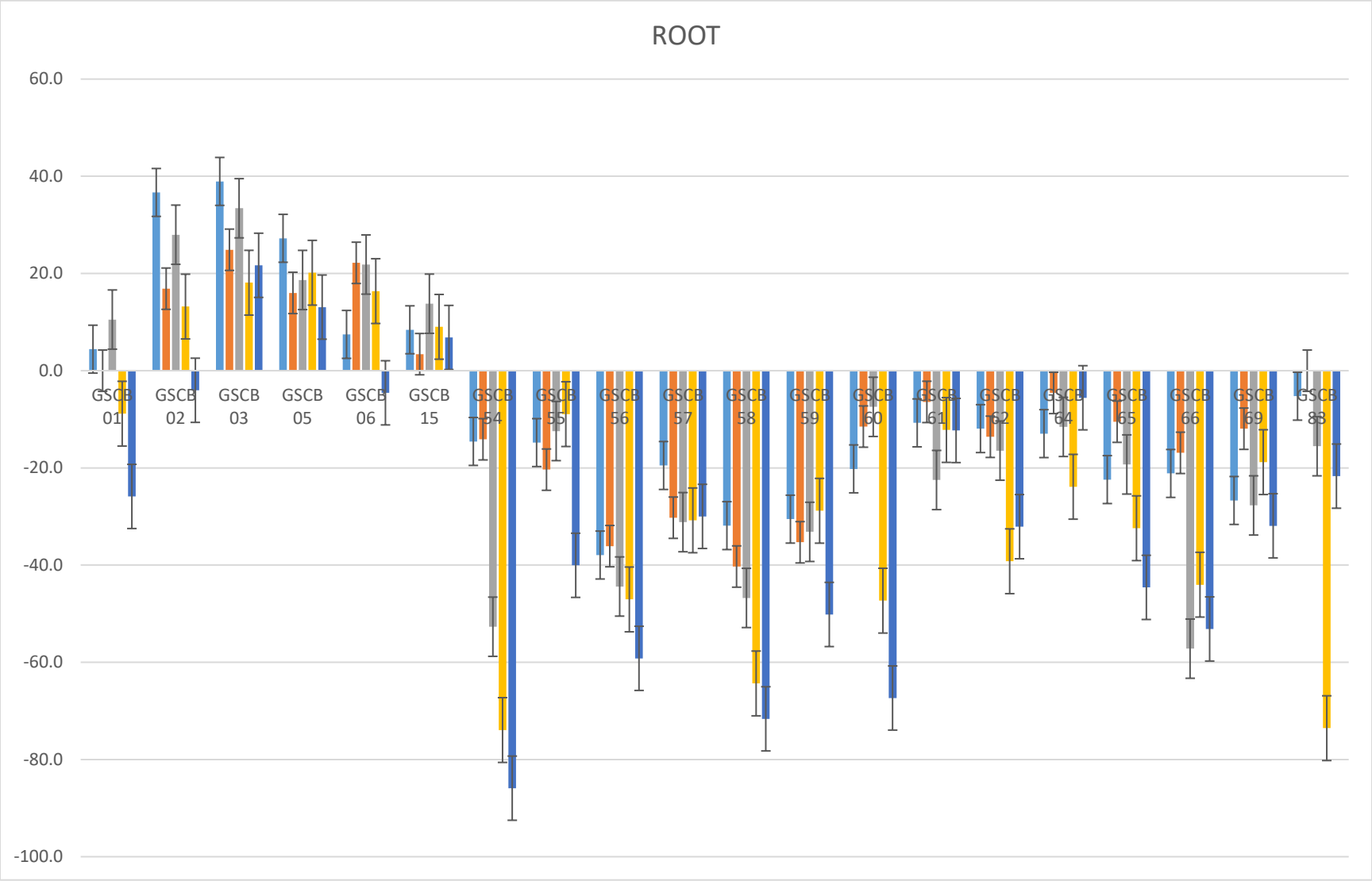
In the graph above, we can see how the different compounds affected the stem growth in cucumber seeds; some inhibition while others showed stimulation. Topping the list of inhibition this time around, we have GSCB 56 with almost 80% at four of its higher concentartions, followed by GSCB 58 with over 60% at 500 micro moles concentration. Compounds GSCB 15, 54, 57, and 59 recorded between 50 and 59 percent inhibition in at least one of their concentrations. GSCB 05 and 83 have their highest percentage inhibition of 34.1 and 31.8 at 300 μM and 500 μM concentrations respectively. The compound GSCB 55, recorded 16.4% as its highest inhibition at 300 μM concentration, with 26.4% stimulation at its lowest concentration of 50 μM. GSCB 02 and 60 were the only compounds that completely exhibited stimulation, with the highest value of 54% at 300 μM concentration of the former. GSCB 03 showed a greater amount of stimulation at the same concentration with a very minute inhibition of 1.3% at 150 μM concentration. Compounds GSCB 06, 55, 65, and 66 recorded a mixture of very poor inhibition and stimulation as well.

Table 10 - Percentage root elongation in sorghum with respect to the control.

INHIBITION: SORGHUM ROOT					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	4.4	0.00	10.5	-8.8	-25.9
GSCB 02	36.7	16.9	28.0	13.2	-4.0
GSCB 03	38.9	24.9	33.4	18.1	21.7
GSCB 05	27.2	16.0	18.7	20.2	13.1
GSCB 06	7.5	22.2	21.8	16.4	-4.6
GSCB 15	8.4	3.4	13.8	9.0	6.8
GSCB 54	-14.6	-14.1	-52.7	-73.9	-85.9
GSCB 55	-14.8	-20.4	-12.4	-8.9	-40.0
GSCB 56	-37.9	-36.1	-44.4	-47.1	-59.2
GSCB 57	-19.5	-30.3	-31.2	-30.8	-30.0
GSCB 58	-31.9	-40.3	-46.8	-64.3	-71.6
GSCB 59	-30.5	-35.3	-33.2	-28.8	-50.2
GSCB 60	-20.2	-11.5	-7.4	-47.3	-67.3
GSCB 61	-10.7	-6.4	-22.5	-12.2	-12.3
GSCB 62	-11.9	-13.6	-16.4	-39.2	-32.1
GSCB 64	-12.9	-4.6	-11.6	-23.9	-5.6
GSCB 65	-22.4	-10.5	-19.3	-32.4	-44.6
GSCB 66	-21.1	-16.9	-57.2	-44.0	-53.1
GSCB 69	-26.7	-11.9	-27.7	-18.8	-31.9
GSCB 83	-5.2	0.00	-15.5	-73.6	-21.7

Source: the author.

Figure 19 - A graph showing the percentage root elongation in sorghum.



Source: the author.

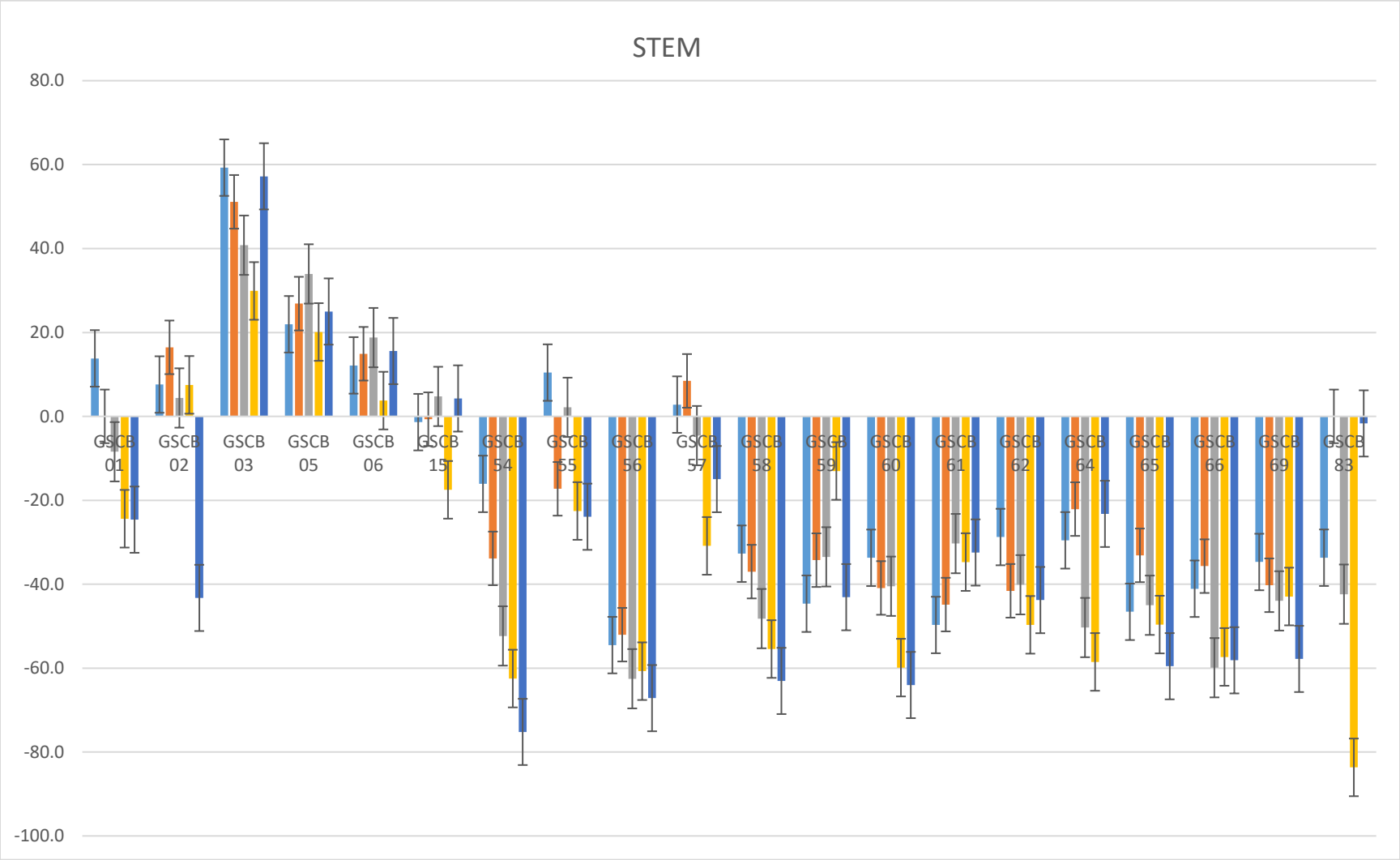
The graph above illustrates how the different test compounds affected the root elongation of the seed of sorghum at distinct concentrations. GSCB 54 topped the list of inhibition with 85.9% at its apex concentration; followed by GSCB 83 with 73.6% at 300 μM concentration, then GSCB 58 with 71.6% at 500 μM concentration. GSCB 60 has 67.3% inhibition at 500 μM, while GSCB 56 recorded its highest percentage inhibition of 59.2 at the same concentration. GSCB 66 recorded its highest percentage inhibition of 57.2 at 150 μM concentration. GSCB 59 has 50.2% inhibition. GSCB 65 and 55 have 44.6% and 40% inhibitions respectively at their 500 μM concentrations. The compounds, GSCB 1, 2, 6, 57, 61, 64, and 69 recorded less than 40% inhibition in at least one of their respective concentrations. However, in compounds GSCB 1, 2 and 6, stimulation was also observed in most of their concentrations. In GSCB 03, 05, and 15, complete stimulation was observed from all their concentrations; with 38.9% stimulation at 50 μM concentration of GSCB 03. In general, most of the tested compounds showed inhibition, with few of the showing stimulation.

Table 11 - Percentage stem elongation in sorghum with respect to the control.

INHIBITION: SORGHUM STEM					
Compounds	50 μM	75 μM	150 μM	300 μM	500 μM
GSCB 01	13.8	0.00	-8.4	-24.4	-24.6
GSCB 02	7.6	16.5	4.4	7.5	-43.3
GSCB 03	59.3	51.1	40.8	29.9	57.2
GSCB 05	22.0	26.9	33.9	20.1	25.0
GSCB 06	12.1	14.9	18.8	3.8	15.6
GSCB 15	-1.4	-0.7	4.7	-17.5	4.3
GSCB 54	-16.1	-33.9	-52.3	-62.5	-75.2
GSCB 55	10.4	-17.3	2.2	-22.5	-23.9
GSCB 56	-54.5	-52.0	-62.5	-60.7	-67.2
GSCB 57	2.8	8.5	-4.6	-30.9	-15.0
GSCB 58	-32.7	-37.0	-48.2	-55.5	-63.1
GSCB 59	-44.6	-34.3	-33.5	-13.0	-43.1
GSCB 60	-33.7	-40.9	-40.5	-59.9	-64.0
GSCB 61	-49.7	-44.9	-30.3	-34.7	-32.4
GSCB 62	-28.8	-41.6	-40.1	-49.7	-43.8
GSCB 64	-29.5	-22.1	-50.3	-58.5	-23.2
GSCB 65	-46.6	-33.1	-45.0	-49.6	-59.5
GSCB 66	-41.1	-35.7	-59.9	-57.3	-58.1
GSCB 69	-34.7	-40.3	-44.0	-42.9	-57.8
GSCB 83	-33.7	0.00	-42.4	-83.7	-1.7

Source: the author.

Figure 20 - A graph showing the percentage stem elongation in sorghum.



Source: the author.

In the graph above, we can see that the stem elongation of the seeds of sorghum, agree with the results of the root elongation in most cases, with compounds GSCB 01, 02, 15, 55, and 57 showing a mix of inhibition and stimulation in some of their different concentrations, with the highest inhibition of 43.3%, and the highest stimulation of 16.5% both experienced in GSCB 02 at 500 μM and 75 μM concentrations respectively. On the other hand, compounds GSCB 03, 05, and 06 showed stimulation completely, with GSCB 03 having the highest of 59.3%, 57.2%, 51.1%, and 40.8% at its 50 μM, 500 μM, 75 μM, and 150 μM concentrations respectively; followed by GSCB 05, having its highest percentage stimulation of 33.9 at 150 μM concentration. GSCB 06 has the least percentage stimulation among the three compounds.

While compounds GSCB 54, 56, 58, 59, 60, 61, 62, 64, 65, 66, 69, and 83 recorded inhibition in all their concentrations; as GSCB 83 topped the list with 83.7% inhibition at its 300 μM concentration. GSCB 54 follows with 75.2% then GSCB 56 with 67.2% inhibition both at 500 μM concentrations, GSCB 60, has 64.0% at 500 μM concentration. GSCB 59 has the least percentage inhibition among the twelve listed compounds above, with 44.6% at its 50 μM concentration. As observed in the root elongation of the seeds of sorghum, majority of the compounds exhibitted inhibitory activy on the stem elongation, with few of them showing stimulation.

CHAPTER 5

CONCLUSION

5. CONCLUSION

A total of twenty compounds were evaluated against five different seed species, namely lettuce, ryegrass, brachiaria, cucumber, and sorghum.

The work focused on the in-vitro root and stem elongation bioassay of the tested seeds, which is one aspect of potential herbicidal activity determination. However, herbicidal activity has different formulations and/or applications, such as pre- and post- germination.

In conclusion, all synthesized compounds exhibited activity in seed germination. However, compounds GSCB 01, 54, 56, and 58 showed superior activity to the commercial herbicide S-metolachlor.

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