RASĀYAN *J. Chem.*
Vol. 19 | No. 4 | 2014-2018 | October-December | 2026
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

IMPROVED GREEN SYNTHESIS OF METRIBUZIN USING AQUEOUS SODIUM BROMIDE: A SUSTAINABLE AND HIGH-YIELD APPROACH

S.D. Yamgar[1,✉], G.B. Kolekar[1], S.R. Yankanchi[1], P.P. Mohire[1], O. S. Nile[1] and V. B. Metkari[2]

[1]Department of Agrochemicals and Pest Management, Shivaji University, Kolhapur-416004 (Maharashtra) India
[2]Department of Pharmaceutics, Adarsh College of Pharmacy, Vita-415311(Maharashtra) India
✉Corresponding author: sdyamgar@yahoo.com

ABSTRACT

Metribuzin is a widely used triazinone herbicide for effective control of broad-leaf and grassy weeds in several agricultural crops. Conventional industrial synthesis of metribuzin involves the use of hazardous reagents such as methyl bromide and bromine, resulting in moderate yields, higher production costs, and environmental concerns. In the present study, an improved and environmentally benign synthetic route for metribuzin has been developed using aqueous sodium bromide as a brominating agent under controlled reaction conditions. The process demonstrates enhanced yield (90–92%) compared to the conventional method (86–88%) while eliminating the direct use of elemental bromine and chlorine. The synthesized metribuzin was characterized by melting point, HPLC, NMR, and IR spectroscopy, and the analytical data were found to be in good agreement with standard specifications. Furthermore, antifungal and antibacterial activities of the final product were evaluated and showed comparable performance to the commercial reference standard. The developed process offers significant economic and ecological advantages, including cost reduction, waste minimization, and zero effluent generation, making it suitable for sustainable agrochemical manufacturing.

Keywords: Metribuzin, triazinone, green synthesis, sodium bromide, herbicide, sustainable agrochemicals

RASĀYAN *J. Chem.*, Vol. 19, No.4, 2026

INTRODUCTION

Metribuzin is a selective systemic herbicide belonging to the triazinone class and is widely used for the effective control of broad-leaf and grassy weeds in a variety of agricultural crops, including soybean, potato, wheat, barley, sugarcane, tomato, peas, and lentils. Owing to its dual pre- and post-emergence activity, high herbicidal efficiency, and favorable cost-to-performance ratio, metribuzin has become an indispensable component of modern weed management programs.[1] Its mode of action involves inhibition of photosystem II, leading to disruption of electron transport during photosynthesis and subsequent plant death, which makes it particularly effective against a broad spectrum of weeds.[2]

Commercial production of metribuzin is traditionally carried out through methylation of triazinone intermediates using methyl bromide or methyl chloride in the presence of strong acidic catalysts.[3] Although these conventional synthetic routes are well established, they present several inherent limitations. The use of methyl bromide and bromine-based reagents raises significant concerns due to their high toxicity, ozone-depleting potential, stringent handling requirements, and increasing regulatory restrictions worldwide. Furthermore, these processes often result in moderate product yields, formation of undesirable by-products such as iso-metribuzin, and increased operational costs associated with reagent procurement, effluent treatment, and waste disposal. [4]

In recent years, the agrochemical industry has faced growing pressure to adopt sustainable and environmentally benign manufacturing practices. [5] Regulatory frameworks, coupled with the principles of green chemistry, emphasize the reduction or elimination of hazardous reagents, improved atom economy, valorization of industrial by-products, and minimization of waste generation. Several studies have

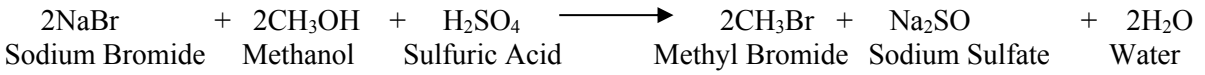
reported alternative synthetic approaches for triazinone derivatives; however, many of these methods still rely on hazardous halogenating agents or fail to demonstrate clear advantages in terms of yield, scalability, and environmental impact. [6]

Against this background, the development of an efficient, cost-effective, and eco-friendly synthesis of metribuzin remains highly desirable. In the present work, we report an improved synthetic process employing aqueous sodium bromide as an alternative bromine source for the in-situ generation of methyl bromide. Sodium bromide, often available as an industrial by-product, is utilized as a value-added raw material, thereby transforming waste into a useful reagent. [7] The proposed process eliminates the direct use of elemental bromine and chlorine, improves reaction efficiency, and significantly enhances overall yield compared to conventional methods.[8]

The developed route aligns closely with green chemistry principles by reducing hazardous chemical usage, improving process safety, lowering production costs, and achieving zero effluent discharge.[9] Moreover, the synthesized metribuzin meets commercial quality specifications and exhibits comparable physicochemical and biological properties to standard products. The present study thus demonstrates a technically viable and environmentally sustainable approach for large-scale metribuzin production, offering significant advantages for industrial agrochemical manufacturing. [10]

Synthesis Reaction Scheme

The synthesis of metribuzin described in this study proceeds through a two-stage process involving in-situ generation of methyl bromide followed by alkylation of the triazinone intermediate.



EXPERIMENTAL

Raw Materials

All chemicals used were of technical or analytical grade and were used as received. Triazinone was obtained with 95% purity, while sodium bromide solution (72.5%) was sourced from industrial by-product streams. Methanol, sulphuric acid, Catalyst 1, and Catalyst 2 were of standard commercial grades.

Table-1: Details of chemical used

S. No.	Raw materials	Mol. Wt.	Qty(gm)	Purity	Gm/mol	M/R
1	Triazinone	200	200	95	1	1
2	caustic lye	40	85	48	1.02	1.02
3	water	18	408	100		
4	SBS	104	3	99	0.028	0.028
5	2-ethyl hexanol	130	1.2	99	0.009	0.009
6	Aq NaBr solution	103	185	72.5	1.34	1
7	MEOH	32	65	99	2.01	1.5
8	sulphuric acid	98	143	98	1.49	1.1
9	Catalyst 1	34	13.5	50	0.198	
10	Catalyst 2	293.82	1		0.003	
11	water for washing	18				
12	caustic flakes	40				

Preparation of Sodium Triazinone Solution

Triazinone was suspended in water in a clean and dry round-bottom flask under stirring. Aqueous caustic lye solution was added gradually over 30 minutes while maintaining the pH above 10. The reaction mixture was stirred further until complete dissolution of the solid, yielding a clear sodium triazinone solution.

In-situ Generation of Methyl Bromide and Metribuzin Formation

In a separate closed reaction system, aqueous sodium bromide solution and methanol were charged and stirred at room temperature. Concentrated sulphuric acid was added slowly over 1–2 hours, resulting in an exothermic reaction and in-situ generation of methyl bromide gas. The evolved gas was directed into the sodium triazinone solution maintained at pH >10.5. The reaction temperature was gradually increased to 50–55 °C and subsequently raised to 110 °C to ensure completion of methylation.[11] Reaction progress was monitored by HPLC, ensuring residual triazinone content below 1%.

Iso-Metribuzin Degradation

The crude reaction mass was filtered, and the wet cake was subjected to iso-metribuzin degradation. The wet solid was suspended in water, followed by the addition of Catalyst 2 at 25–30^{0}C. Catalyst 1 solution was added slowly, and the mixture was stirred for 1–2 hours until iso-metribuzin impurity was reduced below 0.5%. The pH was adjusted to 6.0–6.5 using caustic lye.

Isolation and Drying

The final product was filtered, washed with hot water, and dried at 65–70 °C to constant weight with moisture content below 0.5%. The dried sample was subjected to analytical characterization.

RESULTS AND DISCUSSION

The developed process resulted in a significant improvement in yield (90–92%) compared to the conventional synthesis route (87–88%). The final product was obtained as an off-white crystalline solid with a melting point of 125 °C, consistent with reported literature values.[12]

HPLC analysis confirmed high purity and compliance with commercial specifications. Structural confirmation was achieved through NMR and IR spectroscopy, which matched the reference standard. The antifungal and antibacterial activity studies demonstrated comparable biological efficacy to the marketed metribuzin formulation. The use of aqueous sodium bromide not only eliminates the need for elemental bromine and chlorine but also enables valorization of industrial waste streams, thereby contributing to circular economy practices. [13]

Chromatography Study

The GC–FID chromatogram of the Metribuzin sample shows a peak at RT = 5.04 min, which exactly matches the retention time of the Metribuzin standard, confirming the identity of Metribuzin in the sample. The internal standard, Dibutyl Sebacate, elutes at 8.48 min in both chromatograms, indicating good system stability and reproducibility.

The area percentage of Metribuzin in the sample (87.99%) is very close to that of the standard (87.50%), suggesting consistent detector response and absence of matrix interference at the analyte retention time. Slight variation in peak area between standard and sample is normal and acceptable, and is utilized for quantitative estimation using the internal standard method. Overall, the results demonstrate that the sample conforms to the standard in terms of retention time, peak purity, and chromatographic behavior, confirming that the method is specific, selective, and suitable for quantitative determination of Metribuzin in the sample.

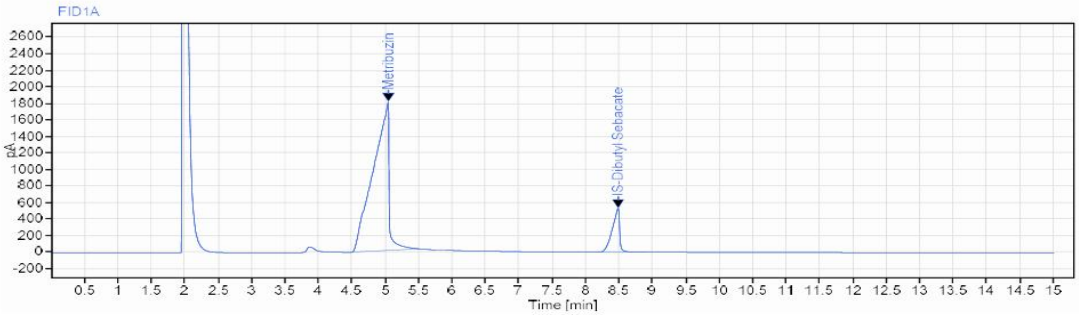


Fig.-1: Metribuzin Standard Chromatogram

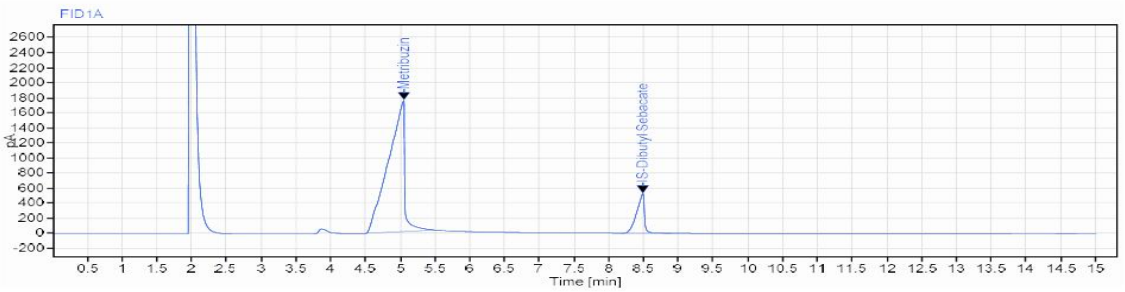


Fig.-2: Metribuzin Sample Chromatogram

Table-2: Comparison: Metribuzin Standard vs Sample (GC–FID)

Parameter	Standard	Sample	Observation
Detector	FID	FID	Same method
Retention Time (min)	5.04	5.04	Exact match
IS RT (min)	8.48	8.48	Consistent
Metribuzin Area	28479.12	29700.53	Slightly higher in sample
IS Area	4069.75	4055.10	Comparable
Metribuzin Area %	87.50	87.99	Comparable
Peak Shape	Sharp, symmetric	Sharp, symmetric	No distortion
Interference	None	None	Method selective

Fourier Transform Infra-Red Study

The FT-IR spectrum of the Metribuzin sample shows all characteristic absorption bands corresponding to the functional groups present in Metribuzin, including secondary amine (N–H), carbonyl (C=O), triazine ring (C=N and C–N), methoxy (C–O–C), and chloro (C–Cl) functionalities.

The positions and intensities of these bands closely match those observed in the Metribuzin standard, with no additional or missing peaks. Minor variations in band intensity are acceptable and may be attributed to sample preparation or concentration differences.

The absence of extra peaks in the sample spectrum indicates no detectable impurities or degradation products.

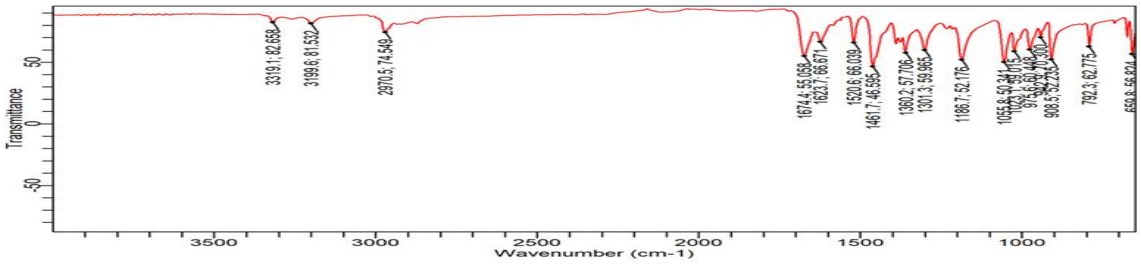


Fig.-3: Metribuzin Standard IR

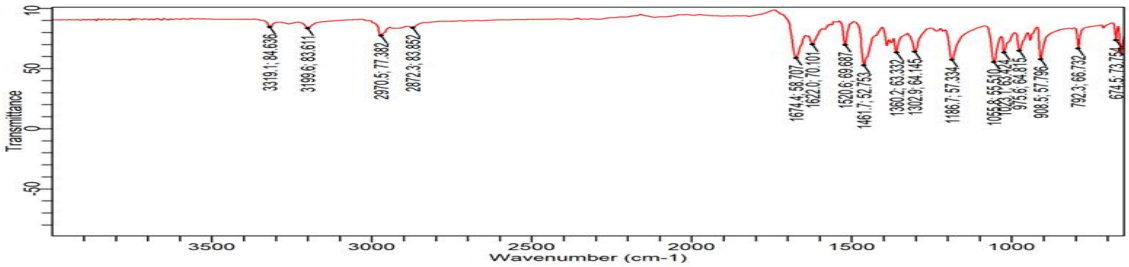


Fig.-4: Metribuzin Sample IR

CONCLUSION

An efficient and environmentally sustainable synthesis of metribuzin has been developed, addressing the limitations of conventional manufacturing methods. The optimized process minimizes hazardous

chemicals, reduces energy consumption, and lowers waste generation while improving reaction selectivity and overall yield. It ensures high purity, reproducibility, and scalability, making it economically viable for industrial production. The methodology follows green chemistry principles and represents a promising alternative for the commercial manufacture of metribuzin.

ACKNOWLEDGMENTS

The authors are grateful to Department of Agrochemicals and Pest Management, Shivaji University, Kolhapur, for allowing the facility for this work.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-12:Responsible Consumption and Production*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

S.D. Yamgar https://orcid.org/0009-0006-4107-2424
G.B. Kolekar https://orcid.org/0000-0002-1874-3043
S.R. Yankanchi https://orcid.org/0000-0002-0886-7608
P.P. Mohire https://orcid.org/0000-0003-4644-1111
O. S. Nile https://orcid.org/0000-0002-8662-0459
V. B. Metkari https://orcid.org/0000-0003-3589-8933

Cite this article as: S. D. Yamgar *et al.*, *Rasayan J. Chem.*, 19(4), 2014-2018(2026), https://doi.org/10.31788/RJC.2026.1949750

REFERENCES

1. D. Samir, R. Selma, and S. Asma, *Pharmaceutical and Biosciences Journal,* **8,** 10(2020), https://doi.org/10.20510/ukjpb/8/i4/1593522789
2. O. Ay, G. Dikmen, and O. Koyuncu, *Journal of Molecular Structure*, **1297,** 136869(2024), https://doi.org/10.1016/j.molstruc.2023.136869
3. E. Jackman, *Journal of Heterocyclic Chemistry*, **27** 1053(1990), https://doi.org/10.1021/jm00400a003
4. N. Ibrahim, *Journal of Heterocyclic Chemistry*, **81**, 1393(2010), https://doi.org/10.5155/eurjchem.1.4.388-396.154
5. S. Hamama, G. El-Bana, S. Shaaban, O. Habib, and H. Zoorob, *Royal Society of Chemistry*, **6,** 24010(2016), https://doi.org/10.1039/C5RA26433B
6. V. Asha, S. Pooja, and S. Starling, *Asian Journal of Chemistry*, **37,** 12(2025), https://doi.org/10.14233/ajchem.2025.34567
7. C. Cimanga, and V. Pullabhotla, *Asian Journal of Chemistry*, **37,** 7(2025), https://doi.org/10.14233/ajchem.2025.33269
8. K. Barbour, and W. Geigle, US Patent US4435568A, (1984)
9. L. Qi, N. Li, and H. LI, *Chemistry Select*, **10**, 6(2025), https://doi.org/10.1002/slct.202404833
10. L. Pengpeng, and H. Kan, *Journal of Environment and Health*, **31(5)**, (2017), https://doi.org/10.16241/j.cnki.1001-5914
11. H. Sun, Y. Liu, and Z. Kexueban, **29**, 127(1999)
12. J. Wang, L. Shen, L. Cai, H. Yang, Y. Zhang, Z. Zhang, H. Zhang, F. Wang, Z. Li, *Journal of Molecular Structure,* **1318**, 2(2024), https://doi.org/10.1016/j.molstruc.2024.139427

[RJC-9750/2026]