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Bacterial Oxidation of Naphtharene to 1-Naphthol

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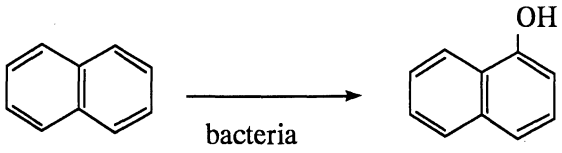
The oxidation of naphtharene in a liquid culture was carried out in the presence of *Bacillus cereus*. 1-Naphthol was obtained in 11-20% yield and the selectivity of 65-77% at 28 ℃ and pH 7.0 after 12-24 h. The ratio of 1-naphthol to 2-naphthol was 94:6.

The degradation of naphthalene (**1**) with bacteria or fungi has been established to give various metabolites.[1] In the presence of a fungi *Cunninghamera elegans*, **1** has been oxidized to give 1-naphthol (**2**) in a 67.9% selectivity among six metabolites.[2] Recently a bacteria *Rhodococcus sp. M192* has been revealed to give 2-methylnaphthol from 2-methylnaphthalene,[3] a precursor of menadion (vitamin K_3). Authors separated a naturally living bacteria *Bacillus cereus* from soil of our campus by using agar plate and found that it acts as a catalyst for the oxidation of **1** to **2** in higher selection.

The oxidation of **1** was carried out as follows. In a 30 ml L-shaped test tube was added 10 ml liquid culture[4] and inoculated a small amount of *B. cereus*. The increase of *B. cereus* was followed photometrically by its absorbance at 370 nm and saturated after 10 h. The doubling time was 2 h. After the increase of bacteria stopped (12 h), 15 μ mol of **1** in 0.5 ml acetone was added and incubation was further continued for 12 h at 28 ℃. The products were analyzed with HPLC by using a silica-gel column (C-18, 4.6 mm ϕ x 150 mm) under a gradient flow of MeOH-H_2O (3:7 to 9:1) and detected at 230 nm. The oxidation of **1** under various conditions was shown in Table 1. Under the lack of **1**, no product was detected. When **1** was added to the culture solution,



1 **2**

2 was obtained as a major product. The oxidation took place from 23 ℃ and optimum pH and temperature were 7.0 and 28 ℃, respectively. The selectivity to **2** fall into 64.8 to 76.9% between the reaction temperature from 23 to 28℃. A higher reaction temperature (33 ℃) decreased the selectivity. The yield of **2** was increased with increase in reaction time and reached 19.7% after 24 h. The ratio of **2** /2-naphthol (**3**)= 94/6 in our experiments was comparable to that obtained in *C. elegans* (**2** / **3**=96/4) .[2] Also, in a physiological salt solution (100 ml) **1** (180 μmol) was oxidized to give **2** in 15.4% yield in the presence of *B. cereus* (3.9 g, wet) at 28 ℃ for 12 h. Fine crystals of **2** obtained by treating on a silica-gel column (Kiesel gel 60, Merck Co., ethyl ether-petroleum ether 2:8) were in accord with the authentic sample in NMR, GC-Mass and elemental analyses. We believe that it was first example of the selective oxidation of **1** to **2** with bacteria. A similar tendency of products and selectivity between a bacteria *B. cereus* and a fungi *C. elegans* suggests the presence of a common oxidation system. Since various chemicals and pharmaceuticals are expected to be produced under mild conditions, further application to several hydrocarbons is in progress in our laboratory.

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Table 1. The oxidation of **1** in the presence of *B. Cereus* under various conditions

Entry	**1**	Temp	Time	pH	Conversion	Yield of **2** [a]
	μmol	℃	h		%	%
1	0	28	12	7.0	0	0 (0)
2	15	23	12	7.0	6.5	5.0 (76.9)
3	15	28	12	7.0	17.9	11.6 (64.8)
4	15	33	12	7.0	7.9	2.1 (26.6)
5	15	28	12	5.0	0	0 (0)
6	15	28	12	8.1	18.7	10.8 (57.8)
7	180	28	24	7.0	-	19.7 (-) [b]

a) Figures in parentheses show the selectivity to **2**. b) Culture solution of 250 ml was used.

References

1) C. L. Poh and R. C. Bayly, *J. Bacteriolog*, **143**, 59 (1980).

2) C. E. Cernigria and D. T. Gibson, *Appl. Environ. Microbiol* ., **34**, 363 (1977).

3) Y. Tani, J. P. 6-22775 (1994).

4) A nutrient broth, 10 g of bonito extract, 10 g of pepton, 2 g of NaCl, and water to make 10 dm^3 was used.

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