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Biocatalysis using plant material: A green access to asymmetric reduction

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Abstract: Green techniques for organic synthesis are innovative trends with considerable applications; in which biocatalysis is one who have gained a special scope in literature. In recent years, a considerable amount of literature on bio-catalytic asymmetric reduction of aldehydes and ketones in the production of chiral alcohols is documented. This review focuses on selected examples of bioreduction of aldehydes and ketones using different plant material. Considering a variety of organic reaction schemes, only substrate and plant material used for bioreduction, with some important reactions are taken under consideration.
Keywords: Plant material, Green chemistry, Biocatalysis, Enantioselective reduction.

Introduction:

Reduction of carbonyl group is one of the important reactions in organic chemistry. There are numerous chemical methods are available to reduce carbonyl group. Moreover, some methods are designed with application of enzymes. There is no need to explain the advantages of enzymatic reactions with respect to their selectivity (regio, chemo and enantioselectivity) and their application in different applied fields [1-5]. This greener application is not only limited to commercial enzymes but a crude plant extract is also used for reduction of organic compounds. Decomposition of organic matter is an oxidation process therefore in presence of such matter one can use it for reduction of another substance.

Asymetric reduction of prochiral ketones produces chiral alcohols those are important building blocks in chemical and pharmaceutical industry. The production of these optically active alcohols using biocatalytic methods is getting more attention in last two decades. [6]. In reducing prochiral ketones Baker's yeast which was the most widely used microorganism for reduction of prochiral ketones yielding the corresponding optically active alcohols [7], similarly immobolized plant cell culture was also investigated [8].

Production of chiral alcohols

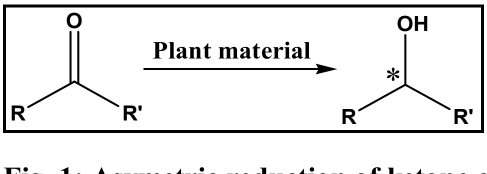


Fig. 1: Asymetric reduction of ketone catalyzed by plant material.

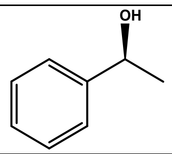
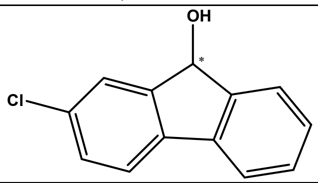
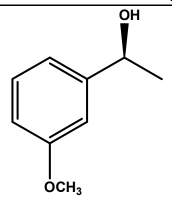
Chiral compounds are the most important building blocks in the chemical and pharmaceutical industry for the production of chemical catalysts, liquid crystals, flavors, agrochemicals, or drugs [9]. Optically active secondary alcohols are commonly used as intermediates for the introduction of chirality into the product [10].

At present use of chemical methods is not the only option for production of chiral compounds, use of enzyme or biocatalytic methods are also developing. These methods include use of crude or purified enzyme or plant material (Fig. 1).

Bioreduction of aldehyde and ketone using plant material

The direct use of plant material instead of isolating enzymes or handling biotechnological processes would be easy option for organic chemists. Biotransformation is not limited to microorganisms and purified enzymes, in recent years use of whole plant cells and plant culture have been studied as potential agents for biotransformation reactions. Several examples of whole plants were reported as sources of reductase activity with alcohol dehydrogenase systems [11]. Some excellent examples considering yield and enantiomeric excess (ee) of asymmetric reduction using plant material are shown in table 1.

Table 1: Product of bioreduction of ketone to chiral alcohol

Product	Biocatalyst	Conversion %	ee	Ref.
	Apiaceae	96	99.99	23
	Grape	97	>99	28
	água-de-coco do Ceará (Coconut water)	98	99	12

Coconut water (*Cocos nucifera* L.) was used as a biocatalyst to reduce different aliphatic and aromatic aldehydes and ketones with excellent yield and high enantiomeric excess [12]. Similarly, ACC (água-de-coco do Ceará) and BFJ (Borassus flabellifer juice) are refreshing beverages derived from Cocos nucifera L. and B. flabellifer L. were reported for the reduction of aromatic aldehydes [13]. The results demonstrates that electron donating group present either at para or meta position of aromatic aldehydes showed better activity in the presence of both juices, but ortho substituted aromatic aldehydes did not produce any alcohol, which may be due to steric effect on the enzyme's active site. In addition, methoxy group present at para rather than meta position also led to increased yield within 15–30 h. These biocatalysts were used not only to reduce aromatic aldehydes but also for decarboxylation of substituted cinnamic acid (Fig. 2). Whereas in another study, necessity of hydroxyl group at fourth position for the decarboxylation of the benzoic and cinnamic acid derivatives was suggested [14]. In this study banana (*Musa sapientum*) and maize (*Zea maiz*) leaves were used as a biocatalyst. In general, higher yields were obtained using leaves of maize than banana, regardless of whether the substituent was activating or deactivating the aromatic ring. It is also interesting to note that banana leaves were unable to reduce the unsubstituted aldehydes.

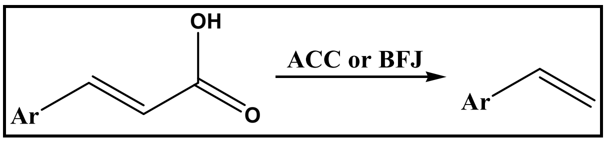


Fig. 2: Decarboxylation of substituted cinnamic acid by ACC and BFJ.

The *Aloe vera* extract can be used as a biocatalyst for reduction of different aromatic aldehydes [15]. When carried out under microwave irradiation, this reaction was performed in a short reaction time. In this study, a simple, fast and green biotechnological method for the preparation of a wide range of alcohols of industrial and pharmaceutical interest is reported. Moreover, use of soyabean (*Glycine max*) seeds were (tritured and used as a catalyst after removal of fats in hexane) suggested for the stereoselective reduction of different aliphatic and aromatic aldehydes [16]. Whereas, use of bark of *Passiflora edulis* for the reduction of aromatic aldehydes and ketones was also reported with good yields and moderate enantioselectivity [17].

Roots of plant material:

In several cases, bioreduction was performed by using roots of different plant material. Baldassarre et al. [18] investigated the use of roots of carrot (*Daucus carota*) for reduction of 2-methylcyclohexanone to afford opticaly active alcohol. Similary the carrot roots was also used for the reduction of substituted acetophenone to chiral alcohol as per Prelog's rule [19]. Moreover, these are also used for reduction of aromatic, heteroaromatic and aliphatic ketones [20]. In another study [21] enantioselective reduction of heteroaryl methyl ketone was carried out using caroot roots as a biocatalyst to give chiral alcohol with good yield. Along with carrot roots; *Brassica rapa* was also used for the reduction of β-ketoester [22], where different results were obtained in sterile and nonsterile condition.

Roots of some weeds were also studied and reported as a biocatalyst in the stereoselective reduction of acetophenone where they found highest stereoselectivity with *Eryngium horridum* [23]. They studied reduction of different substituted acetophenones and found conversion with high eanantiomeric excess. Reduction of benzaldehyde using root of wild plants collected from Punilla Valley (Province of Córdoba, Argentina) have been reported; most of the species studied showed almost quantitative yields for the reduction reaction. However, reduction of benzaldehyde occurred in the shortest period of time using Conium maculatum (Apiaceae) and was selected for the further experiments with different substituted benzaldehyde, in which monosubstituted benzyl alcohols were obtained in higher yields [24].

Andrade et al. [25] reported bioreduction of acetophenone derivative as well as biooxidation of 1-phenyl ethanol derivative using different biocatalysts like burdock roots (*Arctium lappa* L.), potato tubers, beet roots (*Beta vulgaris* L.), yam tubers (*Dioscorea alata* L.), chive roots (*Allium schoenoprasum* L.), coriander roots (*Coriandrum sativum* L.), ginger roots, taro tubers (*Colocasia esculenta* L. Schott), lotus roots, manioc roots (*Manihot esculenta Crantz*), arracacharoots (*Arracacia xanthorrhiza Bancroft*), turnip roots (*Brassica rapa* L.), radish roots (*Raphanus sativus* L.) and yacon roots (*Polymnia sonchifolia*). Bioreduction of different aldehyde ketones using *Manihot esculenta* and *Manihot dulcis* roots as a biocatalyst to give opticaly active alcohols with good yield [26].

Fruits and Vegetables:

Different vegetables like broccoli (B. oleracea var. italica), cauliflower (B. Oleracea var. botrytis), spinach beet (B. vulgaris var. cicla), and spinach (Spinacia oleraceae) were used for the reduction of aromatic ketones [27]. In another study, [28] vegetables like potato (*Solanum tuberosum* L.), plum (*Prunus* spp.), scallion (*Allium fistulosum* L. var. caespitosum), topinambur (*Hippophae Rhamnoides* Linn.), onion (*Allium cepa* L.), and garlic (*Allium saticum* L.) Some studies were reported with use of fruits like grape (*Vitis vinifera* L.), apple (*Malus pumila* Mill.), banana (*Musa balbisiana* Colla), cherry (*Prunus pseudocerasus* Lindl.), pear (*Pyrus pyrifolia* (Burm.) Nak.), strawberry (*Fragaria ananassa* Duch.), orange (*Citus reticulate* Blanco), jujube (*Zizyphus jujuba* Mill.) as a reducing agents for nitro-polycyclic aromatic ketones. Alves et al. [29] investigated enantioselective reduction of various aromatic aldehyde and ketone with moderate to good yield and enantiomeric excess using different vegetables such as Ginger (*Zingiber officinale)*, yam (*Colocasia esculenta* L.), turmeric (*Curcuma longa)*, potato (*Solanum tuberosum)*, gherkin *(Cucumis anguria* L.), okra (*Abelmoschus esculentus),* hot peppers (*Capsicum chinense*), green peppers (*Capsicum annum*), cabbage (*Brassica oleracea*), cucumber (*sativum Cucumis*), beans (pods *Vigna unguiculata*), Coriander (*sativum Coriandrum*)*,* scallions (*Allium fistulosum* L.) and lettuce *(Lactuca sativa*). Moreover, freshly ripened fruit clementine mandarin (*Citrus reticulata*) was used for the reduction of prochiral ketones [30].

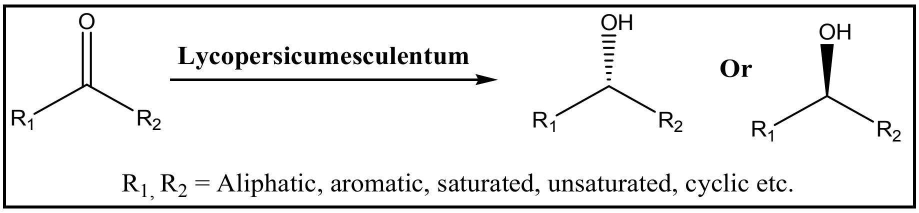


Fig. 3: Asymetric reduction of ketone using *Lycopersicumesculentum* (tomato) at RT

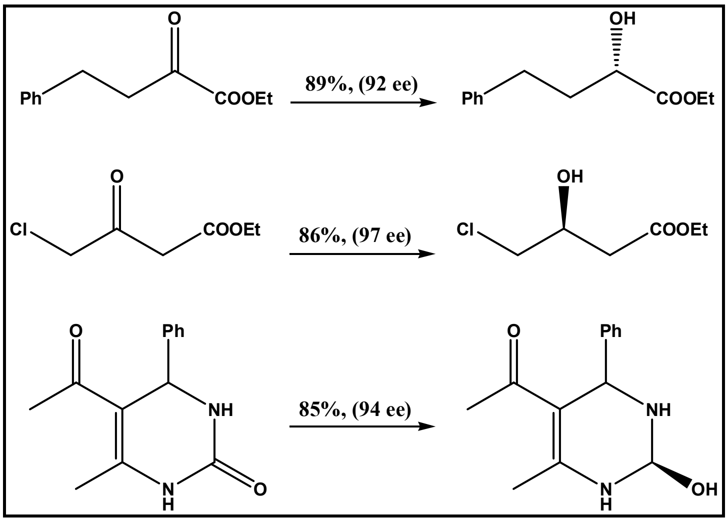


Fig. 4: Reduction of carbonyl compounds by *Lycopersicumesculentum* (tomato) at RT

Biocatalysis using plant material can be a powerful tool for the production of alcohols for wide range of substrates, as shown in fig. 3, in which tomato (*Lycopersicumesculentum)* was used for asymmetric reduction. In this process, the inner portion of the ripen tomato fruit with seeds and the thin external part was removed and the rest were cut carefully into about 2 mm thin and 1cm long slices, those were then soaked in deionized water for 18 hours and then used as the biocatalytic system [31]. Some interesting examples using this catalyst are as shown in fig. 4, where one carbonyl group is selectively reduced in presence of another reducible group.

Utsukihara et al. [32] reported the stereoselective reduction of camphorquinones using different vegetables like carrot, potato, sweet potato, apple, Japanese radish, cucumber, burdock and onion. Similarly, Xie et at. [33] investigated use of different fruits and vegetables like apple (*Malus pumila*), banana (*Musa balbisiana*), orange (*Citrus reticulate*), potato (*Solanum tuberosum*), strawberry (*Fragaria ananassa*), scallion (*Allium fistulosum*), plum (*Prunus* spp.), garlic (*Allium sativum*), onion, cherry (*Prunus pseudocerasus*), jujube (*Zizyphus jujube*), topinambur (*Helianthus tuberosus*) and grape (*Vitis* spp.) as biocatalyst for reduction of fluorenones and got moderate to good yield with enantiomeric excess. Yang et al. [34] investigated reduction of prochiral simple and substituted aromatic ketones, β-ketoester with enantiomeric excess using fruits like Apple (*Malus pumila*), carrot (*Daucus carota*), cucumber (*Cucumis sativus*), onion (*Allium cepa*), potato (*Soanum tuberosum*), radish (*Raphanus sativus*) and sweet potato (*Ipomoea batatas*). In another study Chang et al. [35], has reported the detailed study of bioreduction of acetophenone using different fruits like apple, carrot, cucumber, onion, potato, radish and sweet potato. Considering reaction yield and enantioselectivity, they found carrot was the best catalyst for this reaction. Several studies discussed above are summarised in table 2 showing use of different plant material as a biocatalyst for the reduction of carbonyl compounds.

Table 2: Bioreduction using different plant materials

Biosource	Substrate	Ref.
Roots of carrot	2-methylcyclohexanone	18
	Substituted Acetophenone	19
	Aromatic, heteroaromatic and aliphatic ketones	20
	Heteroaryl methyl ketones	21
Roots of *Manihot esculenta* and *Manihot dulcis*	Aliphatic and aromatic aldehydes and ketones	26
Roots of wild plant Conium maculatum (Apiaceae)	Benzaldehyde	24
Roots of carrot and *Brassica rapa*	β-ketoester	22
Roots of weeds	Acetophenone	23
Tubers of potato, yam, taro and roots of chive, coriander, burdock, ginger, lotus, beet, manioc, arracacha, turnip, radish and yacon	Acetophenone derivatives	25
Carrot, potato, sweet potato, apple, Japanese radish, cucumber, burdock and onion	Camphorquinones	32
Barks of *Passiflora edulis*	Aromatic aldehydes and ketones	17
Apple, carrot, cucumber, onion, potato, radish and sweet potato	Substituted Acetophenone, β-ketoester	34
Apple, banana, orange, potato, strawberry, scallion, plum, garlic, onion, cherry, jujube, topinambur and grape	Fluorenones	33
Coconut water	Aliphatic and aromatic aldehydes and ketones	12
Broccoli, cauliflower, spinach beet, and spinach	Aromatic ketones	27
Apple, carrot, cucumber, onion, potato, radish, sweet potato	Acetophenone	35
Aloe vera (with microwave irradiation)	Aromatic aldehydes	15
Coconut water and toddy palm	Aromatic aldehydes	13
Soyabean	Aromatic aldehydes and ketones	16
Banana and maize	Benzaldehyde	14
Clementine mandarin	Aromatic ketones	30
Ginger, yam, turmeric, potato, gherkin, okra, hot peppers, green peppers, cabbage, cucumber, beans, Coriander, scallions and lettuce	Aromatic and aliphatic aldehydes and ketones	29

Conclusion

Asymmetric reduction of prochiral ketones is important transformation in organic synthesis to get important intermediates. Although traditional methods for the enantioselective synthesis of chiral alcohol are extensively developed, biocatalytic approaches remain extremely attractive for several reasons like their selectivity and environmentally friendly approach. Bioreduction by using plant material is gaining attention in the last few years. Considering the huge taxonomy use of plant material instead of purified enzyme gives many options for biocatalysis. In near few years, it is anticipated that more plant materials will discovered as an efficient biocatalysts. This article is dedicated to green chemistry and an attempt to suggest 'go green' for all academic and industrial researchers.

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