

Note

Resolution and Synthesis of (*S*)-1-(2-Naphthyl)ethanol with Immobilized Pea Protein: As a New BiocatalystHiroyuki NAGAOKA^{*,***} and Hiroshi KAYAHARA^{**,†}^{*}The United Graduate School of Agricultural Science, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan^{**}Department of Bioscience and Biotechnology, Shinshu University, 8304 Minamiminowa, Kamiina, Nagano 399-4598 Japan^{***}Sanyo Shokuhin Co., Ltd., 555-4 Asakura, Maebashi, Gunma 371-0811, Japan

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(*S*)-1-(2-Naphthyl)ethanol was yielded by immobilized pea (*Pisum sativum* L.) protein (IPP) from (*R,S*) 2-naphthyl ethanol (>99% ee, yield; about 50%), in which the (*R*)-enantiomer was selectively oxidized to 2-acetonaphthone. IPP could be reused consecutively at least three times without any decrease of yield and optical purity.

Key words: immobilized pea protein; selective oxidation; biotransformation; (±) 2-naphthyl ethanol; (*S*)-1-(2-naphthyl)ethanol

Recently, baker's yeast,¹⁾ lipase,²⁾ cultured plant cells,³⁾ and bacteria⁴⁾ have been found to be useful biocatalysts in synthesizing chiral compounds.

We report here new catalysts, *i.e.* pea (*Pisum sativum* L.) protein as the method of resolution and synthesis of racemic alcohol more stereoselectively and more economically than the above-mentioned biocatalysts. Additionally, this method may have such merits as the ease in separation the catalyst from the reaction solution and its reuse it without any decrease in yield and optical purity.

Pea protein (PP) powder was obtained from Orugano Co. Ltd., which was prepared by the spray dry method from a water extract of hulled and milled pea seeds under low pressure. The PP was immobilized as follows:³⁾ the protein powder (20 g) was dissolved in distilled water (200 ml), and 5% aq. sodium arginate (250 ml) was poured into the solution with stirring. When the homogeneous solution was added dropwise to 0.6% aq. calcium chloride solution (2000 ml), calcium arginate gel beads (ϕ = about 4 mm) involving the pea protein were made. After the beads were kept further in the calcium chloride solution for 5 h, the beads were separated from the solution and washed with distilled water.

Then, the immobilized pea protein (IPP) was used for the resolution of (±) 2-naphthyl ethanol (*I*). That is, 200 mg of *I* was added to distilled water containing IPP at 33–37°C in the absence of any organic solvent, buffer, or surfactant without stirring. After filtration, the separation of (*S*)-alcohol and 2-acetonaphthone was done with silica gel chromatography (elution solvent; hexane:ethyl acetate = 9:1). *I* was biotransformed into (*S*)-alcohol with excellent optical yield (>99% ee, yield: about 50%) through the stereoselective oxidation of its

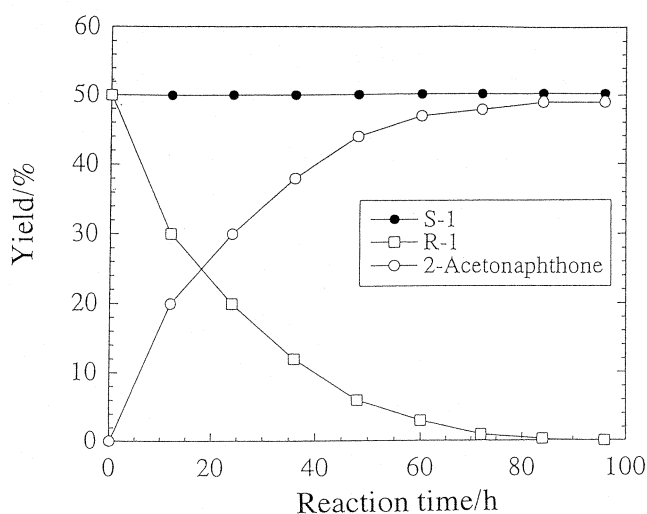


Fig. 1. Biotransformation of (*S*)-1-(2-Naphthyl)ethanol with Immobilized Pea (*Pisum sativum* L.) Protein through Selective Oxidation of Its (*R*)-Enantiomer to 2-Acetonaphthone.

Table 1. Chiral Resolution of Racemic 1-(2-Naphthyl)ethanol Using Immobilized Pea Protein (IPP) and Consecutive Reuse (2nd, 3rd) of IPP

Reuse	Time/h ^a	Resolved Alcohol	OP/% ee ^b	CY/% ^c
1st	96	S	99	50
2nd	48	S	99	50
3rd	36	S	99	50

^a Reaction time.^b Optical purity measured by HPLC.^c Chemical yield.

(*R*)-isomer to 2-acetonaphthone in the way depicted in Fig. 1. HPLC analysis was done by using a Chiralcel OB column (elution solvent; hexane:2-propanol = 9:1, flow rate; 0.5 cm³ min⁻¹, retention time = 14.2 min (99.9%, (*S*)-alcohol), 18.1 min (0.1%, (*R*)-alcohol).

As can be seen in Table 1, IPP was found to be reusable at least three times with acceleration in the reaction rate without any decrease of yield and optical purity.

This acceleration may be due to a steric change of the catalyst in favor of fitting the substrate during the process of reaction.

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We suggest that pea protein powder may be very useful in stereoselectively catalytic reactions of the powder as a new biotransformation of chiral compound, in which the reaction condition are mild (35°C, pH=7) and needs no preincubation or bacteria-free operation in contrast to the case of cultured plant cell.

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