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Biotransformation of Some Compounds using Potato

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ABSTRACT

Biocatalysts have been considered as suitable biochemical systems for the biotransformation of exogenous substrates. For the last 20 years plant cell cultures have been used for the biotransformation of compounds such as terpenoids and alkaloids. In the last decade, various examples of the reduction of ketones to chiral alcohols are reported using fungi or algae. It is known that various enzymes are included in some vegetables and catalyse the oxidation, reduction and hydrolysis of ester. In particular, potatoes contain the enzymes such as polyphenol oxidase (PPO), lypoxygenase (LOX), *Solanum tuberosum* epoxide hydrolase (StEH), hydroperoxide lyase (HPOlyase), reductase, and hydroxylase. Mironowicz (1998) first reported that the use of whole plant cells from potato and topinambur tubers for the hydrolysis of acetates results in the production of alcohols. Recently, the use of plant enzymatic systems and genetic manipulation approaches to biotransformation has steadily increasing over the past half decade. More recently, we reported that the biotransformation of camphorquinone, 1,2-cyclohexanedione and 2-methylcyclohexanone using various vegetables gives the corresponding alcohols as reduction products. Moreover, other studies have shown the studied oxidation of bisphenol A by polyphenol oxidase in vegetables. The availability of the enzymatic system using vegetables is low cost, with ease of work-up and eco-friendly system for all advantages. In this paper the reduction of various ketones, oxidation of some compounds and hydrolysis of ester with potatoes in vegetables are described.

Keywords: hydrolysis, oxidation, reduction, *Solanum tuberosum*

CONTENTS

INTRODUCTION

In the past few decades, biocatalysis has undergone significant development, and a number of biocatalytic reactions have been introduced and optimized for the transformation of organic compounds. Ishihara *et al*. (2003) summarized the advances in the biotransformation of exogenous substrates by cultured cells that have been reported over the past 25 years. Also, Nakamura *et al*. (2003) reviewed recent advances in the asymmetric reduction of ketones by biocatalysts.

It is known that various useful enzymes are found in vegetables. Mironowicz (1998) first reported on the use of whole plant cells derived from potato (*Solanum tuberosum*) and topinambur (*Helianthus tuberosus*) tubers for the hydrolysis of acetates and the production of the alcohols. The plant enzymes available, and the chemical compounds, which can undergo biotransformation mediated by these plant enzymes, vary. Yadav *et al.* (2002) reported that the reduction of various ketones such as acetophenones, α-azido aryl ketones, β-ketoesters, aliphatic acyclic and cyclic ketones gives corresponding optically active secondary alcohols with moderate to excellent chemical yields using carrot (*Daucus carota*). We reported (Utsukihara *et al*. 2006) on a convenient and simple procedure for the preparation of α-hydroxycamphor from (+)- and (-)-camphorquinones from various vegetables including potato, by a reduction process under mild conditions. Gargouri and Legoy (2002) reported that a two-enzyme system involving a lipase from a *Pseudomonas* sp. and an extract of potato tubers containing lipoxygenase were used to convert triacylglycerols to 9-hydroperoxy fatty acids. Additionally, polyphenol oxidase (tyrosinase) and peroxidase are obtained from the potato. Furthermore, other vegetables such as carrot, celery (*Apium graveolens* L. var. *rapaceum*), horseradish (*Armoracia lapathifolia* Gilib.) and banana (*Musa sapientum*) can be used biotransformation. (Mączka and Mironowicz 2002; Comasseto *et al.* 2004; Mączka and Mironowicz 2004;

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Mączka and Mironowicz 2004; Scarpi *et al.* 2005; Bruni *et al.* 2006a, 2006b; Machado *et al.* 2006; Yadav *et al.* 2008). This method is an eco-friendly environmental reduction system employing vegetables as biocatalysts. The advantages of the reduction are the easy availability and low cost of materials. Furthermore, biocatalytic reactions are generally safety. The reaction conditions are mild using water as solvent at room temperature. However, synthesizing more complex molecules is difficult due to low solubility of the substrates.

The use of plant genetic manipulation approaches to biotransformation has been steadily increasing over the past half decade. For example, epoxide hydrolases (*St*EH) from potato (*Solanum tuberosum*) catalyzes racemic styrene oxide derivatives (Monterde *et al.* 2004; Mateo *et al.* 2007; Pihlanto *et al*. 2008). The potato (*Solanum tuberosum*) *St*EH in the enzymatic extract was prepared by overexpression in *Escherichia coli* BL21. Isolated enzymes and the plant parts such as roots and leaves are used as biocatalysts as well as chemical catalysts or enzymes.

In this review, the biotransformation of the exogenous substrates by potato (*Solanum tuberosum*) and other vegetables are summarized according to the three chemical reaction classes i.e. reduction, oxidation and hydrolysis.

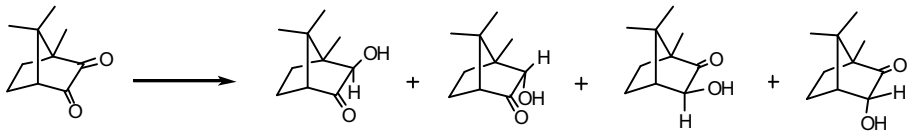
REDUCTION

Reduction of ketones

It is known that acetophenones and other ketones are reduced to their corresponding alcohols with excellent stereoselectivity using carrot (*Daucus carota*). However, there are a few reports that reduce ketones with other vegetables. In the following list of vegetables, carrot (*D. carota*), potato (*Solanum tuberosum*), sweet potato (*Ipomoea batatas*), apple (*Malus pumila*), Japanese radish (*Raphanus sativus*), cucumber (*Cucumis sativus*), burdock (*Arctium lappa*) onion (*Allium cepa*), ornamental cabbage (*Brassica oleracea botrytis*), pumpkin (*Cucurbita maxima*, *Cucurbita pepo*), globe artichoke (*Cynara scolimus*), fennel (*Foeniculum vulgare*), banana (*Musa sapientum*), topinambur (*Helianthus tuberosus*), celery (*Apium graveolens* L. var. *rapaceum*), horseradish (*Armoracia lapathifolia* Gilib.) and cassava (*Manihot dulcis* Crantz, *Manihot esculenta* Crantz) have been tested in biotransformations.

(+)-Camphorquinone (**1**) afforded a mixture of diastereoisomers of three α-keto alcohols: (+)-2*R*-*exo*-hydroxyepicamphor (**1a**), (-)-3*S*-*exo*-hydroxycamphor (**1c**) and (+)-3*R*-*endo*-hydroxycamphor (**1d**). However, (-)-2*S*-*endo*-hydroxyepicamphor (**1b**) could not be obtained from (+)-camphorquinone (**1**) using carrot (*D. carota*). These results are shown in **Table 1**. Reduction of (+)-camphorquinone (**1**) with burdock (*A. lappa*) provided (-)-3*S*-*exo*-hydroxycamphor (**1c**) in high selectivity of 100%. Reduction of (+)-camphorquinone (**1**) from apple (*M. pumila*), Japanese radish (*R. sativus*), cucumber (*C. sativus*) and onion (*A. cepa*) were transformed to (-)-3*S*-*exo*-hydroxycamphor (**1c**) as the major products. However, the reduction of (+)-camphorquinone (**1**) by potato (*S. tuberosum*), gave no selectivity. On the contrary, sweet potato (*I. batatas*) gave (+)-2*R*-*exo*-hydroxyepicamphor (**1a**) in 79% selectivity.

(-)-Camphorquinone (**2**) was transformed to give the corresponding four isomers: (-)-2*S*-*exo*-hydroxyepicamphor (**2a**), (+)-2*R*-*endo*-hydroxyepicamphor (**2b**), (+)-3*R*-*exo*-hydroxycamphor (**2c**) and (-)-3*S*-*endo*-hydroxycamphor (**2d**). (-)-Camphorquinone (**2**) with various vegetables was transformed to the corresponding four isomers. Reduction of (-)-camphorquinone (**2**) with onion (*A. cepa*) provided

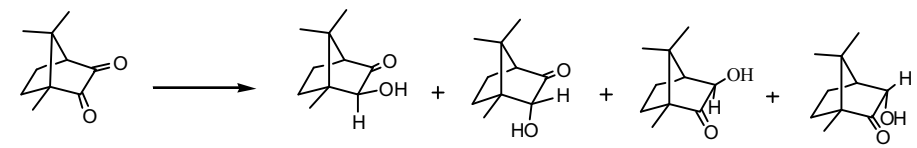


1 **1a** **1b** **1c** **1d**

Table 1 Reduction of (+)-camphorquinone (**1**) by various vegetables.

Vegetable	Yield (%)[a]	Product ratio (%)[b]				Reference
		1a	1b	1c	1d	
Potato (*Solanum tuberosum*)	89	36	-	27	37	Utsukihara *et al*. 2006
Carrot (*Daucus carota*)	88	4	-	88	8	Utsukihara *et al*. 2006
Sweet potato (*Ipomoea batatas*)	86	79	-	14	7	Utsukihara *et al*. 2006
Apple (*Malus pumila*)	84	5	-	59	36	Utsukihara *et al*. 2006
Radish (*Raphanus sativus*)	82	20	-	63	17	Utsukihara *et al*. 2006
Cucumber (*Cucumis sativus*)	85	19	-	49	32	Utsukihara *et al*. 2006
Burdock (*Arctium lappa*)	81	-	-	100	-	Utsukihara *et al*. 2006
Onion (*Allium cepa*)	84	20	-	63	17	Utsukihara *et al*. 2006

[a] Isolated yields.
[b] Relative intensities by ^{1}H NMR peak area.

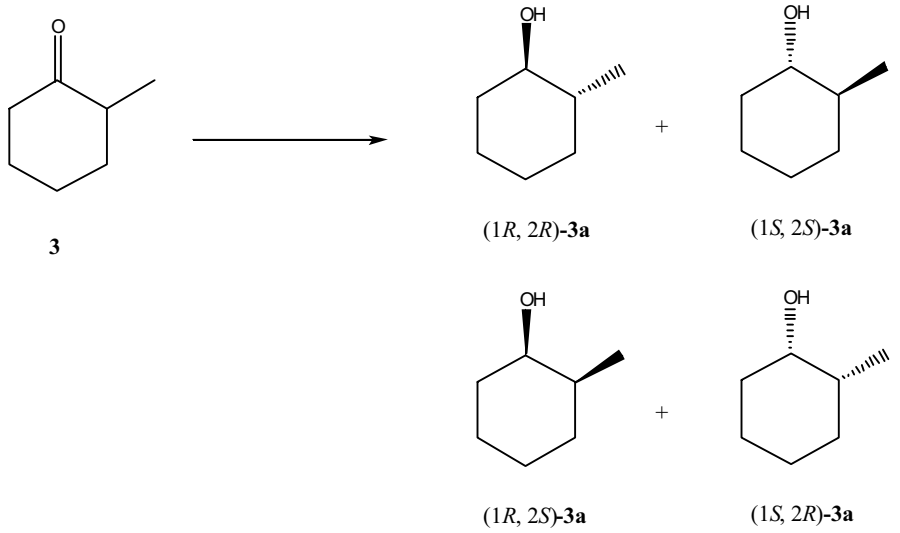


2 **2a** **2b** **2c** **2d**

Table 2 Reduction of (-)-camphorquinone (**2**) by various vegetables.

Vegetable	Yield (%)[a]	Product ratio (%)[b]				Reference
		2a	2b	2c	2d	
Potato (*Solanum tuberosum*)	82	32	36	26	6	Utsukihara *et al*. 2006
Carrot (*Daucus carota*)	87	52	15	28	5	Utsukihara *et al*. 2006
Sweet potato (*Ipomoea batatas*)	86	43	20	30	7	Utsukihara *et al*. 2006
Apple (*Malus pumila*)	84	17	19	49	15	Utsukihara *et al*. 2006
Radish (*Raphanus sativus*)	84	47	10	35	8	Utsukihara *et al*. 2006
Cucumber (*Cucumis sativus*)	82	35	8	45	12	Utsukihara *et al*. 2006
Burdock (*Arctium lappa*)	81	36	36	28	-	Utsukihara *et al*. 2006
Onion (*Allium cepa*)	85	-	9	85	6	Utsukihara *et al*. 2006

[a] Isolated yields.
[b] Relative intensities by ^{1}H NMR peak area.



3

(1*R*, 2*R*)-**3a**

(1*S*, 2*S*)-**3a**

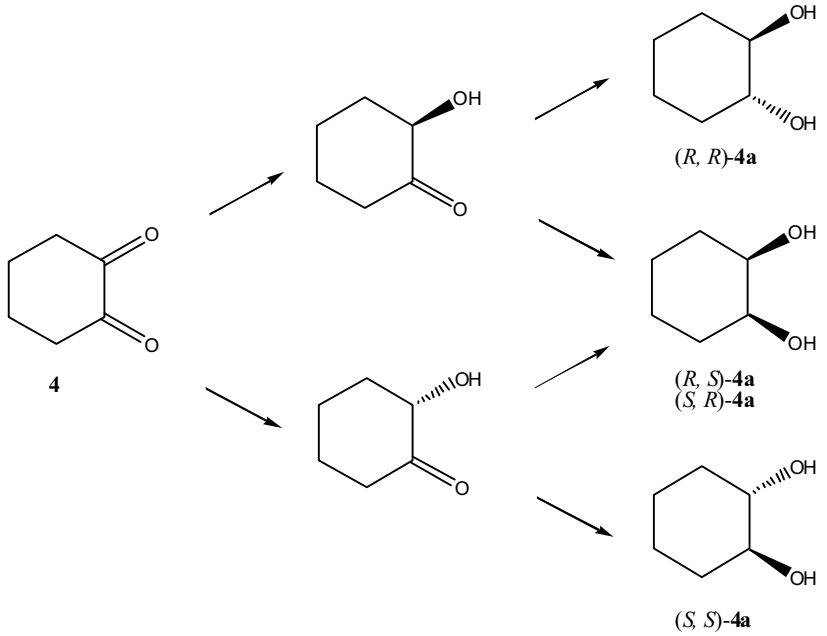
(1*R*, 2*S*)-**3a**

(1*S*, 2*R*)-**3a**

Table 3 Reduction of 2-methylcyclohexanone (**3**) by various vegetables.

Vegetable	Yield (%)[a]	*cis*-Alcohol ratio/ee. (%)[b]	*trans*-Alcohol ratio/ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	38	8	92/77 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Carrot (*Daucus carota*)	67	48/100 (1*S*, 2*R*)	52/100 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Sweet potato (*Ipomoea batatas*)	61	70/37 (1*S*, 2*R*)	30/90 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Apple (*Malus pumila*)	18	77/95 (1*S*, 2*R*)	23/50 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Radish (*Raphanus sativus*)	14	36/77 (1*S*, 2*R*)	64/73 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Cucumber (*Cucumis sativus*)	15	24/75 (1*S*, 2*R*)	76/81 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Burdock (*Arctium lappa*)	66	53/70 (1*S*, 2*R*)	47/88 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Onion (*Allium cepa*)	49	39/80 (1*S*, 2*R*)	61/90 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Ornamental cabbage (*Brassica oleracea botrytis*)	17	65/20 (1*S*, 2*R*)	35/92 (1*S*, 2*S*)	Bruni *et al*. 2006
Carrot (*Daucus carota*)	100	46/20 (1*S*, 2*R*)	54/90 (1*S*, 2*S*)	Bruni *et al*. 2006
Pumpkin (*Cucurbita maxima*)	60	57/24 (1*S*, 2*R*)	43/92 (1*S*, 2*S*)	Bruni *et al*. 2006
Globe artichoke (*Cynara scolimus*)	93	68/10 (1*S*, 2*R*)	32/70 (1*S*, 2*S*)	Bruni *et al*. 2006
Fennel (*Foeniculum volgare*)	78	33/30 (1*S*, 2*R*)	67/92 (1*S*, 2*S*)	Bruni *et al*. 2006
Banana (*Musa sapientum*)	27	56/20 (1*S*, 2*R*)	44/20 (1*S*, 2*S*)	Bruni *et al*. 2006

[a] Isolated yields.
[b] GLC peak area.



4

(*R, R*)-**4a**

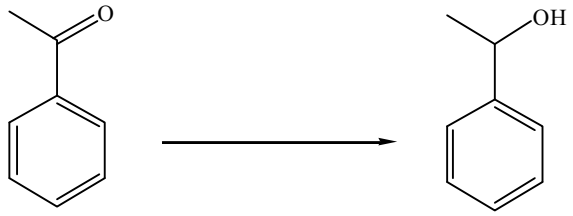
(*R, S*)-**4a**
(*S, R*)-**4a**

(*S, S*)-**4a**

Table 4 Reduction of 1,2-cyclohexanedione (**4**) by various vegetables.

Vegetable	Yield (%)[a]	de. (%)[b]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	22	28	2 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Carrot (*Daucus carota*)	30	72	87 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Sweet potato (*Ipomoea batatas*)	26	44	58 (1*R*, 2*R*)	Utsukihara *et al*. 2006
Apple (*Malus pumila*)	46	56	90 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Radish (*Raphanus sativus*)	43	80	19 (1*R*, 2*R*)	Utsukihara *et al*. 2006
Cucumber (*Cucumis sativus*)	40	56	62 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Burdock (*Arctium lappa*)	34	62	91 (1*S*, 2*S*)	Utsukihara *et al*. 2006
Onion (*Allium cepa*)	43	60	85 (1*S*, 2*S*)	Utsukihara *et al*. 2006

[a] Isolated yields.
[b] GLC peak area.

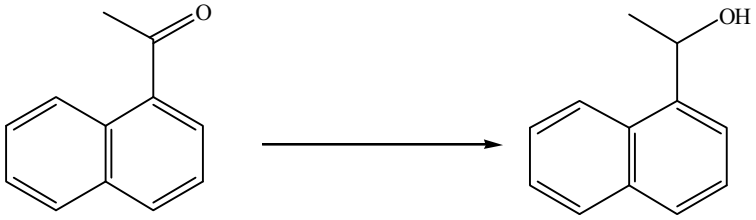


5 **5a**

Table 5 Reduction of acetophenone (**5**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	1	20 (*R*)	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	1	15 (*R*)	Mironowicz 1998
Carrot (*Daucus carota*)	73	92 (*S*)	Yadav *et al*. 2002
Carrot (*Daucus carota*)	100	100 (*S*)	Bruni *et al*. 2002
Carrot (*Daucus carota*)	4	82 (*S*)	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	100	100 (*S*)	Bruni *et al*. 2006
Celery (*Apium graveolens* L. var. *rapaceum*)	20	85 (*S*)	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	5	88 (*S*)	Maczka and Mironowicz 2002
Fennel (*Foeniculum vulgare*)	80	100 (*S*)	Bruni *et al*. 2006
Fennel (*Foeniculum vulgare*)	37	100 (*S*)	Bruni *et al*. 2002
Pumpkin (*Cucurbita maxima*)	79	90 (*S*)	Bruni *et al*. 2006
Banana (*Musa sapientum*)	55	100 (*S*)	Bruni *et al*. 2006
Pumpkin (*Cucurbita pepo*)	10	100 (*S*)	Bruni *et al*. 2002
Pumpkin (*Cucurbita pepo*)	20	89 (*S*)	Bruni *et al*. 2006
Globe artichoke (*Cynara scolimus*)	15	48 (*S*)	Bruni *et al*. 2006
Ornamental cabbage (*Brassica oleracea botrytis*)	52	78 (*R*)	Bruni *et al*. 2006
Cassava (*Manihot dulcis* Crantz*)*	83	97 (*S*)	Machado *et al*. 2006
Cassava (*Manihot esculenta* Crantz*)*	80	95 (*S*)	Machado *et al*. 2006

[a] Isolated yields.
[b] GLC peak area.



6 **6a**

Table 6 Reduction of 1'-acetonaphtone (**6**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	4	-	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	3	100 (*S*)	Mironowicz 1998
Celery (*Apium graveolens* L. var. *rapaceum*)	8	0	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	0	-	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	0	-	Maczka and Mironowicz 2002

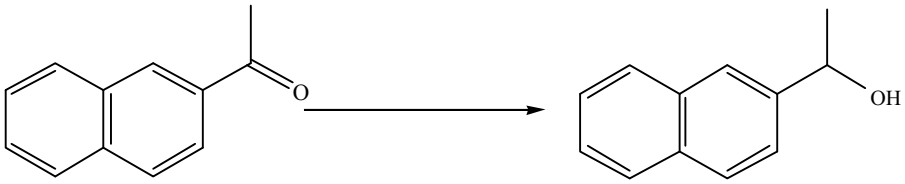
[a] Isolated yields.
[b] GLC peak area.

(+)-3*R*-*exo*-hydroxycamphor (**2c**) in 85% selectivity. However, apple (*M. pumila*), and cucumber (*C. sativus*) transformed **2** to (+)-3*R*-*exo*-hydroxycamphor (**2c**), whereas reduction of (-)-camphorquinone (**2**) by potato (*S. tuberosum*), gave no selectivity. The yields and products formed by each of the vegetables are summarized in **Tables 1** and **2**. From these results, it was found that only hydroxy ketones were obtained and diols were not afforded.

2-Methylcyclohexanone (**3**) was reduced to give *trans*- and *cis*-2-methylcyclohexanol (**3a**). These results are shown in **Table 3**. In the case of the potato (*S. tuberosum*), the reduction was high diastereomeric excess (*trans*-2-methylcyclohexanol, 84%).

Biotransformation of 1,2-cyclohexanedione (**4**) using various vegetables to the reduced product *trans*-1,2-cyclohexanediol in high selectivity has been achieved. These results are shown in **Table 4**. From these results, it was found that only diols were obtained while hydroxy ketones were not afforded. The enantioselective reduction of **4** using burdock (*A. lappa*) resulted in 91% enantiomeric excess of (1*S*, 2*S*)-*trans*-1,2-cyclohexanediol (**4a**) at full conversion. Moreover, carrot (*D. carota*), apple (*M. pumila*), and onion (*A. cepa*) provided (1*S*, 2*S*)-*trans*-1,2-cyclohexanediol (**4a**) in high enantiomeric excess. On the contrary, sweet potato (*I. batatas*) and radish (*R. sativus*) gave (1*R*, 2*R*)-*trans*-1,2-cyclohexanediol (**4a**) as major products. In the case of radish (*R. sativus*), the diastereomeric excess of the *trans*-1,2-cyclohexanediol ((*R*, *R*)-**4a,** (*S*, *S*)-**4a**) was 80% at complete conversion. On the contrary, burdock (*A. lappa*) provided *trans*-1,2-cyclohexanediol in good diastereomeric excess (60%). Whereas, potato (*S. tuberosum*) provided 1,2-cyclohexanediol (**4a**) in low diastereomeric and enantiomeric excess.

Carrot reduces the prochiral ketone, acetophenone (**5**), to the (*S*)-phenylethanol (**5a**) (ee. 82-100%). In the case of potato (*S. tuberosum*) and topinambur (*H. tuberosus*), lower yields are obtained with low enantiomeric excess. Potato (*S. tuberosum*), topinambur (*H. tuberosus*) and ornamental cabbage (*B. oleracea botrytis*) gave the product with *R*-configuration alcohol. On the hand, the alcohols produced using other plants had *S*-configuration, which is in agreement with Prelog's rule. These results are shown in **Table 5**.

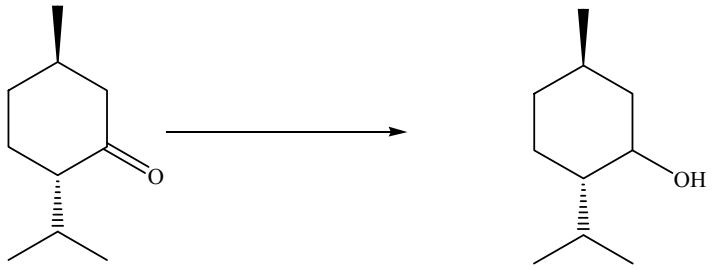


7 **7a**

Table 7 Reduction of 2'-acetonaphtone (**7**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	4	100 (*S*)	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	23	100 (*S*)	Mironowicz 1998
Celery (*Apium graveolens* L. var. *rapaceum*)	19	72 (*S*)	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	70	97 (*S*)	Yadav *et al*. 2002
Carrot (*Daucus carota*)	100	100 (*S*)	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	0	-	Maczka and Mironowicz 2002

[a] Isolated yields.
[b] GLC peak area.



8 **8a**

Table 8 Reduction of menthone (**8**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	1	33 (1*R*)	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	1	88 (1*R*)	Mironowicz 1998
Celery (*Apium graveolens* L. var. *rapaceum*)	8	-	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	2	-	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	11	22 (1*S*)	Maczka and Mironowicz 2002

[a] Isolated yields.
[b] GLC peak area.

1'-Acetonaphtone (**6**) was reduced to give alcohol **6a**. In the case of potato (*S. tuberosum*), the reduction was low yield. Other plants such as carrot (*D. carota*), horseradish (*A. lapathifolia* Gilib.) and celery (*A. graveolens* L. var. *rapaceum*) showed poor reduction activity. These results are shown in **Table 6**.

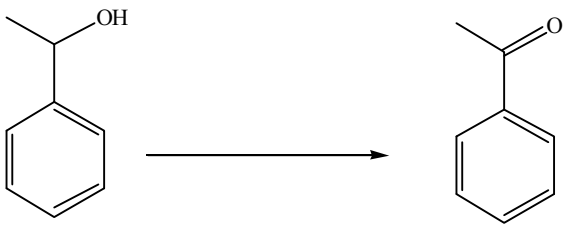
2'-Acetonaphtone (**7**) was reduced to give **7a**. In the case of potato (*S. tuberosum*), the reduction was high enantiomeric excess (*S*-alcohol, 100%), but low yields (4%) resulted. In almost all the cases, good enantiomeric excess (72-100%) was observed. When, carrot (*D. carota*) was provided **7a** in high enantiomeric excess (100%), a high chemical yield (100%) was generated. These results are shown in **Table 7**.

Menthone (**8**) was reduced to give menthol (**8a**). Potato (*S. tuberosum*) and topinambur (*H. tuberosus*) gave (1*R*) – menthol (**8a**). On the contrary, 1*S*-alcohol was obtained with celery (*A. graveolens* L. var. *rapaceum*). All the cases, reduction of **8** using plants resulted in low chemical yield (1-11%). These results are shown in **Table 8**.

OXIDATION

Oxidation of alcohols

Enantioselective oxidation is useful for the preparation of

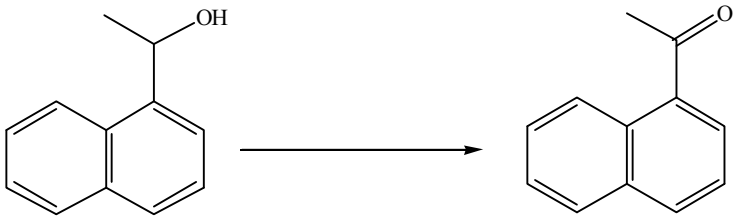


5a **5**

Table 9 Oxidation of 1-phenylethanol (**5a**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	14	-	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	43	80 (*R*)	Mironowicz 1998
Celery (*Apium graveolens* L. var *rapaceum*)	29	69 (*R*)	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	11	-	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	-	-	Maczka and Mironowicz 2002

[a] Isolated yields.
[b] GLC peak area.

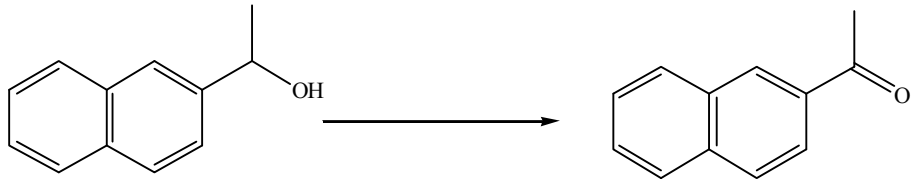


6a **6**

Table 10 Oxidation of 1-(1-naphthyl)ethanol (**6a**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	10	4 (*R*)	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	2	6 (*R*)	Mironowicz 1998
Celery (*Apium graveolens* L. var *rapaceum*)	0	-	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	0	-	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	0	-	Maczka and Mironowicz 2002

[a] Isolated yields.
[b] GLC peak area.

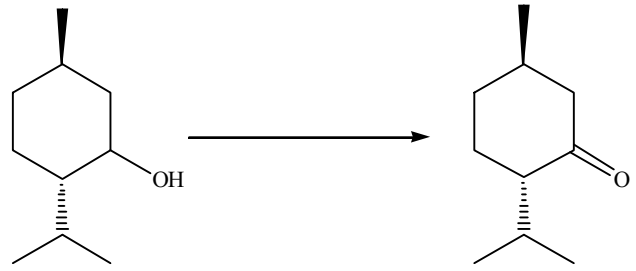


7a **7**

Table 11 Oxidation of 1-(naphthyl)ethanol (**7a**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	4	5 (*R*)	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	46	95 (*R*)	Mironowicz 1998
Celery (*Apium graveolens* L. var *rapaceum*)	60	35 (*S*)	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	0	-	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	0	-	Maczka and Mironowicz 2002

[a] Isolated yields.
[b] GLC peak area.



8a **8**

Table 12 Oxidation of menthone (**8a**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	1	-	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	1	1 (1*R*)	Mironowicz 1998
Celery (*Apium graveolens* L. var *rapaceum*)	-	-	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	-	-	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	-	-	Maczka and Mironowicz 2002

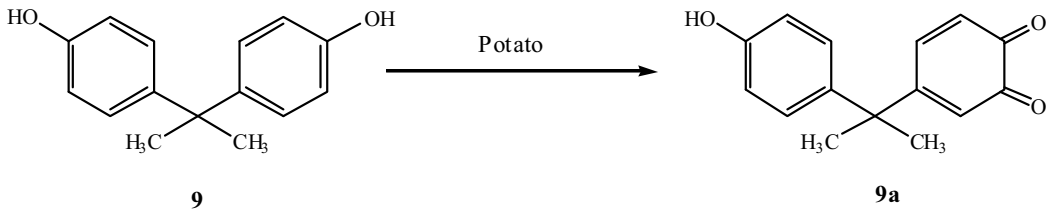
[a] Isolated yields.
[b] GLC peak area.

chiral alcohols and ketones from racemic hydroxyl compounds. Alcohols are converted to the corresponding ketones by the potato. The oxidation of recemic 1-phenylethanol (**5a**) by potato (*S. tuberosum*) tubers yielded acetophenone (**5**). The biotransformation of 1-(1-naphthyl)ethanol (**6a**) and 1-(2-naphthyl)ethanol (**7a**) with potato (*S. tuberosum*) gave 1'-acetonaphthone (**6**) and 2'-acetonaphthone (**7**), respectively. However, compounds **6a** and **7a** were obtained in low yield and low optical purities (4-5% ee.). The biotransformation of menthol (**8a**) was low for conversion of ketone. These results are shown in **Table 9**, **10**, **11** and **12**.

Potato polyphenol oxidase

Bisphenol A (2,2-bis(4-hydroxyphenol)propane) (**9**) is generally used as a starting material (**Fig. 1**) for polymers including polycarbonates, epoxy resins, phenol resins, polyesters and polyacrylates. Krishnan *et al.* (1993) and Olea *et al.* (1996) reported the estrogenic activity of **9**. It was suggested that the toxicity and biological activity of the reaction product and metabolites should be investigated from the viewpoint of risk assessment of the contaminants for human health and the environment.

Recently, degradation of bisphenol A by manganese peroxidase and laccase from basidioomycetes were reported (Hirano *et al*. 2000; Tanaka *et al*. 2000; Tsutsumi *et al*.



9 **9a**

Fig. 1 Oxigenation of bisphenol A (**9**) to quinines by potato.

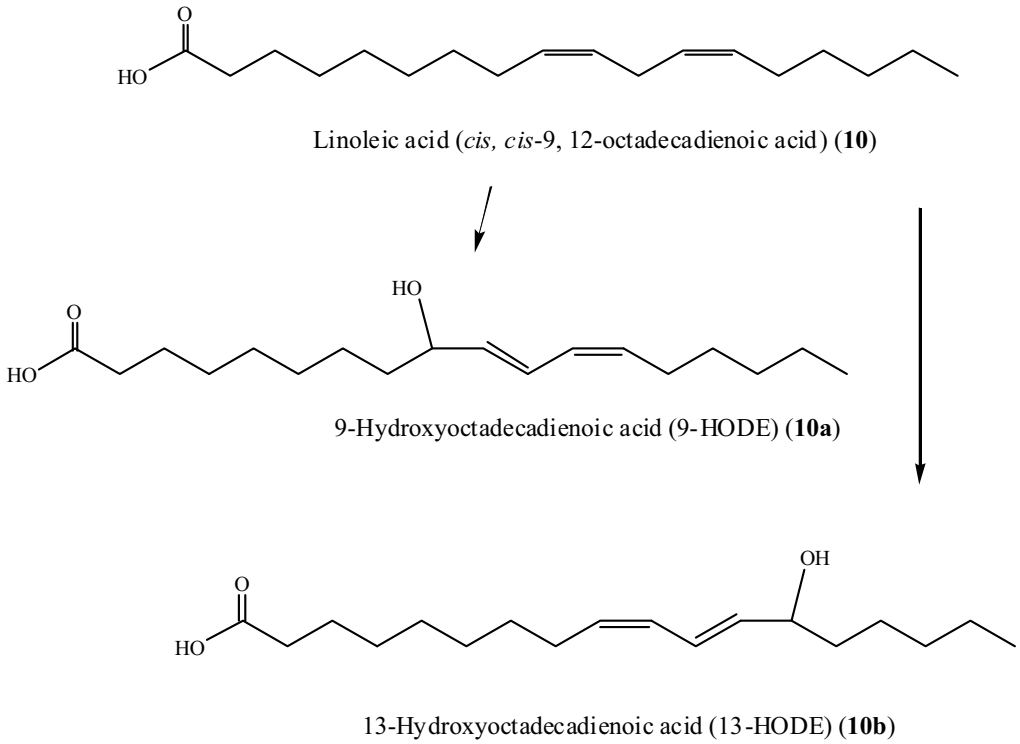


Fig. 2 Linoleic acid (**10**) incubated with potato lipoxygenase.

2001). There are some reports on removal of bisphenol A from aqueous solution using peroxidase from other sources (Caza *et al*. 1999; Sakurai *et al*. 2001; Chai *et al*. 2003, 2005). Yoshida *et al*. (2002) reported that the crude enzyme solutions of fruits and vegetables, potato (*S. tuberosum*), mushroom (*Agaricaceae*), eggplant (*Solanum melongena*), burdock (*A. lappa*), and yacon (*Polymnia sonchifolia* Poeppig & Endlicher) showed remarkable oxidative activity on bisphenol A. The highest activity was observed in potato (*S. tuberosum*), and the major product obtained by the enzymatic oxygenation was the monoquinone derivative of bisphenol A, accompanied a small amount of the bisquinone derivative. Tubers of 10 potatoes (Norin 1, Hokkai 86, Hokkai 87, Hokkai 88, Irish Cobbler, Sayaka, Touya, Toyoshiro, Beniakari and Hokkaikogane) (Yoshida *et al*. 2002) were tested for the oxidative activity of bisphenol A. These potatoes were obtained from the National Agricultural Research Center for Hokkaido Region. Among them, it was found that Norrin 1, which shows strong discoloration after peeling and/or cooking, had the highest activity. On the other hand, Hokkai 87, Toyoshiro, and Hokkaikogane showed very low oxidative activity.

Potato lipoxygenase

Wallerstein *et al.* (1947) described procedures for the assay of oxidase activity in potato (*S. tuberosum*), based on macerating the potato (*S. tuberosum*) in the presence of *p*-cresol and catechol, and determining the resulting depth of color formation photometrically after stabilization in 80% acetone.

Laties *et al.* (1972) reported that the respiration of fresh potato (*S. tuberosum*) slices is inhibited up to 30% by imidazole as an inhibitor of α-oxidation of long chain fatty acid.

Lipoxygenases are one of the most widely studied enzymes at the present time and occur in more than 60 species of plants and animals. Lipoxygenases catalyse the oxygenation of polyunsaturated fatty acids (PUFA) containing a *cis*, *cis*-1,4-pentadiene unit to form conjugated hydroperoxydienoic acid. Soybean lipoxygenase is the most extensively studied and the molecular structure has been reported.

Incubation of linoleic acid (**10**) with the purified potato (*S. tuberosum*) lipoxygenase under O_2 atmosphere resulted in a mixture of 9 and 13-hydroperoxyoctadecadienoic acid (**10a**, **10b**) being formed (Nikolaev *et al.* 1990; **Fig. 2**). Stereochemical analysis of the respective methyl-hydroperoxyoctadecadienoic acids revealed that the 9-isomer (**10a**) was in *S*-configration and 13-hydroperoxyoctadecadienoic acid (**10b**) was a mixture of *S* (39%) and *R* (61%).

Butovich *et al*. (1998) studied the aerobic oxidation of linoleyl alcohol (**11**) by potato (*S. tuberosum*) tuber lipoxygenase in the presence of 0.02% non-ionic detergent Lubrol PX and 0.1 mM sodium dodecyl sulfate.

Moreover, dioxygenation of linoleyl alcohol (**11**; **Fig. 3**) was obtained by possible positional isomeric hydroperoxides and the major products of the enzymatic oxidation of linoleyl alcohol (**11**) by potato (*S. tuberosum*) lipoxygenase were characterized by GC-MS (Gas Chromatography-Mass Spectrometer) analysis. The products were isolated, hydrogenated with H_2 over Pd (Palladium) on carbon, and ana-

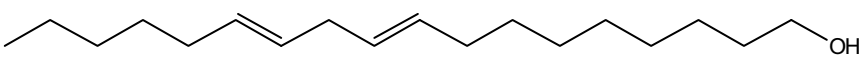
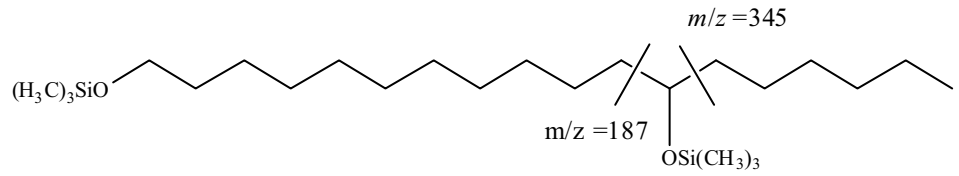
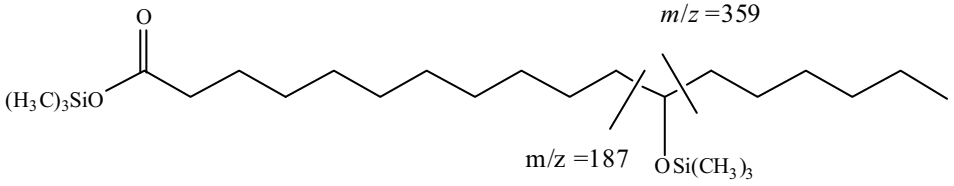


Fig. 3 Linoleyl alcohol (**11**).

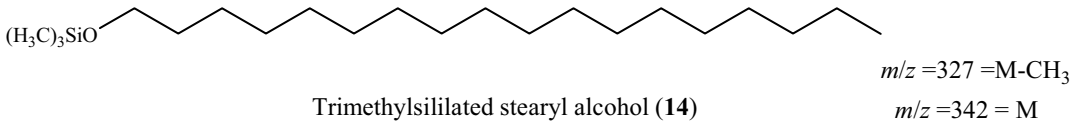


12-Hydroxystearyl alcohol (**12**)

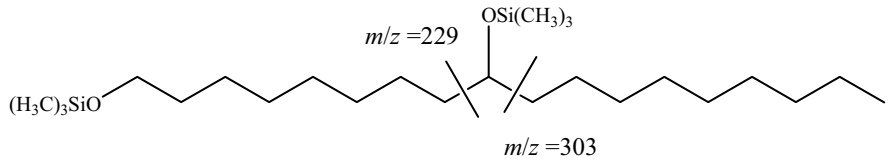


12-Hydroxystearic acid (**13**)

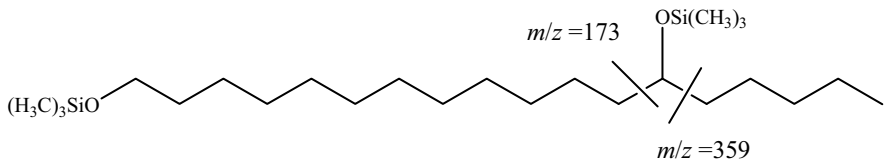
Fig. 4 12-hydroxystearyl alcohol (**12**) and 12-hydroxystearic acid (**13**).



Trimethylsililated stearyl alcohol (**14**)



Trimethylsililated 9-hydroxystearyl alcohol (**15**)



Trimethylsililated 13-hydroxystearyl alcohol (**16**)

Fig. 5 Compounds **14**, **15** and **16**.

lyzed by GC-MS. The fragmentation patterns of GC-MS analysis of O-TMS (Trimethylsilane) derivatives of two model compounds showed the presence of two major fragments with *m*/*z* 187 and 345 for 12-hydroxystearyl alcohol (**12**), and 187 and 359 for 12-hydroxystearic acid (**13**; **Fig. 4**).

The GC-MS analysis of the reaction products of enzymatic oxidation of linoleyl alcohol (**11**) revealed unreacted linoleyl alcohol (stearyl alcohol) and two of its disililated and hydrogenated hydroxy derivatives, 9-hydroxy- (**15**; **Fig. 5**) and 13-hydroxystearyl alcohol (**16**; **Fig. 5**) in an almost equimolar ratio. 9-Hydroxystearyl alcohol (**15**) was split into two major fragments with *m*/*z* ratios of 229 and 303, while 13-hydroxystearyl alcohol (**16**) gave two ions with *m*/*z* 173 and 359. From these results, it was found that the dioxygenation of linoleyl alcohol (**11**) by potato (*S. tuberosum*) tuber lipoxygenase leads to the formation of two positional isomeric products 9- and 13-hydroperoxyoctadecadien-1-ols.

Additionally, Butovich *et al.* (2000) examined the stereospecificity and double-bond conformation of primary dioxygenation products of linoleyl alcohol (**11**) catalyzed by potato (*S. tuberosum*) lipoxygenase. Four oxidation products (A, B, C and D) were revealed on HPLC (High-performance liquid Chromatography). The oxidation products were treated with $NaBH_4$ (sodium tetrahydroborate), and the resulting products were analyzed by HPLC. The treatment led to a mixture of four new products, E, F, G and H, free of the primary reactions products A-D. Compounds A-D reacted with *N*,*N*-dimethyl-*p*-phenylenediamine to give pink products. No color change in such reaction was detected with compounds E-H. Hence, compounds A-D were likely to be hydroperoxidase, while compounds E-H were presumably hydroxyl derivatives of linoleyl alcohol (**11**). Treatment of individual products A-D with $NaBH_4$ and reduced products proved that the compounds E, F, G and H were formed from A, B, C and D, respectively (**Fig. 6**).

To confirm the geometry of conjugated double bonds of the product, the ^{1}H NMR spectra of compounds E-H were measured and analyzed. Based on all the spectrometric and HPLC observations presented, the following structure assignments were made: compound A, 13-hydroperoxy-9*Z*, 11*E*-octadecadien-1-ol; compound B, 13-hydroperoxy-9*E*, 11*E*-octadecadien-1-ol; compound C, 9-hydroperoxy-10*E*, 12*Z*-octadecadien-1-ol; compound D, 9-hydroperoxy-10*E*, 12*E*-octadecadien-1-ol.

A new potato tuber lipoxygenase full-length cDNA sequence has been isolated from potato tubers and expressed

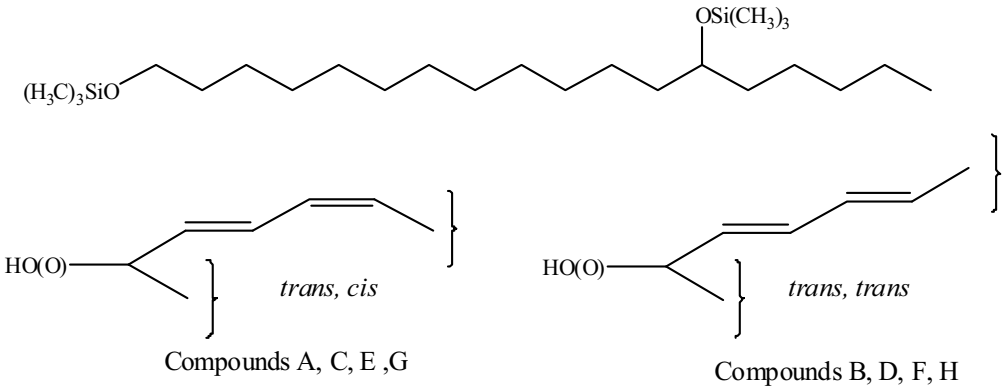


Fig. 6 Structure assignments of compounds A-H.

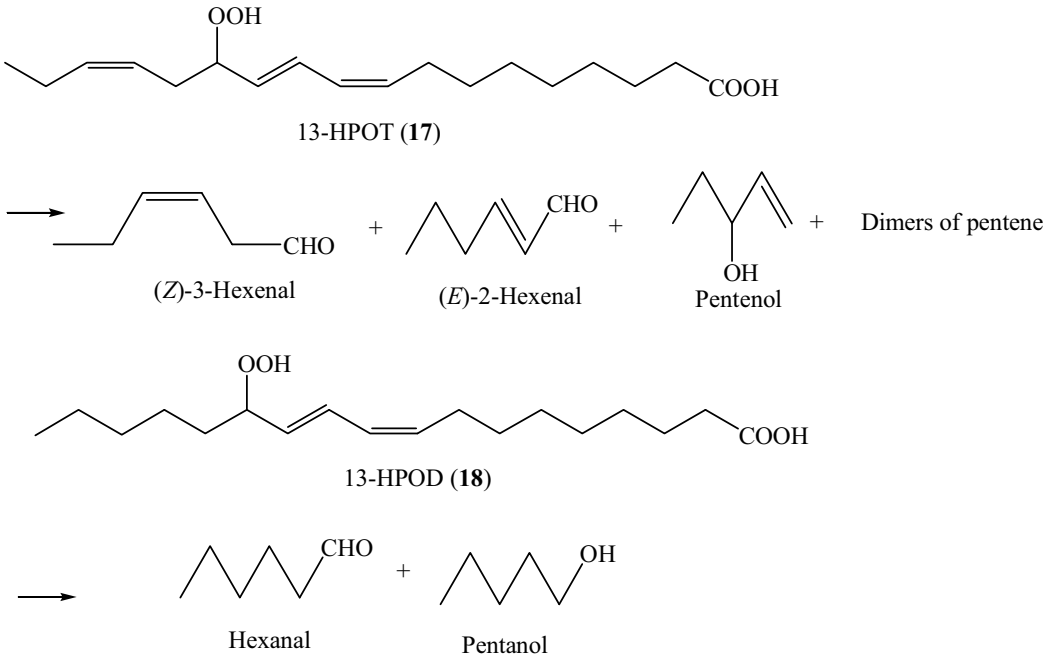


Fig. 7 Biotransformation of fatty acid hydroperoxides by potato.

in *Escherichia coli* for the characterization of novel recombinant lipoxygenase (potato 13/9- lipoxygenase) (Hughes *et al*. 2001). The authors used a homology model of pea 9/13-lipoxygenase to superimpose and compared the linoleate-binding pockets of different potato (*S. tuberosum*) lipoxygenases of known positional specificity. And then tested this model by using site-directed mutagenesis to identify some primary determinations of linoleate binding to potato 13/9-lipoxygenase and concluded that the mechanism determining positional specificity described for a cucumber lipoxygenase dose not apply to potato 13/9- lipoxygenase.

Cleavage of 13-hydroperoxy-9*Z*, 11*E*, 15*Z*-octadecatrienoic acid (13-HPOT) (**17**), 13-hydroperoxy-9Z, 11*E*-octadecatrienoic acid (13-HPOD) (**18**), 9-HPOT and 9-HPOD by potato (*S. tuberosum*) tuber cell-free extracts was investigated by Fauconnier *et al.* (2002). 13-HPOT (**17**) and 13-HPOD (**18**) were degraded almost completely while 9-HPOT and 9-HPOD were partially transformed. By GC-MS analysis of the volatile compounds formed during the reactions, it was found that (*Z*)-3-hexenal, (*E*)-2-hexenal, pentenols and dimers of pentene were obtained from 13-HPOT (**17**), while from 13-HPOD (**18**), hexanal and pentan-1-ol were formed.

Moreover, Triton X-100 was omitted in the extraction

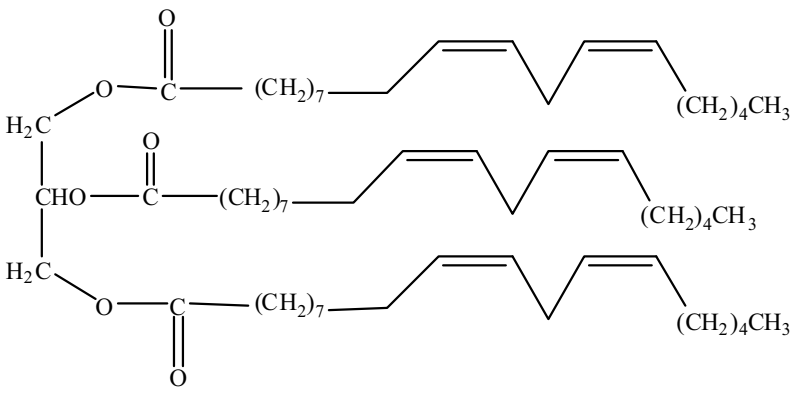


Fig. 8 Trilinolein (**19**).

buffer, and only pentenols and dimers of pentene were identified from 13-HPOT (**17**) and pentanol from 13-HPOD (**18**).

Gargouri and Legoy (2002) reported that a two-enzyme system, involving a lipase from a *Pseudomonas* sp. and an extract of potato (*S. tuberosum*) tubers containing lipoxygenase were used to convert triacylglycerols to 9-hydroperoxy fatty acids. For example, the lipase-catalyzed hydrolysis (linoleic acid/trilinolein) of lipoxygenase-catalyzed oxygennation (hydroperoxy linoleic acid/ linoleic acid) and of the total conversion of trilinolein (**19**; **Fig. 8**) to hydroperoxy linoleic acid was studied.

Co-oxidation of β-carotene in the presence of linoleic acid was catalyzed by potato (*S. tuberosum*) lipoxygenases described by Aziz *et al*. (1999). The rate of co-oxidation was dependent on the concentration of both linoleic acid and β-carotene. The maximum rate of co-oxidation occured at a molar ratio of linoleic acid to β-carotene of 16:1.

Eschen-Lippold *et al*. (2007) reported the reaction of divinyl ether-containing polyunsaturated fatty acids in transgenic potato (*S. tuberosum*) paints. The divinyl ethers colneleic acid (**21**) and colnelenic acid (**23**) were obtained from linoleic acid (**10**) and α-linolenic acid (**10′**), respectively (**Fig. 9**).

Suspension cultures of potato (*S. tuberosum*) and *Arabidopsis* were incubated with (+)- and (-)-abscisin acid (**24**) (Windsor and Zeevaart 1997). The pathway of inactivation of abscisin acid (**24**) proceeded with hydroxylation, yielding 8'-hydroxy abscisin acid (**25**) which is unstable and then rearranges to phaseic acid (**26**) (**Fig. 10**).

Potato hydroperoxide lyase

Hamberg (1999) reported on the products formed on incubating [1-^{14}C]linoleic acid (**10**) with a whole homogenate preparation of potato (*S. tuberosum*) leaves and clarified the transformation mechanism. The labeled oxidation products

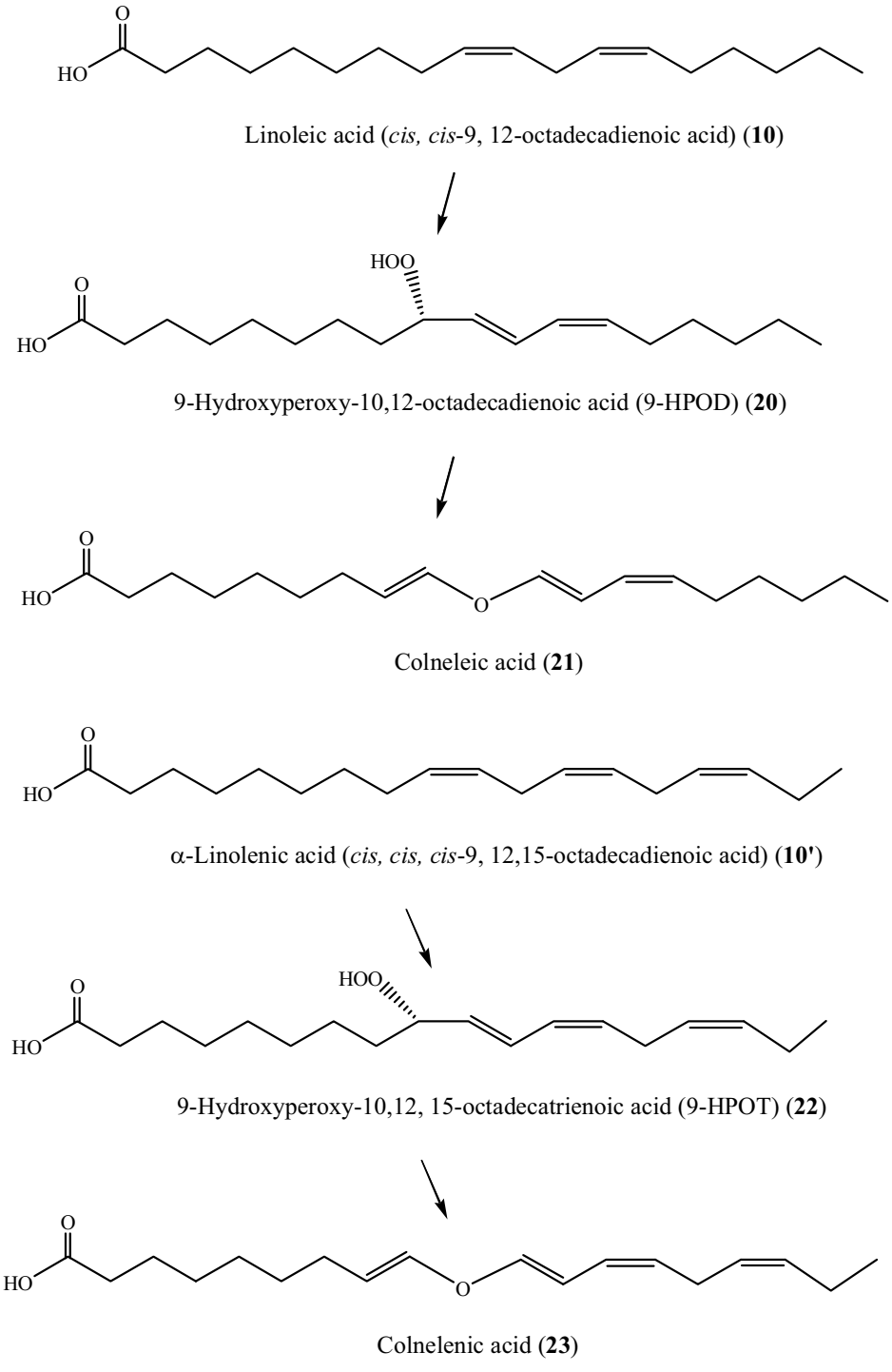
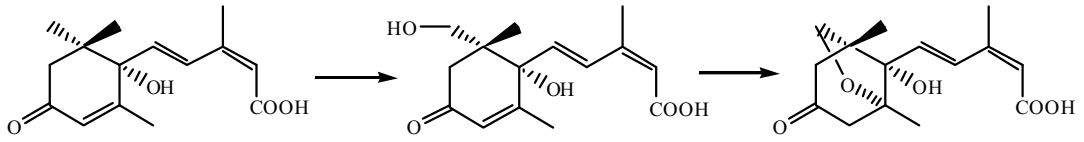
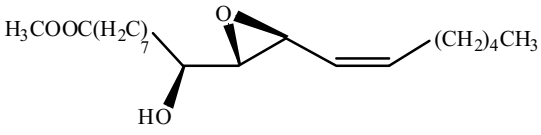


Fig. 9 Biotransformation of linoleic acid (**10**) and α-linolenic acid (**10′**).

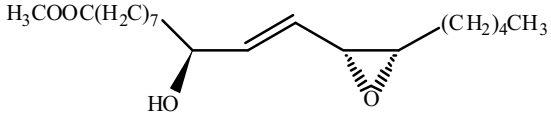


Abscisin acid (**24**) 8'-Hydroxyabscisin acid (**25**) Phaseic acid (**26**)

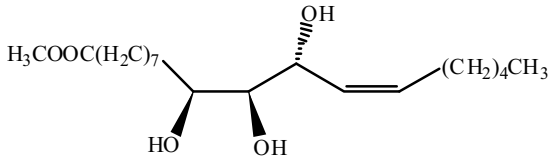
Fig. 10 Oxidation of abscisin acid (**24**) by potato.



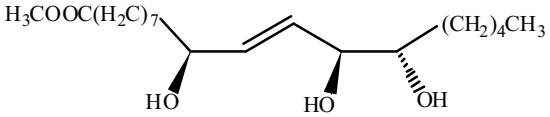
Methyl 10(*S*), 11(*S*)-epoxy-9(*S*)-hydroxy-12(*Z*)-octadecenoate (**27**)



Methyl 12(*R*), 13(*S*)-epoxy-9(*S*)-hydroxy-10(*E*)-octadecenoate (**28**)



Methyl 9(*S*), 10(*S*),11(*R*)-trihydroxy-12(*Z*)-octadecenoate (**29**)



Methyl 9(*S*), 12(*S*),13(*S*)-trihydroxy-10(*E*)-octadecenoate (**30**)

Fig. 11 Biosynthesis of trihydroxy oxylipins in potato leaves.

obtained by HPLC were contaminated by chlorophyll and other pigments. The reaction products were analyzed by straight-phase radio high-performance liquid chromatography (SP-radio-HPLC). The methyl-esterified product was found to contain four major radioactive oxidation products, i.e., the epoxy alcohols, methyl 10(*S*), 11(*S*)-epoxy-9(*S*)-hydroxy-12(*Z*)-octadecenoate (**27**), methyl 12(*R*), 13(*S*)-epoxy-9(*S*)-hydroxy-10(*E*)-octadecenoate (**28**), the trihydroxy derivatives, methyl 9(*S*), 10(*S*), 11(*R*)-trihydroxy-12(*Z*)-octadecenoate (**29**) and methyl 9(*S*), 12(*S*), 13(*S*)-trihydroxy-10(*E*)-octadecenoate (**30**) (**Fig. 11**).

Hydroperoxide lyases catalyzed the cleavage of fatty acid hydroperoxides to aldehydes and oxoacids (Vancanneyt *et al*. 2001). A hydroperoxide lyases activity present in potato leaves has been characterized and shown to specifically cleave 13-hydroperoxides of both linoleic and inoleic acid to yield hexanol and 3-hexanol, respectively, and 12-oxo-dodecenoic acid.

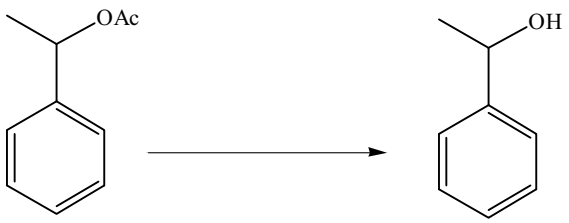
HYDROLYSIS

Hydrolysis of acetoxy group

Optically active alcohols have been obtained either by well known method of asymmetric reduction of ketone, or enantioselective hydrolysis of racemic esters. Plant cell enzymes are able to catalyze reactions with high regio- and stereoselectivity. Racemic acetates; 1-phenylethyl acetate (**5c**), 1-(1'-naphthyl)ethyl acetate (**6c**), 1-(2'-naphthyl)ethyl acetate (**7c**) and menthyl acetate (**8c**) were hydrolyzed by the vegetable extracts.

The hydrolysis of racemic acetate **5c** by potato (*S. tuberosum*) was accompanied by hydroxylation of the resulting 1-phenylethanol (**5a**). The absolute configuration of **5a** was *R* with low enantiomeric excess (17%). **Table 13** shows the efficiency of biotransformation of racemic acetates **5c**. Carrot (*D. carota*), topinambur (*H. tuberosus*) and celery (*A. graveolens* L. var. *rapaceum*) gave *R*-configuration. However, horseradish (*A. lapathifolia* Gilib.) provided *S*-configuration.

Other racemic acetates **6c**, **7c** were generated by plant

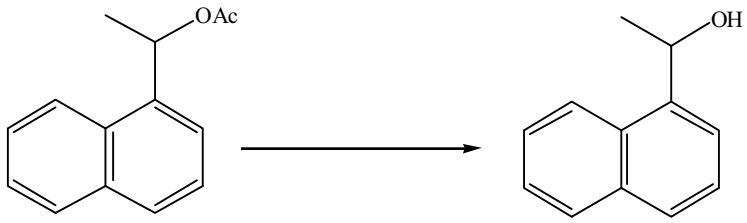


5c **5a**

Table 13 Hydrolysis of 1-phenylethyl acetate (**5c**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	88	17 (*R*)	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	58	42 (*R*)	Mironowicz 1998
Celery (*Apium graveolens* L. var *rapaceum*)	61	47 (*R*)	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	91	11 (*R*)	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	62	41 (*S*)	Maczka and Mironowicz 2002

[a] Isolated yields.
[b] GLC peak area.

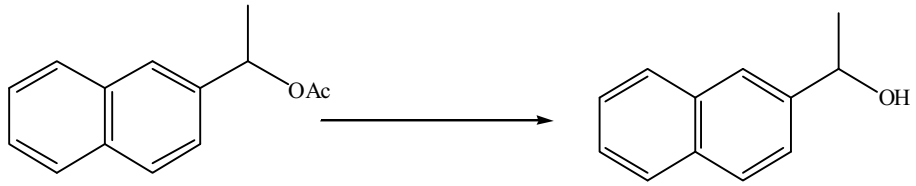


6c **6**

Table 14 Hydrolysis of 1-(1-naphthyl)ethyl acetate (**6c**) by various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	73	37 (*R*)	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	43	68 (*R*)	Mironowicz 1998
Celery (*Apium graveolens* L. var *rapaceum*)	48	68 (*R*)	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	64	75 (*R*)	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	20	53 (*S*)	Maczka and Mironowicz 2002

[a] Isolated yields.
[b] GLC peak area.

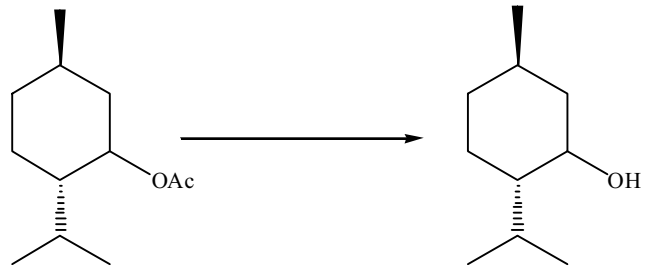


7c **7**

Table 15 Hydrolysis of 1-(2-naphthyl)ethyl acetate (**7c**) various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	86	26 (*S*)	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	56	66 (*R*)	Mironowicz 1998
Celery (*Apium graveolens* L. var *rapaceum*)	55	33 (*R*)	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	74	50 (*R*)	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	14	0	Maczka and Mironowicz 2002

[a] Isolated yields.
[b] GLC peak area.



8c **8a**

Table 16 Hydrolysis of menthyl acetate (**8c**) various vegetables.

Vegetable	Yield (%)[a]	ee. (%)[b]	Reference
Potato (*Solanum tuberosum*)	63	69 (1*R*)	Mironowicz 1998
Topinambur (*Helianthus tuberosus*)	19	25 (1*R*)	Mironowicz 1998
Celery (*Apium graveolens* L. var *rapaceum*)	-	-	Maczka and Mironowicz 2002
Carrot (*Daucus carota*)	-	-	Maczka and Mironowicz 2002
Horseradish (*Armoracia lapathifolia Gilic*)	-	-	Maczka and Mironowicz 2002

[a] Isolated yields.
[b] GLC peak area.

hydrolysis, and shown in **Tables 14** and **15**. In the case of potato (*S. tuberosum*), 1-(1'-naphthyl)ethyl acetate (**6c**) and 1-(2'-naphthyl)ethyl acetate (**7c**) proceeded in good yield (73%, 86%), but in low enantiomeric excess (37%, 26%) .

The hydrolysis of menthyl acetate (**8c**) proceeded selectively. The results of the transformation are presented in **Table 16**. Potato provided menthol (**8a**) in good yield and enantiomeric excess. On the other hand, it was found that other plants, such as carrot (*D. carota*), horseradish (*A. lapathifolia* Gilib.) and celery (*A. graveolens* L. var. *rapaceum*) showed no hydrolysis for **8c**.

Potato epoxide hydrolase

Potato (*S. tuberosum*) and cress (*Nasturtium officinale*) soluble epoxide hydrolases catalyze the hydrolysis of epoxide (**Fig. 12**) or arene oxides to their corresponding diols (Morisseau *et al*. 2000). Moreover, the hydrolysis of racemic styrene oxide derivatives proceeds using the recombinant potato (*S. tuberosum*) epoxide hydrolase (*St*EH). The *St*EH enzymatic extract used in the study herein was prepared by over-expression in *Escherichia coli* BL21 (DE3) (Monterde *et al*. 2004).

The *meta*- and *para*-chlorostyrene diol derivatives are important building blocks for the synthesis of various biologically active molecules. The *St*EH afforded the cor-

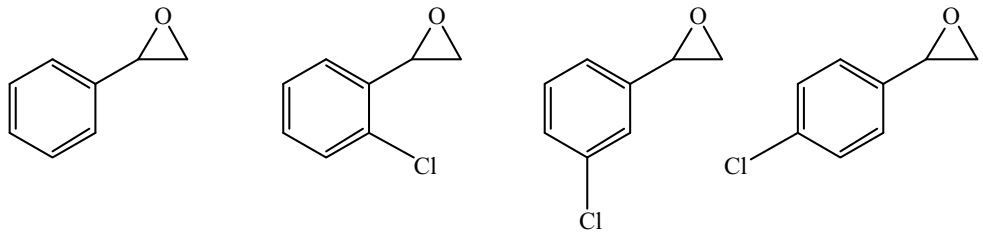


Fig. 12 Structure of the racemic epoxides.

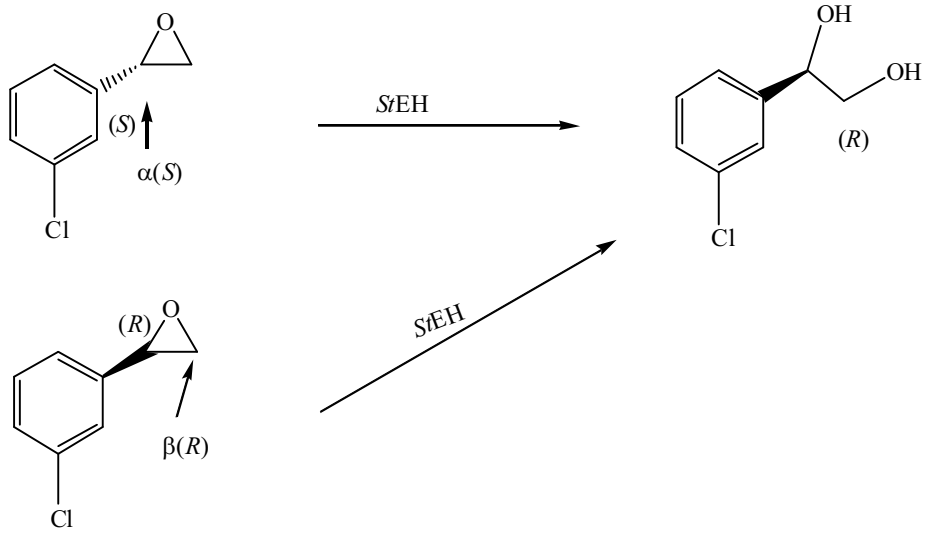


Fig. 13 Hydrolysis of racemic *meta*-chlorostyrene oxide.

responding (*R*)-diol in good to excellent enantiomeric excess. For example, hydrolysis of racemic *meta*-chlorostyrene oxide led to a conversion ratio of 57%. The remaining epoxide exhibited a 61% (*R*) enantiomeric excess, while the produced diol exhibited an enantiomeric excess as high as 94% (*R*). The (*S*)-enantiomer should be essentially attacked at the substituted (benzylic) carbon atom, thus leading to the (*R*)-diol by inversion of configuration, whereas the (*R*)-enantiomer should be essentially attacked at the substituted carbon atom, affording the diol of unchanged (*R*)-configuration. The *meta*-chlorostyrene oxide and *para*-chlorostyrene oxide were indeed preferably attacked at the benzylic position [α(*S*)>97%], whereas the (*R*)-enantiomer was attacked at the terminal carbon atom [β(*R*)>92%] [i.e., the determination of the so-called regioselectivity coefficients α(*R*), β(*R*), α(*S*), β(*S*)]. This behavior is illustrated for racemic *meta*-chlorostyrene oxide in **Fig. 13** (Monterde *et al.* 2004).

Moreover, Mateo *et al*. (2007) reported that the covalent immobilization of *St*EH was explored using highly activated Sepa-beads-epoxy or Glyoxyl-agarose based supports. A Glyoxyl-agarose immobilizate, prepared under optimized experimental conditions, led to a material exhibiting excellent thermal and chemical stability. This afforded a Glyoxyl-agarose-*St*EH immobilizate retaining 80% initial enzymatic activity and a stabilization factor of at least 300 at 60°C, as compared to the free enzyme.

CONCLUSION

As can be seen from the examples, it was found that potato (*S. tuberosum*) has the biochemical ability to transform substrates such as various organic compounds. Therefore, the biotransformation by potato (*S. tuberosum*) is considered to serve as important tools for the structural modification of molecules to give useful compounds. The availability of the enzymatic system using potato (*S. tuberosum*) is low cost, with ease of work-up and eco-friendly system for all advantages.

In the future, the development methods to utilize the reaction processes will be necessary for the practical applications of biotransformation with potato (*S. tuberosum*).

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