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BIOTRANSFORMATIONS OF RACEMIC ACETATES BY POTATO AND TOPINAMBUR TUBERS*

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Key Word Index—*Solanum tuberosum*; Solanaceae; potato; *Helianthus tuberosus*; biotransformation; enantiospecific hydrolysis of acetates: (±)-1-phenylethyl acetate; (±)-1-(1-naphthyl)ethyl acetate; (±)-1-(2-naphthyl)ethyl acetate; menthyl acetate.

Abstract—The hydrolysis of acetates: (±)-1-phenylethyl ((±)-**1**), (±)-1-(1-naphthyl)ethyl ((±)-**2**), (±)-1-(2-naphthyl)ethyl ((±)-**3**) and (±)-menthyl ((±)-**4**) with the use of potato and topinambur (artichoke) tubers results in the production of alcohols, which in the same environment are oxygenated to ketones. Pure *S*-1-phenylethyl acetate has been produced. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

In our earlier study [2] we found that enzymes present in apples and some vegetables can hydrolyse ester bonds in acetates of aromatic-aliphatic alcohols [3]. The purpose of the present investigation was to study the hydrolysis of (±)-1-phenylethyl ((±)-**1**), (±)-1-(1-naphthyl)ethyl ((±)-**2**), (±)-1-(2-naphthyl)ethyl ((±)-**3**) and (±)-menthyl ((±)-**4**) racemic acetates to determine their enantiospecificity.

RESULTS

Racemic acetates **1**–**4** are hydrolysed to secondary alcohols by the enzymes present in potatoes (*Solanum tuberosum*, cv. Saturna) and topinambur (*Helianthus tuberosus*, artichoke). In the same environment the alcohols are oxygenated to ketones (Scheme 1).

Table 1 shows the efficiency of transformations of racemic acetates **1**–**4** after 48 hr. Among substrates **1**–**4** only the transformation of (±)-1-phenylethyl acetate ((±)-**1**) by potato tubers leads to complete hydrolysis within the standard 48 hr (Table 1). This does not prove enantiospecificity of this reaction, therefore the length of biotransformation of (±)-1-phenylethyl acetate ((±)-**1**) was reduced to 4, 8, 20 and 32 hr. The hydrolysis (Table 1) of the *R*-(+)-enantiomer of 1-phenylethyl acetate (*R*-(+)-**1**) was faster than that of *S*-acetate (*S*-(−)-**1**); *S*-enantiomer (20% of *S*-(−)-**1**) was the only unreacted enantiomer identified in the transformation mixture after 20 hr of hydrolysis of the racemic acetate (±)-**1** (Fig. 1).

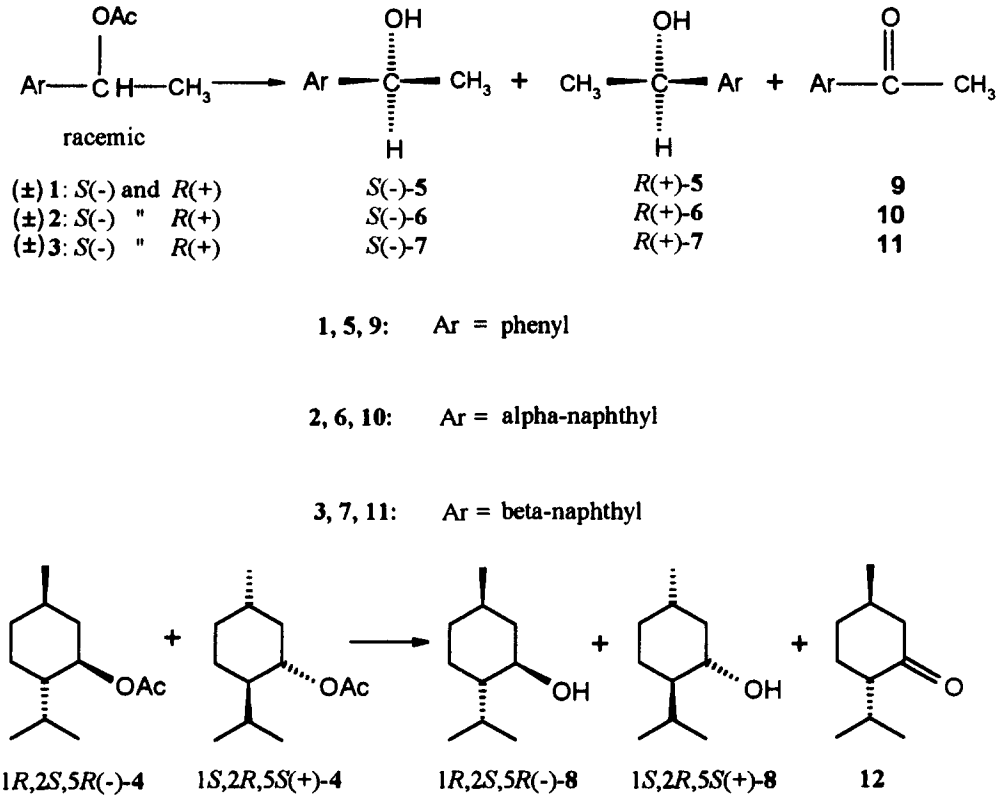
The hydrolysis of racemic 1-phenylethyl acetate ((±)**1**) by potato tubers was accompanied by oxygenation of the resulting 1-phenylethanol (**5**) to acetophenone (**9**), reaching 12% after 8 hr of the transformation process (remaining at this level to the end of the 48 hr biotransformation). It was quite likely that acetophenone (**9**) produced during the transformation was reduced to 1-phenylethanol (**5**) by the enzymes present in potato tubers. For this reason, biotransformations of alcohols: (±)-**5**, (±)-**6**, (±)-**7** and (±)-**8** and ketones **9**, **10**, **11**, **12** were carried out separately. The results are shown in Tables 2 and 3.

Pure *S*-enantiomers of alcohols **6** and **7** were obtained during the reduction of methylnaphthyl ketones **10** and **11** (Table 3). Using topinambur, the *R*-enantiomers of alcohols **5** and **7** (as the unreacted substrates) were obtained during oxygenation of these racemic alcohols (enantiomeric efficiency, e.e. = 80 and 95%, respectively, Table 2). No deracemization [4] of alcohols **5**–**8** during their oxygenation has been found.

DISCUSSION

Comparison of the results obtained in the present study with those obtained earlier [5] shows that the transformation capability of potato and topinambur tubers is comparable with those observed for whole intact plants in the same conditions; this ability of plant, tissue cultures and cell suspension is markedly weaker. The capability of the enzyme system present in potato and topinambur to carry out enantiospecific

* Part XLI in the series Biotransformations. For part XL see ref. [1].



Scheme 1. Substrates and products of biotransformation by means of potato and topinambur.

Table 1. Efficiency of 48 hr hydrolysis of racemic acetates **1**, **2**, **3**, **4**

	Contents of the reaction mixture									
	Potato					Topinambur				
Substrates (acetates)	Alcohol yield; [%]	e.e.† [%]	Ketone [%]	Unreacted acetates yield; [%]	e.e.† [%]	Alcohol yield; [%]	e.e.† [%]	Ketone [%]	Unreacted acetates yield; [%]	e.e.† [%]
(±)-**1**	88;	17(*R*-**5**)*	12(**9**)	0;	0	58;	42(*R*-**5**)	28(**9**)	13;	69(*S*)
(±)-**2**	73;	37(*R*-**6**)	trace of (**10**)	26;	88(*S*)	43;	68(*R*-**6**)	2(**10**)	55;	55(*S*)
(±)-**3**	86;	26(*R*-**7**)	3(**11**)	10;	54(*S*)	56;	66(*R*-**7**)	16(**11**)	28;	71(*S*)
(±)-**4**	63;	69(1*R*-**8**)	trace of (**12**)	36;	13(1*S*)	19;	25(1*R*-**8**)	trace of (**12**)	80;	8(1*S*)

* The hydrolysis of (±)-**1** by potato was repeated in shorter time period (Fig. 1).
† e.e. = enantomeric efficiency.

biotransfomations is much higher than that of examined whole plants, tissue cultures or cell suspensions.

EXPERIMENTAL

General. GC: Hewlett-Packard 5890, FID, carrier gas—H_2 using Chrompack WCOT Fused Silica, Chirasil-Val (0.25 mm × 25 m) capillary column for **1** (column temp. 125° const., injection temp. 250°), for **2** and **3** (column temp. 100°/5 min; 0.5°/1 min; 116° const., injection temp. 250°) and Chirasil-DEX CB (0.25 mm × 25 m) for **4** (column temp. 80°/1 min; 1°/1 min; 110° const., injection temp. 250°). TLC: silica gel 60 F_{254} pre-coated aluminium sheets (layer thickness 0.2 mm, Merck) with *n*-hexane-EtOAc (8:1) for **1** and **2**, *n*-hexane-Et_2O (5:1) for **3** and benzene-EtOAc (10:3) for **4**. CC: silica gel with *n*-hexane-acetone (20:1 for **1**, 30:1 for **2** and 35:1 for **3**).

Biocatalysers. Potato tubers (*Solanum tuberosum cv.* Saturna) were obtained from Flesner Polski, Oława (Poland). Topinambur (*Helianthus tuberosus*, artichoke) was from the Experiment Station of Agricultural University, Wrocław, Poland. All transformations were carried out at the time when the vegetables were suitable for consumption.

Biotransformation. Healthy tubers were blended

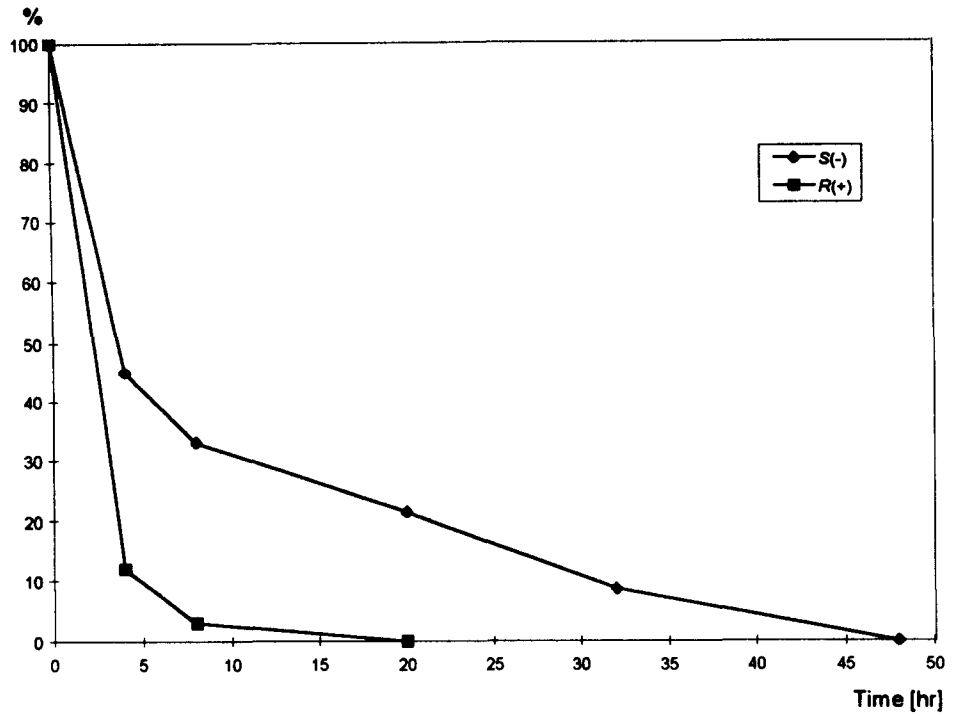


Fig. 1. Rate of the hydrolysis of enantiomeric 1-phenylethyl acetates (**1**).

Table 2. Efficiency of 48 hr oxygenation of racemic alcohols **5**, **6**, **7**, **8**

Substrates	Potato 'Saturna' Ketone [%]	Potato 'Saturna' e.e.* Unreacted alcohol [%]	Topinambur Ketone [%]	Topinambur e.e.* Unreacted alcohol [%]
(±)-1-Phenylethanol ((±)-**5**)	14(**9**)	no enantiosp.	43(**9**)	80(*R*)
(±)-1-(1-Naphthyl)ethanol ((±)-**6**)	10(**10**)	4(*R*)	2(**10**)	6(*R*)
(±)-1-(2-Naphthyl)ethanol ((±)-**7**)	4(**11**)	5(*R*)	46(**11**)	95(*R*)
(±)-Menthol ((±)-**8**)	1(**12**)	no enantiosp.	1(**12**)	1(1*R*)

* e.e. = enantomeric efficiency.

Table 3. Efficiency of 48 hr reduction of ketones **9**, **10**, **11** and **12**

Substrates	Potato 'Saturna' Alcohol yield; [%]	Potato 'Saturna' e.e.* [%]	Topinambur Alcohol yield; [%]	Topinambur e.e. [%]
Acetophenone (**9**)	1;	20(*R*-**5**)	1;	15(*R*-**5**)
Methyl-1-naphthyl ketone (**10**)	4;	no enantiosp.	3;	100(*S*-**6**)
Methyl-2-naphthyl ketone (**11**)	4;	100(*S*-**7**)	23;	100(*S*-**7**)
Menthone (**12**)	1;	33(1*R*-**8**)	1;	81(1*R*-**8**)

* e.e. = enantomeric efficiency.

using an electric mixer for 2 min and 20 ml (3.5–4.0 g dry wt, 105°, 12 hr) of the pulp was placed in a conical flask with 50 ml of Na-Pi buffer (pH = 5.9). This pulp with 20–30 mg of substrate dissolved in 0.5 ml of acetone was shaken for 48 hr (except for (±)-**1** for which the biotransformations were also carried out for 4, 8, 20 and 32 hr). The course of biotransformation was controlled by means of TLC and GC. Biotransformation mixt. was extracted with $CHCl_3$ into which both the transformation products and unreacted substrates and some compound present in the plant mass have passed. Yield of biotransfor-

mations (Tables 1–3) were determined by means of GC (HP-5 column, without purification) using standard compound to compare R_t.

The interpretation of gas chromatograms obtained by means of chiral columns required comparison with enantiomer standards; therefore after biotransformations the products and unreacted substrates with prevalence of one enantiomer (GC) were isolated using CC. In the case of compound (±)-**1**: from 120 mg: *S*(−)-**1** (unreacted substrate after 20 hr hydrolysis, e.e. = 100%): 17 mg; (±)-**5** (oxygenation by topinambur): 60 mg: *R*(+)-**5** (unreacted substrate, e.e. = 80%): 24 mg; (±)-**7** (oxygenation by topinambur): 75 mg: *R*(+)-**7** (unreacted substrate, e.e. = 95%): 23 mg; **11** (reduction by topinambur): from 125 mg: *S*(−)-**7** (e.e. = 100%): 12 mg.

The experiments were performed in several replications for confirmation of the results and for isolation of adequate quantities of the products (optical rotation measurement and/or CC) all substrates in the buffer soln for the biotransformations were stable under these conditions.

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