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Edible catalysts for clean chemical reactions: Bioreduction of aromatic ketones and biooxidation of secondary alcohols using plants

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Abstract

Bioreduction of acetophenone derivatives **1a–e** and biooxidation of (*RS*)-1-phenylethanol derivatives **2a–e** have been evaluated using edible plants as biocatalysts. Chiral (*R*)- and (*S*)-alcohols were prepared by different plants in up to 98% of enantiomeric excess. Ketones can also be prepared from alcohol oxidation using this clean protocol.

Keywords: Biotransformation; Biooxidation; Bioreduction; Plants; Root; Ketone; Alcohol

1. Introduction

In recent years, chemical reactions using plant cell cultures and part of plants as biocatalysts have received great attention [1–3]. This crescent interest is due to the wide biotechnological potential of the enzymatic reactions. The biocatalytic transformations using plants can be applied in phytoremediation of organic pollutants [4,5], bioreduction of ketones [6–18], enzymatic lactonization [19], hydrolysis of esters [11,20-24], addition of hydrogen cyanide [25] and hydroxylation and oxidation reactions [26]. Among these applications, we can mention the current interest in the preparation of chiral alcohols from ketone reduction by the use of plant cell cultures [6,10,15], *Phaeseolus aureus* L. [9], *Daucus carota* L. and celeriac roots [7,8,11–14]. These reactions are based on the utilization of these plants as enzymatic source (alcohol dehydrogenases and their cofactors) to reduce prochiral ketones.

Recently, we disclosed our results on the reduction of organoseleno- and organothio-acetophenones using *Daucus carota* root as catalysts [7]. The corresponding chiral alcohols were prepared in up to 99% enantiomeric excess. We have also reported the results of the bioreduction of organoselenoacetophenones using whole fungal cells [27]. It was found that some fungal strains give (*R*)- and (*S*)-alcohols with high enantioselectivity (up to 99%). However, in view of the good results on the use of *D. carota* root in bioreduction reactions, we focused our attention on the study of new biocatalysts, which could be easily manipulated and used for important organic transformations. In this paper we report our results in the bioreduction of ketones (Scheme 1) and alcohol biooxidation by enzymatic systems of different plants (Scheme 2).

2. Experimental

2.1. General methods

Solvents were purified by standard procedures [28]. Acetophenone and 4′-nitroacetophenone were purchased from Merck. 4′-Bromoacetophenone, 4′-methylacetophenone and 4′-aminoacetophenone were purchased from Aldrich. These chemicals were used without further purification. 4′-methylselenoacetophenone was prepared according to our previous report [27]. Thin-layer chromatography (TLC) was performed using precoated plates (Aluminum foil, silica gel 60 F_{254} Merck, 0.25mm). Merck 60 silica gel (230–400 mesh) was used for flash chromatography. GC analyses were performed

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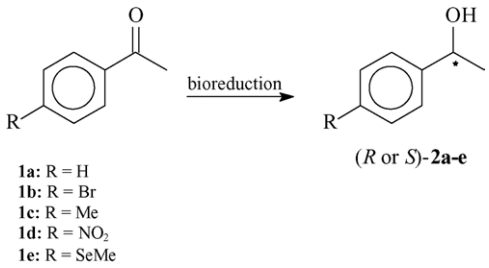


Scheme 1. Bioreduction of ketones **la–e** catalyzed by plants.

in a Shimadzu GC-17A instrument with a FID detector, using hydrogen as a carrier gas (100 kPa). Mass spectra were recorded on a Shimadzu GC–MS QP5050A (70 eV) spectrometer. The fused silica capillary columns used were either a J & W Scientific DB-5 (30 m × 0.25 mm) or a chiral column Chirasil-Dex CB (β-cyclodextrin (25 m × 0.25 mm) for determination of the enantiomeric excesses. Optical rotations were determined on a JASCO DIP-378 polarimeter.

2.2. Biocatalysts

Healthy plants were obtained from a local market: Burdock roots (*Arctium lappa* L.); sweet white potato tubers [*Ipomoea batatas* (L.) Lam.]; sweet red potato tubers [*I. batatas* (L.) Lam.]; potato tubers (*Solanum tuberosum* L.); beet roots (*Beta vulgaris* L.); yam tubers [*Dioscorea alata* L.); chive roots [*Allium schoenoprasum* L.); coriander roots (*Coriandrum sativum* L.); ginger roots (*Zingiber officinale* Roscoe); taro tubers [*Colocasia esculenta* (L.) Schott]; lotus roots (*Nelumbo nucifera* Gaertn.); manioc roots (*Manihot esculenta* Crantz); arracacha roots (*Arracacia xanthorrhiza* Bancroft); turnip roots (*Brassica rapa* L.); radish roots (*Raphanus sativus* L.); yacon roots (*Polymnia sonchifolia*).

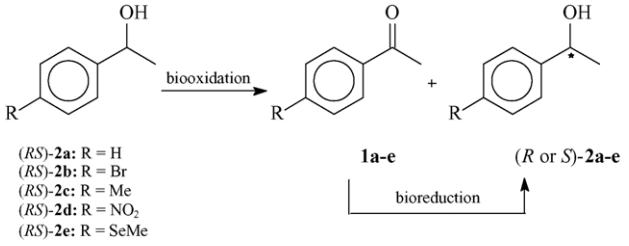
2.3. Synthesis of the raceme alcohols *2a–e* for gas chromatography correlation analysis

The alcohols (RS)-**2a–e** were prepared by reduction of the corresponding acetophenones **1a–e** with sodium borohydride in methanol [30].

2.4. General procedures for biotransformations

The plants were washed with water and then maintained in a 5% sodium hypochlorite aqueous solution for 20 min. Then they were washed with ethanol, manipulated under a sterile laminar flow cabinet and peeled with a sterilised cutter. To increase the contact of the substrate with the biocatalyst, the external layer was removed and the rest was cut into small thin slices (5 mm), except for *C. sativum* and *A. schoenoprasum* roots, which were only sliced.

The plants (20 g), water (80 mL) and the appropriate ketones **1a–e** or alcohols (*RS*)-**2a–e** [liquid compound: 100 μL; solid compound: 100 mg in DMF (1 mL)] were added to an erlenmeyer (250 mL). The biotransformation was carried out in an orbital shaker (160 rpm) at 32 °C for the time indicated in Tables 1–5. The progress of the reaction was monitored by GC analysis.



Scheme 2. Biooxidation of alcohols (*RS*)-**2a–e** catalyzed by plants.

2.5. GC analysis for the enantiomeric excess (e.e.) determination

The reaction progress was monitored periodically by collecting 3 mL samples. These samples were extracted by stirring

Table 1
Biooxidation of (*RS*)-1-phenylethanol(**2a**)

Entry	Biocatalyst	*t* (days)	Alcohol **2a**		Ketone **la**
			c (%)	e.e. (%)	*c* (%)
1	*Attium schoenoprasum*	3	95	7 (*R*)	5
		6	46	>98 (*R*)	54
2	*Arctium lappa*	3	100	6 (*R*)	–
		6	100	4 (*R*)	–
3	*Arracacia xanthorrhiza*	3	98	97 (*S*)	2
		6	12	17 (*S*)	88
4	*Beta vulgaris*	3	78	21 (*S*)	22
		6	77	32 (*S*)	23
5	*Brassica rapa*	3	100	–	–
		6	100	26 (*S*)	–
6	*Colocasia esculenta*	3	67	36 (*R*)	33
		6	33	41 (*R*)	67
7	*Coriandrum sativum*	3	76	25 (*R*)	24
		6	84	19 (*R*)	16
8	*Dioscorea alata*	3	96	4 (*S*)	4
		6	85	6 (*R*)	15
9	*Ipomoea batatas* (white)	3	89	11 (*R*)	11
		6	90	11 (*R*)	10
10	*Ipomoea batatas* (red)	3	95	3 (*R*)	5
		6	95	4 (*R*)	5
11	*Manihot esculenta*	3	90	7 (*R*)	10
		6	87	9 (*R*)	13
12	*Polymnia sonchifolia*	3	100	11 (*S*)	–
		6	99	93 (*S*)	1
13	*Raphanus sativus*	3	51	89 (*S*)	49
		6	26	>98 (*R*)	74
14	*Solanum tuberosum*	3	74	12 (*S*)	26
		6	40	20 (*S*)	60
15	*Zingiber officinale*	3	93	79 (*S*)	7
		6	100	>98 (*S*)	–

t: time (days); *c*: conversion determined by GC analysis using a chiral column; e.e.: enantiomeric excess; Absolute configuration is in parenthesis.

Table 2
Bioreduction of acetophenone (**1a**)

Entry	Biocatalyst	*t* (days)	Alcohol **2a**	
			c (%)	e.e. (%)
1	*Allium schoenoprasum*	3	5	>98 (*S*)
		6	5	>98 (*S*)
2	*Arctium lappa*	3	8	8 (*S*)
		6	21	58 (*S*)
3	*Arracacia xanthorrhiza*	3	44	91 (*S*)
		6	91	66 (*S*)
4	*Beta vulgaris*	3	65	61 (*R*)
		6	83	87 (*R*)
5	*Brassica rapa*	4	4	99 (*S*)
		6	10	99 (*S*)
6	*Colocasia esculenta*	3	24	50 (*S*)
		6	27	6 (*S*)
7	*Coriandrum sativum*	3	56	99 (*S*)
		6	–	–
8	*Dioscorea alata*	3	30	94 (*S*)
		6	47	94 (*S*)
9	*Ipomoea batatas* (white)	3	8	69 (*S*)
		6	18	–
10	*Ipomoea batatas* (red)	3	–	–
		6	–	–
11	*Manihot esculenta*	3	13	29 (*R*)
		6	14	31 (*R*)
12	*Nelumbo nucifera*	3	–	–
		6	–	–
13	*Polymnia sonchifolia*	3	2	47 (*R*)
		6	2	28 (*R*)
14	*Raphanus sativus*	3	10	15 (*S*)
		6	4	79 (*R*)
15	*Solanum tuberosum*	3	3	24 (*R*)
		6	5	7 (*S*)
16	*Zingiber officinale*	3	8	>98 (*S*)
		6	8	>98 (*S*)

t: time (days); *c*:conversionto **2a** was determined by GC analysis using a chiral column; e.e.: enantiomeric excess; Absolute configuration is in parenthesis.

with ethyl acetate (2 mL) followed by centrifugation (6000 rpm, 5 min). The organic phase was analyzed by GC (2 μL) in a chiral capillary column. The products of the biocatalyzed reactions were compared with a racemic mixture previously obtained from chemical reactions (see Section 2.3).

GC conditions (carrier gas: H_2, 100 kPa)—Chiral compounds (*RS*)-**2a**–**e**: method (a): injector 200 °C; detector 220 °C; 110 °C, 3 °C/min until 180 °C; retention time (t_R) of (*RS*)-1-phenylethanol (**2a**): *R*-enantiomer 4.56 min, *S*-enantiomer 4.82 min; (*RS*)-1-(4-bromophenyl)ethanol (**2b**): *R*-enantiomer 12.64 min, *S*-enantiomer 13.30 min; method (b): injector 200 °C; detector 220 °C; 110 °C, 1 °C/min until 180 °C; t_R (min): (*RS*)-1-(4-methylphenyl)ethanol (**2c**): *R*-enantiomer 7.45 min; *S*-enantiomer 8.31 min; method (c): injector 200 °C; detector 220 °C; 150 °C 1 °C/min until 180 °C; t_R (min): (*RS*)-1-(4-nitrophenyl)ethanol (**2d**): *R*-enantiomer 12.94 min, *S*-enantiomer 14.13 min; method (d): injector 200 °C; detector 220 °C; 140 °C (25 min, hold time), 5 °C/min until 180 °C; t_R (min): (*RS*)-1-(4-methylselenophenyl)ethanol (**2e**): *R*-enantiomer 18.22 min, *S*-enantiomer 19.94 min.

2.6. Assignment of the absolute configurations for the alcohols (RS)-*2a–e*

The absolute configurations were attributed by chiral GC correlation with standards (*S*)-1-phenyl-ethanol (**2a**) [29], (*S*)-1-(4-bromophenyl)ethanol (**2b**), (*S*)-1-(4-methylphenyl)ethanol (**2c**), (*S*)-1-(4-nitrophenyl)ethanol (**2d**) and (*S*)-1-(4-methylselenophenyl)ethanol (**2e**) prepared by us as previously reported [7,27,30].

2.7. Preparative scale reactions

The plant (200 g), water (800 mL) and the ketone **1a** or alcohol (*RS*)-**2c** (1000 μL) were added to an Erlenmeyer flask (2 L). After the appropriate conversion time, the mixture was filtered off and the plant suspension was washed with ethyl acetate (100 mL). The aqueous phase was extracted with ethyl acetate (5 mL × 100 mL). The organic phases were combined and dried over $MgSO_4$. The solvent was removed in vacuum and the residue was purified on a silica gel column using a mixture of hexane and ethyl acetate (4:1) as eluent to afford the desired compounds.

- Bioreduction of ketone **1a**: yield of (*S*)-**2a**: 43% (470 mg), $[\alpha]_D^{25} - 58.7°$ (*c* 3.1, $CHCI_3$), e.e. >99%; recovered **1a**: 46% (434 mg) [29].
- Biooxidation of alcohol (*RS*)-**2c**: yield of (*R*)-**2c**: 34% (346 mg), $[\alpha]_D^{25} + 35.6°$ (*c* 3.6, $CHCI_3$), e.e. 64%; yield of **1c**: 26% (257 mg) [30].

3. Results and discussion

3.1. Biooxidations

In order to evaluate the catalytic potential of different plants as oxidizing agents, we decided to use the alcohol oxidation of a racemic mixture to produce the corresponding ketones or the enantiomeric enrichment of the alcohol. We selected 15 plants to carry out the biooxidations. Initially, these chemical reactions were performed by all the biocatalysts in water with (*RS*)-1-phenylethanol as the substrate (Table 1).

As can be seen in Table 1, a kinetic resolution of the racemic 1-phenylethanol was observed with *A. schoenoprasum* and *R. sativus*. After 6 days of reaction with *A. schoenoprasum,* 54% of the alcohol was converted to the ketone, remaining the chiral (*R*)-**2a** in high enantiomeric purity (e.e. >98%, entry 1). On the other hand and more interestingly, the following plants: *A. xanthorrhiza, Z. officinale* and *P. sonchifolia*-showed a characteristic behaviour of a possible deracemization reaction (Scheme 2). The formation of a single enantiomer in high yields (>90%) from the racemate could be proceeding through a two-step

Table 3
Biooxidation of (*RS*)-1-(4-bromophenyl)ethanol (**2b**) and(*RS*)-1-(4-methylphenyl)ethanol (**2c**)

Entry	Biocatalyst	*t* (days)	Alcohol **2b**		Ketone **lb**	Alcohol **2c**		Ketone **lc**
			c (%)	e.e. (%)	*c*(%)	*c* (%)	e e. (%)	*c* (%)
1	*Allium schoenoprasum*	3	94	3 (*S*)	6	7	90 (*R*)	93
		6	63	43 (*S*)	37	–	–	100
2	*Arracacia xanthorrhiza*	3	90	9 (*R*)	10	69	22 (*R*)	31
		6	89	9 (*R*)	11	31	19 (*R*)	69
3	*Beta vulgaris*	3	97	6 (*R*)	3	–	–	–
		6	99	3 (*R*)	1	90	10 (*S*)	2
4	*Brassica rapa*	3	100	–	–	75	10 (*S*)	25
		6	100	–	–	78	10 (*S*)	22
5	*Colocasia esculenta*	3	92	–	8	77	4 (*R*)	23
		6	86	11 (*R*)	14	69	14 (*R*)	31
6	*Coriandrum sativum*	4	99	–	1	13	49 (*R*)	87
		6	94	3 (*R*)	6	–	–	100
7	*Dioscorea alata*	3	44	73 (*S*)	56	70	10 (*R*)	30
		6	47	83 (*S*)	53	73	23 (*R*)	27
8	*Ipomoea batatas* (white)	3	95	5 (*R*)	5	80	26 (*R*)	20
		6	95	7 (*R*)	5	72	38 (*R*)	28
9	*Manihot esculenta*	3	100	8 (*R*)		78	27 (*R*)	22
		6	97	4 (*R*)	3	64	15 (*R*)	35
10	*Raphanus sativus*	3	99	–		92	–	8
		6	100	–	–	93	–	7
11	*Solanum tuberosum*	3	99	2 (*S*)	1	32	86 (*R*)	68
		6	90	5 (*S*)	10	4	>98 (*R*)	96
12	*Zingiber officinale*	3	97	3 (*R*)	3	89	–	11
		6	88	4 (*S*)	12	60	53 (*R*)	40

t: time (days); *c*: conversion determined by GC analysis using a chiral column; e.e.: enantiomeric excess; Absolute configuration is in parenthesis.

redox-sequence (one enantiomer is selectively oxidized to the corresponding ketone which is reduced in a second step by another redox enzyme displaying opposite stereochemical preference). For example, by the use of *Z. officinale,* the racemic 1-phenylethanol (**2a**) was transformed into the chiral (*S*)-**2a** in excellent optical purity after 6 days of biotransformation (e.e. >98%, Table 1, entry 15). *A. xanthorrhiza* and *P. sonchifolia* (entries 3 and 12) also converted the (*RS*)-1-phenylethanol (**2a**) into a single enantiomer [(*S*)-**2a**] after 3 and 6 days of reaction, respectively. In this case, the values of enatiomeric excess were still high. More important is the fact that these results have led to the possibility of employing different plants to obtain both (*R*)- and (*S*)-enantiomers of 1-phenylethanol.

After this screening test, we decided to investigate additional substrates using 12 plants according to their activity in biooxidation reactions.

Using (*RS*)-1-(4-bromophenyl)ethanol (**2b**), we observed that the best biocatalyst for this alcohol oxidation was *D. alata*. The alcohol (*R*)-**2b** was oxidized into the corresponding ketone **1b** in 53% leaving the precursor (*S*)-**2b** unreacted with 83% e.e. (Table 3, entry 6).

A complete oxidation process was observed when *A. schoenoprasum, C. sativum* and *S. tuberosum* were reacted with (*RS*)-1-(4-methylphenyl)ethanol (**2c**) (Table 3, entries 1, 6 and 11). In relation to the enantioselectivity of this reaction, low enantiomeric excesses were observed using all the plants, except *S. tuberosum* which after 3 days of biotransformation (biooxidation) gave the (*R*)-**2c** in 86% e.e. with 32% yield (Table 3, entry 11).

In the case of (*RS*)-1-(4-nitrophenyl)ethanol (**2d**), an unexpected reaction was also observed by the use of several plants as potential oxidant. Besides the alcohol oxidation, we observed the reduction of the nitro group into amino group. In this way, we obtained 4′-aminoacetophenone in high conversion using *A. xanthorrhiza* and *B. vulgaris* (86 and 92%, respectively) (Table 4, entries 2 and 3). In several cases, low alcohol oxidation was observed, and consequently low enantiomeric excess of the unreacted alcohol.

In view of these results concerning nitro reduction, we carried out the biotransformation of nitrobenzene with *B. vulgaris*. After 8 days of reaction, aniline was obtained in 52 % as isolated yield (Scheme 3).

Z. officinale and *C. sativum* were the best catalysts for the complete oxidation of (*RS*)-1-(4-methylselenophenyl)ethanol (**2e**) into the ketone **1e** (Table 4, entries 6 and 12). The highest enantiomeric excesses were obtained by the use of *B. vulgaris* and *C. sativum* as biocatalysts after 3 days of biotransformation (77 and 79% e.e., respectively) (Table 4, entries 3 and 6).

Table 4
Biooxidation of (*RS*)-1-(4-mtrophenyl)ethanol (**2d**) and(*RS*)-1-(4-methylselenophenyl)ethanol (**2e**)

Entry	Biocatalyst	*t* (days)	Alcohol **2d**		Ketone **1d**	Alcohol **2e**		Ketone **1e**
			c (%)	e.e. (%)	*c* (%)	*c* (%)	e.e. (%)	*c* (%)
1	*Allium schoenoprasum*	3	99	–	1	85	11 (*R*)	15
		6	99	–	1	12	76 (*S*)	88
2	*Arracacia xanthorrhiza*	3	67	9 (*R*)	33[a]	79	25 (*R*)	21
		6	14	18 (*R*)	86[a]	60	53 (*R*)	40
3	*Beta vulgaris*	3	77	18(*S*)	23[a]	55	79 (*R*)	45
		6	–	–	92[a]	56	76 (*R*)	44
4	*Brassica rapa*	3	100	–	–	93	9 (*R*)	7
		6	98	4 (*R*)	1	99	9 (*R*)	1
5	*Colocasia esculenta*	3	99	–	1	96	4 (*R*)	4
		6	93	4 (*R*)	6[a]	95	4 (*R*)	5
6	*Coriandrum sativum*	4	100	–	–	54	77 (*R*)	46
		6	100	–	–	1	–	100
7	*Dioscoea alata*	3	97	–	2[a]	91	12 (*R*)	9
		6	97	–	3[a]	92	15 (*R*)	8
8	*Ipomoea batatas* (white)	3	99	–	1	94	10 (*R*)	6
		6	99	–	1	89	14 (*R*)	11
9	*Manihot esculenta*	3	97	–	3	68	19 (*R*)	32
		6	97	–	3	58	23 (*R*)	42
10	*Raphanus sativus*	3	99	–	l[a]	100	7 (*R*)	–
		6	97	–	3[a]	99	8 (*R*)	1
11	*Solanum tuberosum*	3	98	–	l[a]	99	7 (*R*)	1
		6	97	–	2[a]	95	9 (*R*)	5
12	*Zingiber officinale*	3	99	–	1	97	8 (*R*)	3
		6	98	3 (*S*)	1	–	–	100

t: time (days); *c*: conversion determined by GC analysis using a chiral column; e.e.: enantiomeric excess; Absolute configuration is in parenthesis.
[a] 4′-Aminoacetophenone. It was detected by GC–MS analysis and evaluated by comparison with commercial authentic sample.

The complete biooxidation observed with the alcohols **2c** and **2e** suggest an environmentally friendly protocol for oxidation reactions. A "green" method of biocatalytic oxidation using microorganism was already described [31] and thus, the use of plants presented here can be applied for this purpose.

3.2. Bioreduction

As substrate model for the enantioselective bioreduction reaction, we selected acetophenone (**2a**) (Scheme 1). We carried out its bioreduction using 17 edible plants. High enantioselectivities (>90% e.e.) and moderate values of conversion (44–57%) were observed by the use of *A. xanthorrhiza*, *C. sativum* and *D. alata* as biocatalysts (Table 2). Although high values of optical purity were also obtained with *A. schoenoprasum*, *R. sativus* and *Z. officinale*, the conversion of the reaction was in a lower extension (Table 2). Unfortunately, the reduction of acetophenone with *Z. officinale* did not match the result previously presented (Table 1, entry 15). In this case, it is possible that a two-step redox reaction can be occurring and the low yield observed can represent a higher activity of the biooxidation than the bioreduction reaction, furnishing the initial ketone.

Scheme 3. Bioreduction of nitrobenzene by *Beta vulgaris* (beet).

Additional bioreductions were carried out with ten plants as catalysts with aromatic substituted ketones (Scheme 1). For the enantioselective reduction of 4′-bromoacetophenone (**1b**), we observed high enantioselectivity but low values of conversion using *A. schoenoprasum*, *A. xanthorrhiza*, *C. esculenta*, *D. alata* and *R. sativus* as catalysts (Table 5, entries 1, 3, 6, 8 and 10). The catalyst, which gave the best conversion (55%) was *M. esculenta* for (*R*)-**2b** with 89% e.e. (Table 5, entry 9). The alcohol (*S*)-2b was obtained using *A. xanthorrhiza* in 17% yield and 98% e.e. (Table 5, entry 3). *B. vulgaris* and 4′-methylacetophenone (**1c**) lead to the formation of the alcohol (*R*)-**2c** in 86% e.e. and 22% yield (Table 5, entry 4). Most of the plants tested with compound **1c** gave (*S*)-**2c** in poor yields and >98% e.e. (Table 5; entries 1, 5, 9 and 10).

4′-Nitroacetophenone (**1d**) was reduced into the corresponding alcohol (*S*)-**2d** in high e.e. (95%) and conversion (79%) by the use of *A. xanthorrhiza* (Table 5, entry 3). Nitro reduction was also observed by several plants, which gave 4′-aminoacetophenone as side-product. *C. esculenta* lead to

Table 5
Bioreduction of acetophenone derivatives **1b**–**e**.

Entry	Biocatalyst	*t* (days)	Alcohol **2b**		Alcohol **2c**		Alcohol **2d**		Alcohol **2e**	
			c (%)	e.e. (%)	*c* (%)	e.e. (%)	*c* (%)	e.e. (%)	*c* (%)	e.e. (%)
1	*Allium schoenoprasum*	3	3	>98 (*S*)	1	>98 (*S*)	3	10 (*R*)	1	>98 (*S*)
		6	5	>98 (*S*)	–	–	21 (31[a])	48 (*S*)	4	>98 (*S*)
2	*Arctium lappa*	3	–	–	1	>98 (*S*)	–	–	–	–
		6	–	–	1	>98 (*S*)	9	25	4	44 (*S*)
3	*Arracacia xanthorrhiza*	3	14	>98 (*S*)	32	78 (*R*)	68 (6[a])	96 (*S*)	21	>98 (*S*)
		6	17	>98 (*S*)	–	–	79 (9[a])	95 (*S*)	10	>98 (*S*)
4	*Beta vulgaris*	3	10	>99 (*S*)	22	86 (*R*)	–	–	–	–
		6	12	>99 (*S*)	27	87 (*R*)	–	–	4	44 (*S*)
5	*Brassica rapa*	3	–	–	3	>98 (*S*)	–	–	–	–
		6	–	–	3	>98 (*S*)	-	–	–	–
6	*Colocasia esculenta*	3	6	>98 (*S*)	13	38 (*S*)	73 (24[a])	–	18	71 (*S*)
		6	11	>98 (*S*)	18	35 (*S*)	(100[a])	–	19	71(*S*)
7	*Coriandrum sativum*	3	–	–	–	–	16	>98 (*S*)	2	>98 (*S*)
		6	13	66 (*S*)	–	–	16	96 (*S*)	–	–
8	*Dioscorea alata*	3	3	>98 (*S*)	7	29 (*S*)	21	87 (*S*)	1	27 (*R*)
		6	3	>98 (*S*)	11	25 (*S*)	24	86 (*S*)	3	10 (*S*)
9	*Manihot esculenta*	3	50	>90 (*R*)	2	>98 (*S*)	51 (19[a])	91 (*S*)	–	–
		6	55	89 (*R*)	3	>98 (*S*)	56 (20[a])	91 (*S*)	9	>98 (*S*)
10	*Raphanus sativus*	3	4	>98 (*S*)	1	>98 (*S*)	2	>98 (*S*)	–	–
		6	6	>98 (*S*)	1	>98 (*S*)	2	64 (*S*)	2	66 (*S*)

t: time (days); *c*: conversion to **2b**–**e** was determined by GC analysis using a chiral column; e.e.: enantiomeric excess; Absolute configuration is in parenthesis.
[a] 4′-Aminoacetophenone. It was detected by GC–MS analysis and evaluated by comparison with commercial authentic sample.

complete reduction of the nitro group into amino after 6 days of biotransformation (Table 5, entry 6).

The last substrate used was 4′-methylselenoacetophenone (**1e**) and we obtained the highest enantiomeric excess and conversion when *A. xanthorrhiza* was used as catalyst (Table 5, entry 3, conversion 21 %, e.e. >98%).

In order to apply these plants in higher scale reactions, we used *A. xanthorrhiza* for bioreduction of acetophenone (**1a**) and *C. sativum* for biooxidation of (*RS*)-1-(4-methylphenyl)ethanol (**2c**). The bioreduction reaction gave 46% of **1a** and 43% of (*S*)-**2a** (e.e. >99%) as isolated yield. The biooxidation reaction gave 26% of **1c** and 34% of (*R*)-**2c** (e.e. 64%).

4. Conclusion

In conclusion, we have successfully synthesized several chiral (*S*)- and (*R*)-alcohols in up to 98% of enantiomeric excess by bioreduction or biooxidation reactions. Among the plants tested, arracacha roots (*A. xanthorrhiza*) furnished more reproducible and reliable results, which indicate a potential biocatalyst for asymmetric redox reactions. The oxidation of alcohols into ketones catalyzed by plants showed good results. As we observed the nitro reduction performed by different plants, we could also study these reactions for azo dyes biodegradation. These reactions were in several cases very efficient and are considered environmentally friendly, because the residue formed can be used as manure. Other sources of plants will be tested to evaluate the reproducibility.

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