SJIF Impact Factor: 6.711

WORLD JOURNAL OF ADVANCE HEALTHCARE RESEARCH

ISSN: 2457-0400
Volume: 8.
Issue: 11
Page N. 136-141
Year: 2024

Original Article www.wjahr.com

USING PLANTS AS BIOCATALYSTS IN CONDUCTING SOME REDOX REACTIONS

Carol Haddad[1]*, Mohammad Kousara[2] and Rim Salame[3]

[1]Department of Medicinal Chemistry and Quality Control, Faculty of Pharmacy, University of Tishreen, Lattakia, Syria.
[2]Department of Therapeutic Chemistry, Faculty of Pharmacy, University of Tishreen, Lattakia, Syria.
[3]Department of Pharmacognosy, Faculty of Pharmacy, University of Tishreen, Lattakia, Syria.

Article Received date: 22 September 2024 **Article Revised date:** 12 October 2024 **Article Accepted date:** 02 November 2024

***Corresponding Author: Carol Haddad**
Department of Medicinal Chemistry and Quality Control, Faculty of Pharmacy, University of Tishreen, Lattakia, Syria.

ABSTRACT
Biocatalysis utilizes isolated enzymes or whole cells for organic reactions, providing an eco-friendly alternative to conventional chemical synthesis, making it a valuable green technique in chemical synthesis. Plants can be used for reduction, oxidation, and hydrolysis reaction. Utilizing whole plant parts for transformation can be nearly 20 times more efficient than cell cultures, and eliminate the need for complex processing required for isolated enzymes. This study reports the bioreduction of acetophenone and cyclohexanone, as well as the biooxidation of cyclohexanol using various plants as catalysis. Carrot and parsley achieved the best results for the bioreduction of acetophenone and cyclohexanone, while potato demonstrated significant efficiency in the biooxidation of cyclohexanol.

KEYWORDS: Biocatalysis, plants, bioreduction, biooxidation, acetophenone, cyclohexanone, cyclohexanol.

1. INTRODUCTION
Biocatalysis is the use of isolated enzymes or whole cells (such as bacteria, fungi, microalgae and plants) as catalysts in organic reactions. This synthetic approach is distinguished by its ability to provide high enantioselectivity. Moreover, it offers other benefits such as mild reaction conditions, low toxicity, the ability of recycling, and the production of eco-friendly waste. These benefits make biocatalysis the perfect green technique.[1]

Biocatalysts offer several unique characteristics over conventional catalysts. The major advantage of a biocatalyst is its high selectivity. This selectivity is often chiral (stereo-selectivity), positional (regio-selectivity), and functional group specific (chemo-selectivity).This high selectivity is highly desirable in chemical synthesis, offering benefits such as decreased or eliminated need for protecting groups, reduced side reactions, easier separation, and fewer environmental problems. Additional advantages such as high catalytic efficiency and mild operational conditions are also highly attractive in commercial applications.[2,3]

Biocataytic transformations using plants can be utilized in various processes such as the bioreduction of ketones, hudrolysis of esters, enzymatic lactonization, as well as oxidation and hydroxylation reactions.[4] As the utilization of plants for these transformations has advanced, three distinct systems have been used for substrate modification: cell cultures, enzymes derived from plants, and intact plant materials.[5] Bio transformations using parts of plants (roots, tubers, and fruits) are approximately 20 times more efficient compared to cell cultures of the same plants, and it does not require sterile conditions.[6] In addition, there are several advantages for using whole plant cells over isolated enzymes. Firstly, it eliminates the need to handle biological material to obtain a relatively pure enzyme. This simple procedure involves ultracentrifungation, chromatographic apparatus, and minimal amounts of starting material. Moreover, unlike the purified enzymes, biotransformations carried out with whole cells do not require expensive cofactor recycling, as it is automatically done by the cell.[7] In this research, we report our results in the bioreduction of acetophenone and cyclohexanone, and biooxidation of cyclohexanol catalyzed by various plants.

2. MATERIALS AND METHODS
2.1. Materials
Acetophenone (Merck-Schuchardt), cyclohexanaone (Scharlau) and cyclohexanol (Qualikems) were used without further purification.

1-phenylethanol was prepared from acetophenone by reduction with $NaBH_4$.

Fresh carrot (*D.carota*), parsley (*P.crispum*), radish (*R.sativus*), potato (*S.tuberosum*) and apple (*Malus pumila*) were purchased from a local market.

2.2. Methods

Thin-layer chromatography (TLC) was performed using precoated plates (silica gel 60 F254, 0.2mm, Macherey-Nagel). The mixture of hexane: ethyl acetate: methanol (85:10:5) was used as the mobile phase. The detection was performed by UV lamb (254nm) and by vanillin reagent.

HPLC was performed using C_{18}, 5µm (25*0.46). The HPLC was carried out using mobile phase acetonitrile: water (50:50) and RID-10A detector, with 0.8 ml/min flowrate for cyclohexanone and cyclohexanol and 1 ml/min flowrate for acetophenone. Solution of each standard (10 mmol/30ml) was prepared and injected in HPLC to determinate the area under curve.

2.2.1. General procedures for biotransformation

Vegetables were peeled and cut into small thin pieces. Then, 7g of vegetable was added to 30 ml of distilled water. 10mmol of the substrate were added to the suspension. The reaction mixture was then placed in an orbital shaker (150rpm) at room temperature for 3 days. The progress of the reaction was monitored by TLC. After 3 days, the suspension was filtered and monitored by HPLC. The yield was determined by HPLC based on the following equation:

$$\frac{Area\ under\ curve\ (standard)}{concentration\ (standard)} = \frac{Area\ under\ curve\ (sample)}{concentration\ (sample)}$$

3. RESULTS AND DISCUSSIONS

Acetophenone, cyclohexanone and cyclohexaonl have been used as substrates for the biotransformation. Carrot, parsley, radish, and potato were used as biocatalysts for bioreduction of acetophenone and cyclohexanone, while potato and apple were used as biocatalysts for biooxidation of cyclohexaonl.

3.1. Bioreduction of acetophenone

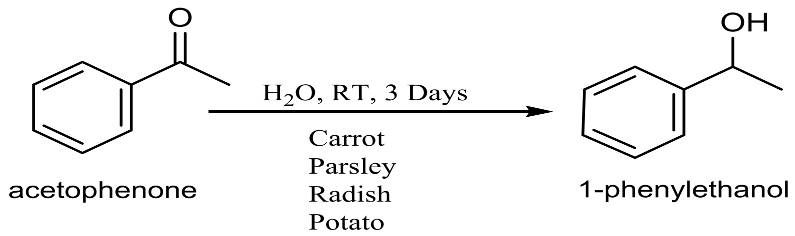

Figure 1: Bioreduction of acetophenone catalyzed by various plants in water.

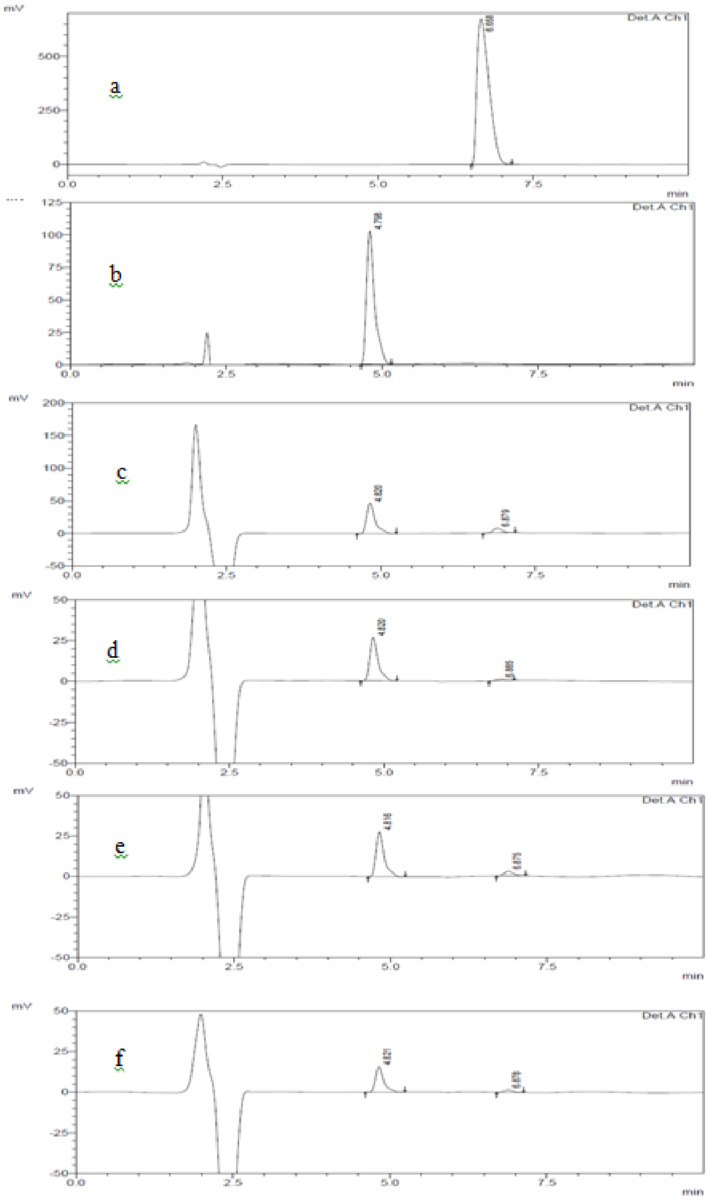

Figure 2: Chromatograms of the standards and acetophenone bioreduction. a: acetophenone standard t_R= 6.658 min, b: 1-phenylethanol standard $t_{R=}$ 4.798 min, c: with carrot, d: with parsley, e: with radish, f: with potato.

All the selected plants successfully reduced acetophenone to 1-phenylethanol in water at room temperature for 3 days (Fig1). Where the highest yield was achieved with carrot (50.26%), followed by parsley and radish, while potato demonstrates the lowest efficiency as shown in (Table 1).

Table 1: Yields of the bioreduction of acetophenone.

Biocatalysis	Yield
Carrot (*D.carota*)	50.26%
Parsley (*P.crispum*)	26.26%
Radish *(R.sativus*)	26.79%
Potato *(S.tuberosum*)	14.98%

3.2. Bioreduction of cyclohexanone

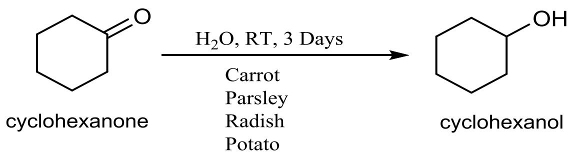

Figure 3: Bioreduction of cyclohexanone catalyzed by various plants in water.

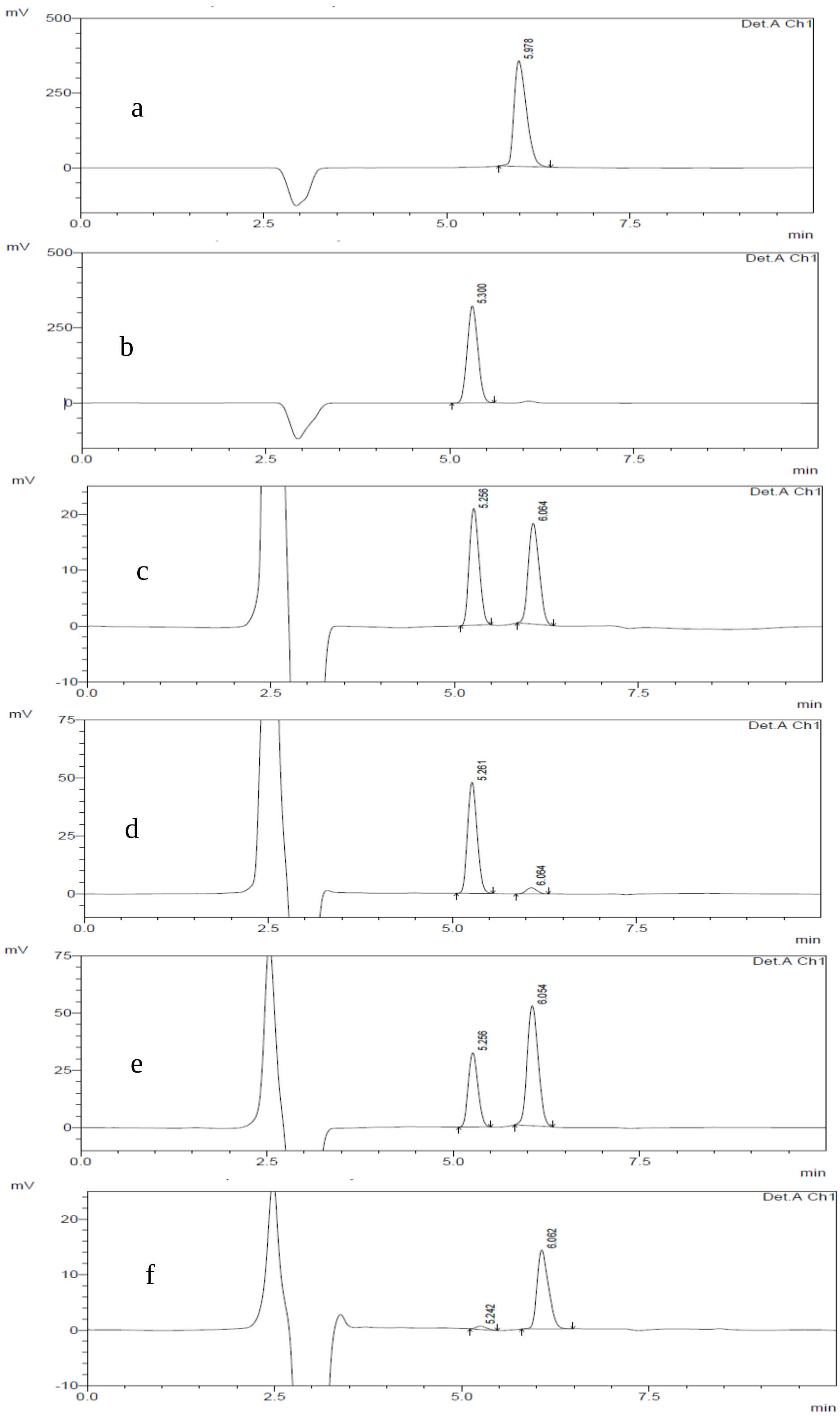

Figure 4: Chromatograms of the standards and cyclohexanone bioreduction. a: cyclohexanone standard $t_{R=}$ 5.978 min, b: cylohexanol standard $t_{R=}$ 5.3 min, c: with carrot, d: with parsley, e: with radish, f: with potato.

Cyclohexanone was reduced to cyclohexanol by all the used plants but with a low yield (Table 2). The best result was obtained with parsley, whereas the bioreduction with potato was the least efficient.

Table 2: Yields of the bioreduction of cyclohexanone.

Biocatalysis	Yield
Carrot (*D.carota*)	8.4%
Parsley (*P.crispum*)	13.29%
Radish (*R.sativus*)	9%
Potato (*S.tuberosum*)	0.17%

3.3. Biooxidation of cyclohexanol

Oxidation of alcohols is valuable in organic synthesis, although it is less commonly employed compared to the reduction of ketones in biotransformations.[8]

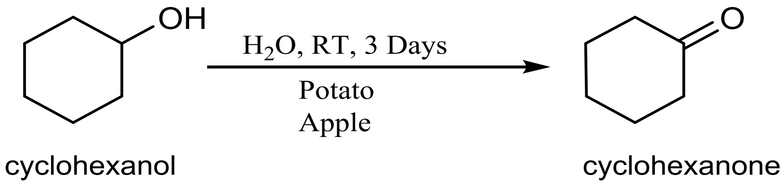

Figure 5: Biooxidation of cyclohexanol catalyzed by plants in water.

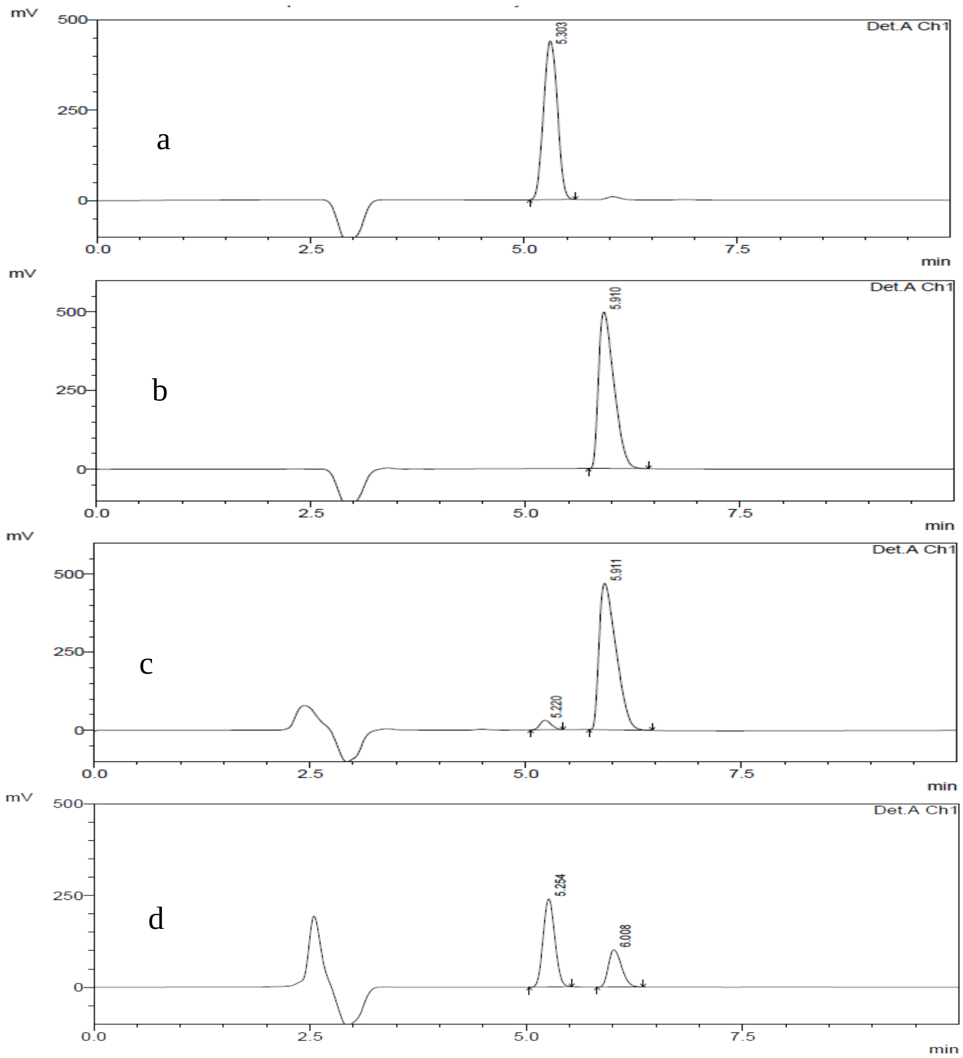

Figure 6: Chromatograms of the standards and cyclohexanol bioreduction. a: cyclohexanol standard $t_{R=}$ 5.303 min, b: cyclohexanone standard $t_{R=}$ 5.910 min, c: with potato, d: with apple.

Both potato and apple oxidized cyclohexanol to cyclohexanone. With potato, we observed a large, clear peak corresponding to cyclohexanone compared to cyclohexanol which appeared as a small peak (Fig 6). The yield obtained with potato was 88.99%, compared to just 16.09% with apple (Table 3).

Table 3: Yields of the biooxidation of cyclohexanol.

Biocatalysis	Yield
Potato (*S.tuberosum*)	88.99%
Apple (*Malus pumila*)	16.09%

The results we obtained demonstrate the effectiveness of plants as biocatalysis in bioreduction and biooxidation reactions. The best bioreduction results were achived with carrot (*D.carota*) and parsley (*P.crispum*), which are recognized to exhibit a relatively high reductase activity.[9] For the biooxidation, the results showed that potato (*S.tuberosum*) act as one of the most effective catalysts, achieving a yield of 88.99%. It is known that peroxidase is found in potato.[10] These finding open up a wide filed for future research to explore new types of plant biocatalysis and the potential for improving reaction yields by adjusting experimental conditions such as temperature, reaction time and concentrations of substrates.

4. CONCLUSION

In this study, we carried out biotransformation to reduce acetophenone and cyclohexanone, and oxidize cyclohexanol by using only water and plant catalysts. The reaction was conducted at room temperature for 3 days without any additives. Acetophenone was reduced to 1-phenylethanol with yields ranging from 50.26% (carrot) to 14.98% (potato). While cyclohexanone was reduced to cyclohexanol with lower yields, from 13.29% (parsley) to 0.17% (potato). The highest yield of the biooxidition of cyclohexanol was achieved with Potato (88.99%). The promising results obtained in this study offer new opportunities for bioreduction or biooxidation of organic compounds using water as a solvent.

5. REFERENCES

1. Garzón-Posse, F.; Becerra-Figueroa, L.; Hernández-Arias, J.; Gamba-Sánchez, D., Whole cells as biocatalysts in organic transformations. Molecules, 2018; 23(6): 1265.
2. Delfino, M., Biocatalytic transformation and analytic characterization of bioactive vegetable substances, 2015.
3. Clouthier, C. M.; Pelletier, J. N., Expanding the organic toolbox: a guide to integrating biocatalysis in synthesis. Chemical Society Reviews, 2012; 41(4): 1585-1605.
4. Khaled, B.; Nedjimi, M. S.; Benmoussa, F., Asymmetric Bioreductionof Ketones with a Pumpkin (cucurbita). Journal of Biochemical Technology, 2019; 10(3-2019): 18-23.
5. Cordell, G. A.; Lemos, T. L.; Monte, F. J.; de Mattos, M. C., Vegetables as chemical reagents. Journal of natural products, 2007; 70(3): 478-492.
6. Krystyna, W., Biotransformation of Isoprenoids and Shikimic Acid Derivatives by a Vegetable Enzymatic System. Zeitschrift fÃ¼r Naturforschung C 2014.
7. Baldassarre, F.; Bertoni, G.; Chiappe, C.; Marioni, F., Preparative synthesis of chiral alcohols by enantioselective reduction with Daucus carota root as biocatalyst. Journal of Molecular Catalysis B: Enzymatic, 2000; 11(1): 55-58.
8. Mączka, W.; Wińska, K.; Grabarczyk, M.; Galek, R., Plant-Mediated enantioselective transformation of indan-1-one and indan-1-ol. Catalysts, 2019; 9(10): 844.
9. Chanysheva, A.; Vorobyova, T.; Zorin, V., Relative reactivity of substituted acetophenones in enantioselective biocatalytic reduction catalyzed by plant cells of Daucus carota and Petroselinum crispum. Tetrahedron, 2019; 75(36): 130494.
10. Utsukihara, T.; Horiuchi, C. A., Production of chiral aromatic alcohol by acetophenone and 1-arylethanol derivatives using vegetables, 2019.