

3,3'-ジメチル-4-メトキシベンゾフェノン(メトキシフェノン,NK-049)の水田土壌中および土壌微生物による代謝

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Metabolism of 3,3'-Dimethyl-4-Methoxybenzophenone (Methoxyphenone, NK-049) in Paddy Soils and by Soil Microorganisms

Akira KUROZUMI, Takashi KUROKAWA, Isamu YAMAGUCHI* and Tomomasa MISATO*

*Ageo Research Laboratory, Agrochemicals Division, Nippon Kayaku Co., Ltd.,
Ageo, Saitama 362, Japan*

**The Institute of Physical and Chemical Research, Wako, Saitama 351, Japan*

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The fate of 3,3'-dimethyl-4-methoxybenzophenone (methoxyphenone, NK-049) in paddy soils and its metabolism by soil microorganisms were investigated by using ^{14}C -NK-049 labeled at carbonyl carbon. NK-049 disappeared rapidly under static ("anaerobic") flooded conditions with half-life of about 10 days. Main products obtained were 3,3'-dimethyl-4-hydroxybenzophenone (NK-049-OH) and $^{14}\text{CO}_2$. Oxidized products of 3- or 3'-methyl group and reduced form at carbonyl group of NK-049 were also detected by thin layer chromatography (*tlc*). After 2 weeks of incubation, radioactivity of NK-049-OH reached 43.0 and 70.8% of the applied radioactivity in Mito soil and Konosu soil, respectively. Significant liberation of $^{14}\text{CO}_2$ (55.0%) was observed in Konosu soil after 6 weeks of incubation, but it was only 0.7% in Mito soil. NK-049-OH was also degraded to yield almost the same amount of $^{14}\text{CO}_2$ in Konosu soil as in the case of NK-049. Under shaking ("aerobic") flooded conditions, $^{14}\text{CO}_2$ was liberated from Konosu soil treated with ^{14}C -NK-049 as under static conditions but little accumulation of NK-049-OH was observed. Microbial metabolites obtained by an isolated microorganism were common with those found in the soil except 3,3'-dimethyl-4-methoxybenzhydrol.

INTRODUCTION

3,3'-Dimethyl-4-methoxybenzophenone (methoxyphenone, NK-049) is a compound with a herbicidal activity synthesized as a derivative of an antibiotic, anisomycin. It has an excellent activity for the control of weeds both in paddy and upland fields.^{1,2)} Studies on the residual analysis of NK-049 in soils and crops have been reported by Izawa *et al.*³⁾ to find the half-lives of NK-049 to be 7-10 days and 23-30 days in the paddy and upland soils, respectively.

Metabolism of NK-049 in rats⁴⁾ and in rice plant^{5,6)} have been studied, but its behavior in soils still remains obscure though it was suggested that NK-049 would be demethylated at methoxy group and oxidized at methyl groups by soil microorganisms.⁷⁾ This paper deals with the fate of NK-049 in paddy soils

under laboratory conditions and the microbial metabolism by isolated soil microorganisms.

MATERIALS AND METHODS

1. Chemicals

^{14}C -NK-049 labeled at carbonyl carbon (5.5 mCi/mmol) was synthesized as described in the previous paper.⁴⁾ ^{14}C -3,3'-Dimethyl-4-hydroxybenzophenone (NK-049-OH, 1.0 mCi/mmol) was prepared by hydrolysis of ^{14}C -NK-049 with hydroiodic acid, and purified by recrystallization from ethanol. Radiochemical purity of ^{14}C -NK-049-OH was more than 99.0%.

Nonradioactive compounds such as 3,3'-dimethyl-4-methoxybenzhydrol, 3'-hydroxymethyl-4-methoxy-3-methylbenzophenone, 3-hydroxymethyl-4-methoxy-3'-methylbenzophenone, 3'-formyl-4-methoxy-3-methylbenzophenone, 3-formyl-4-methoxy-3'-

methylbenzophenone, 3'-carboxy-4-methoxy-3-methylbenzophenone, and 3-carboxy-4-methoxy-3'-methylbenzophenone were used as authentic samples.

2. Soil Samples

Two kinds of paddy soil were obtained from different locations (Konosu in Saitama Pref. and Mito in Ibaragi Pref., Japan). These were crushed and passed through a 0.5 mm sieve, and kept outdoors during storage. The physico-chemical properties of these soils reported by Izawa *et al.*⁸⁾ were as follows: Konosu soil; alluvial soil, clay loam, clay 22.0%, total carbon 1.8%, and cation exchange capacity 14.1 meq/100 g dry soil, Mito soil; volcanic ash soil, clay loam, clay 21.4%, total carbon 2.0%, and cation exchange capacity 15.6 meq/100 g dry soil.

3. Application of NK-049 or NK-049-OH to Soils

Fifty grams (dry weight basis) of soil sample in 200 ml of Erlenmeyer flask were flooded with water of 1 cm deep. The soil was pre-incubated at 30°C under static ("anaerobic") conditions for one week. Then, one ml of methanol solution of ¹⁴C-NK-049 or ¹⁴C-NK-049-OH (2.0 μCi) was added onto the water surface at 20 ppm on dry soil basis. The soil was incubated at 30°C for 6 weeks. Under shaking ("aerobic") conditions, ¹⁴C-NK-049 was added to the flooded Konosu soil without pre-incubation, and the flask was shaken on a reciprocal shaker (Taiyo Incubator M-I^N) at 60 rpm for 4 weeks (30°C). Konosu soil was autoclaved at 120°C (1 kg/cm²) for 30 min prior to the addition of ¹⁴C-NK-049 or ¹⁴C-NK-049-OH in the case of control experiments.

In order to study ¹⁴CO₂ liberation from ¹⁴C-NK-049 or ¹⁴C-NK-049-OH, CO₂-free air was let into the incubation flask, and the gas was captured by an alkaline solution [methylcellosolve/ethanolamine (3:1 v/v)] after passage through toluene layer to trap volatile organic materials. Trap solutions were replaced by the new every week and radio-assayed.

4. Isolation of Microorganisms Capable of Metabolizing NK-049

Konosu soil was pre-incubated with 500 ppm of NK-049 (dry soil basis) at 30°C under static flooded conditions for 4 weeks, and was then suspended in sterilized water. An aliquot of diluted suspension was spread onto mineral-glucose agar medium [0.4% NH₄NO₃, 0.15% KH₂PO₄, 0.15% Na₂HPO₄, 0.02% MgSO₄·7H₂O, 0.0001% FeSO₄·7H₂O, 0.01% CaCl₂·2H₂O, 0.05% yeast extract (Difco), 0.5% glucose, and 2% agar, (pH 6.8)] containing 500 ppm of NK-049, and microorganisms were grown at 30°C for 3 days. Each colony of the microorganisms was inoculated into the mineral-glucose medium (150 ml) containing 5.0 ml of ¹⁴C-NK-049 (0.1 μCi) and incubated at 30°C on a reciprocal shaker at 60 rpm for 5 days. The incubation mixtures were extracted with 150 ml of ethyl acetate and the extracts were subjected to *tlc* (see below), and several microorganisms were chosen according to the capability of metabolizing NK-049.

5. Extraction and Identification of Metabolites of NK-049 from the Soils and the Culture Medium

After removing surface water by decantation the soils were extracted three times with 100 ml of methanol, and filtered through a glass filter packed with a small amount of anhydrous sodium sulfate to make the filtration easy. Surface water and methanol extracts were put together, concentrated *in vacuo*, and the concentrate was extracted with ethyl acetate at pH 2.0. An aliquot of ethyl acetate fraction was spotted on silica gel plate (Merck 60 F₂₅₄, precoated, 0.25 mm thick) together with authentic compounds. The plate was developed in two dimensions with *n*-hexane/ethyl acetate/acetic acid (90:30:2 v/v/v) for the first development and benzene/ethyl acetate/acetic acid (50:20:2 v/v/v) for the second one. *R_f* values of the reference compounds are listed in Table 1.

Metabolites in the residual soils were obtained as follows: Ten grams of residual soil were extracted three times with 100 ml of 1.25 N sodium hydroxide/acetone (1:5), and extracted solution was acidified with hydrochloric acid to pH 2.0, which was concent-

Table 1 *Rf* values of NK-049 and its related compounds.

				<i>Rf</i> value		
R ₁	R ₂	R ₃	X	A*	B**	
-CH ₃	-CH ₃	-CH ₃	-CO-	NK-049	0.68	0.88
-CH ₃	-CH ₃	-CH ₃	>C< ^H _{OH}	M-1	0.50	0.75
-CH ₃	-CH ₃	-H	-CO-	M-2	0.31	0.62
-CH ₂ OH	-CH ₃	-CH ₃	-CO-	M-3	0.16	0.20
-CHO	-CH ₃	-CH ₃	-CO-	M-4	0.40	0.72
-COOH	-CH ₃	-CH ₃	-CO-	M-5	0.20	0.27
-CH ₃	-CHO	-CH ₃	-CO-	M-6	0.30	0.60
-CH ₃	-COOH	-CH ₃	-CO-	M-7	0.06	0.15

A*: *n*-hex: AcOEt: AcOH=90: 30: 2

B**: PhH: AcOEt: AcOH=50: 20: 2

rated *in vacuo*, and re-extracted with ethyl acetate. Ethyl acetate condensate was chromatographed on Florisil column (20 g) with benzene/acetone (2 : 1 v/v). Eluted compounds were analyzed by *tlc* as mentioned above.

Residual soils were also directly subjected to radioassay after wet combustion by using oxidizing solution (25 g CrO₃ in 167 ml H₃PO₄ and 333 ml H₂SO₄) as described by Kametani *et al.*⁸⁾

A selected microorganism was incubated with ¹⁴C-NK-049 (0.1 μCi, 5.0 mg) in the mineral-glucose medium (150 ml) as described earlier, and the cultured broth was extracted two times with 150 ml of ethyl acetate at pH 2.0. The ethyl acetate extract was washed with water two times, dried over anhydrous sodium sulfate, and analyzed by *tlc*. Furthermore, to confirm the chemical structures of the microbial metabolites, ethyl acetate extract was partitioned between *n*-hexane and acetonitrile (3 : 1 v/v), and the condensate of acetonitrile was methylated with diazomethane or acetylated with acetic anhydride and pyridine before GC-MS analysis, when necessary. GC-MS was recorded on Shimadzu LKB-9000 under the conditions of ionizing potential 40 eV, ionizing current about 60 μA, and ion source temperature 270°C. GC-column (glass column of 3 mm in inner diameter and 1.0 m in length) was packed with 3% Silicone OV-17 on chromosorb W HP (80-100 mesh) and/or

2% Dexicil 300 GC on Gaschrom Q (100-120 mesh).

6. Radioassay

Radioactivity was determined with a liquid scintillation spectrometer (Packard Tri-carb 3320) by using either of the following scintillator solutions; A: 4.0 g of PPO and 0.1 g of dimethyl-POPOP in 1,000 ml of toluene; B: 8.0 g of PPO, 0.1 g of dimethyl-POPOP, 100 g of naphthalene and 20 ml of ethylene glycol in 1,000 ml of dioxane; C: 5.0 g of PPO and 0.3 g of dimethyl-POPOP in 1,000 ml of ethanol-amine/methylcellosolve/toluene (1 : 3 : 6 v/v).

RESULTS

1. Fate of NK-049 in Paddy Soils

As summarized in Table 2, NK-049 decreased along with a lapse of time both in Konosu and Mito soils, with half-life of about 10 days, and amount of ¹⁴C-NK-049 after 4 weeks of incubation was 1.0% of the applied radioactivity in Konosu soil and 5.2% in Mito soil, respectively. 3,3'-Dimethyl-4-hydroxybenzophenone (NK-049-OH, M-2) was found as a major product, and its amount reached 70.8% in Konosu soil and 43.0% in Mito soil after 2 weeks of incubation. NK-049-OH decreased gradually in Konosu soil, whereas it remained in almost the same quantity in Mito soil up to 6 weeks. 3,3'-Dimethyl-4-methoxybenzhydrol (M-1), a reduced product at carbonyl group of NK-049, was identified by co-chromatography on *tlc*. Other products extracted from the soil incubated for 2 weeks are shown in Table 3. Oxidized products of NK-049 were identified as 3'-hydroxymethyl-4-methoxy-3-methylbenzophenone (M-3), 3'-carboxy-4-methoxy-3-methylbenzophenone (M-5), and 3-carboxy-4-methoxy-3'-methylbenzophenone (M-7).

In Konosu soil, gaseous radiocarbon compounds trapped with toluene were negligible throughout the experiment, while alkaline trapped radiocarbon rapidly increased after an initial lag of about two weeks, and it reached the half amount of applied radioactivity. However, in Mito soil, negligible radiocarbon was trapped both with toluene and alkaline solution. The radioactive compound trapped

Table 2 Degradation of NK-049 in paddy soils under static and shaking flooded conditions.

Soil (Condition)	Weeks	Distribution of radiocarbon* (%)						
		Methanol extracts				Un- extracted	¹⁴ CO ₂	Total
		NK-049	M-1	M-2	Others			
Konosu (Static)	1	85.6	2.9	9.6	0.4	2.8	0.5	101.8
	2	13.1	2.4	70.8	5.0	4.8	4.2	100.3
	4	1.0	t**	43.2	6.1	6.1	45.2	100.6
	6	0.9	t	25.5	2.0	15.3	55.0	98.7
Mito (Static)	1	65.9	5.6	4.4	7.4	14.1	t	97.4
	2	16.5	6.6	43.0	5.6	25.4	0.2	97.3
	4	5.2	t	47.6	5.3	25.9	0.4	84.4
	6	1.8	t	43.1	10.8	30.8	0.7	87.2
Konosu (Shaking)	4	25.9	t	1.9	9.0	17.5	46.1	100.4

* Percentage of radioactivity to applied ¹⁴C-NK-049.

** t: Less than 0.1%.

Table 3 Other metabolites extracted with methanol after 2 weeks of incubation under static flooded conditions.

Soil	Distribution of radiocarbon* (%)			
	M-3	M-5	M-7	Unknown
Konosu	1.8	0.3	0.1	2.8
Mito	1.5	0.4	0.4	3.3

* Percentage of radioactivity to applied ¹⁴C-NK-049

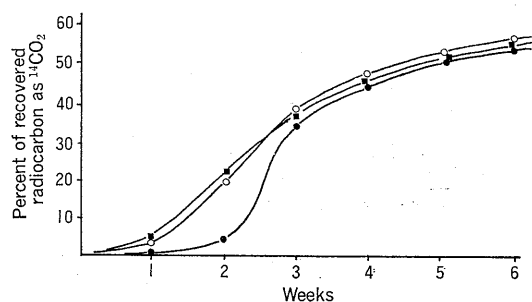


Fig. 1 Liberation of ¹⁴CO₂ from Konosu paddy soil treated with ¹⁴C-NK-049 or ¹⁴C-NK-049-OH.

- : from ¹⁴C-NK-049 (Static condition)
- : from ¹⁴C-NK-049 (Shaking condition)
- : from ¹⁴C-NK-049-OH (Static condition)

by alkaline solution was identified as ¹⁴CO₂ by being converted into Ba¹⁴CO₃ quantitatively.

In order to clarify further degradation of NK-049-OH, the metabolism of ¹⁴C-NK-

049-OH was compared with that of ¹⁴C-NK-049 in Konosu soil under static flooded conditions. However, radioactive materials extracted with methanol were mostly NK-049-OH itself and major degradation product was ¹⁴CO₂. Liberation of ¹⁴CO₂ increased without initial lag in contrast with ¹⁴CO₂ liberation from ¹⁴C-NK-049 treated soil, which had about 2 weeks lag as shown in Fig. 1.

Under shaking ("aerobic") flooded conditions, 25.9% of the applied NK-049 remained and NK-049-OH was 1.9% at 4 weeks of incubation as shown in Table 2. However ¹⁴CO₂ was liberated as shown in Fig. 1 without initial lag as in the case of NK-049-OH under static flooded conditions.

An attempt was made to obtain metabolites

Table 4 Extraction and identification of radiocarbon in the soil residues after 6 weeks of incubation.

Soil	Percent of recovered radiocarbon in the soil residues after methanol extraction		
	Total	Alkaline extract*	Identified as NK-049-OH**
Konosu	15.3	10.1	6.8
Mito	30.8	26.8	18.0

* Extracted with 1.25 N NaOH/acetone (1 : 5 v/v).

** Analyzed by *tlc* followed by column chromatography.

from the residual soil extracted with methanol, and the major material was identified as NK-049-OH by co-chromatography on *tlc* (Table 4). The amount of NK-049-OH reached 6.8% of the applied radioactivity in Konosu soil and 18.0% in Mito soil after 6 weeks of incubation.

In the sterilized soils, NK-049 or NK-049-OH was recovered by 98.7 or 92.0% of the applied amount, respectively, after 6 weeks of incubation. This fact suggests that NK-049 or NK-049-OH is degraded by soil microorganisms.

2. Microbial Metabolites of NK-049

The soil microorganisms capable of degrading NK-049 were selected from Konosu soil by using mineral-glucose medium. One of the microorganisms which belongs to *Bacillus* sp. metabolized NK-049 in mineral-glucose medium efficiently. A typical *tlc* pattern, content, and parent and major fragment peaks of mass spectra of the metabolites are shown in Fig. 2 and Table 5. These metabolites were identified by co-chromatography on *tlc* and mass spectrometry as 3,3'-dimethyl-4-hydroxybenzophenone (M-2), 3'-hydroxymethyl-4-methoxy-3-methylbenzophenone (M-3), 3'-formyl-4-methoxy-3-methylbenzophenone (M-4), 3'-carboxy-4-methoxy-3-methylbenzophenone (M-5), 3-formyl-4-methoxy-3'-methylbenzophenone (M-6), and 3-carboxy-4-methoxy-3'-methylbenzophenone (M-7).

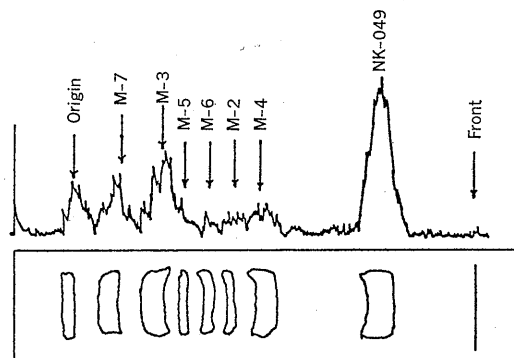


Fig. 2 Radiochromatograms of microbial metabolites of NK-049 in mineral-glucose medium.

Incubation: ^{14}C -NK-049 (333 ppm, 0.1 μCi) was incubated at 30°C for 5 days.

Solvent: *n*-Hex: AcOEt: AcOH=90:30:2

Table 5 Relative amounts of microbial metabolites of NK-049 and their main peaks of mass spectra.

Product	Relative amount (%)	Fragment ions (<i>m/e</i>)
NK-049	36.8	240(M ⁺), 225, 149, 119, 91
M-2	2.6	226 (M ⁺), 211, 135, 119, 91
M-3	14.2	*298(M ⁺), 255, 238, 149
M-4	4.1	254(M ⁺), 149, 133, 105
M-5	2.1	**284(M ⁺), 253, 193, 149
M-6	1.7	254(M ⁺), 163, 135, 119, 91
M-7	6.9	**284(M ⁺), 253, 193, 119
Origin	7.2	—
Others on <i>tlc</i>	5.1	—
Water sol.	9.6	—

* Measured as the methylated product.

** Measured as the acetylated product.

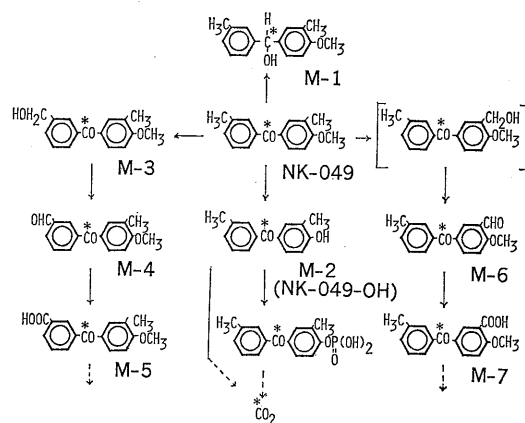


Fig. 3 A proposed metabolic pathway of NK-049 in soils.

The major metabolite was an oxidized product of 3'-methyl group to hydroxymethyl group (M-3).

DISCUSSIONS

The fate of NK-049 in paddy soils under flooded conditions and the microbial metabolism by a microorganism isolated from the paddy soil were investigated. As shown in Table 2, NK-049 was demethylated to NK-049-OH both in Konosu and Mito soils under static flooded conditions with half-life of about 10 days. Furthermore, NK-049-OH disappeared gradually, and $^{14}\text{CO}_2$ was liberated remarkably in Konosu soil, while $^{14}\text{CO}_2$ libera-

tion from Mito soil was not conspicuous. Other metabolites identified from methanol extract of Konosu soil were the reduced product of the compound at carbonyl group (M-1) and the oxidized products of 3- or 3'-methyl group (M-3, M-5, and M-7). These products were also found among the microbial metabolites except M-1.

In the experiments described above, the color of Konosu soil changed from brown to gray under static flooded conditions, and its Eh value was about -50 mV after 4 weeks of incubation, so the soil was supposed to be fairly "anaerobic". On the other hand, under shaking conditions, the soil color did not change and Eh value was about $+300$ mV throughout the incubation. In this case, NK-049-OH did not accumulate in a large quantity. Interestingly, the time course of the liberation of $^{14}\text{CO}_2$ under shaking conditions is similar to that of the incubation of NK-049-OH under static flooded conditions, as shown in Fig. 1. Thus, the degradation process of NK-049 is remarkably affected by soil condition. That is, although the demethylation of methoxy group of KN-049 in the paddy soil is supposed to be a predominant process in both conditions, the accumulation of NK-049-OH was suppressed under shaking conditions, suggesting that KN-049-OH would be metabolized more efficiently to further intermediates to liberate $^{14}\text{CO}_2$.

As mentioned earlier, microbial metabolites of NK-049 were found among the products from the soil treated with NK-049. However, in this microbial culture, the major compound was not NK-049-OH but M-3, an oxidized product at 3'-methyl group of NK-049. Since this microorganism has a remarkable ability to phosphorylate NK-049-OH⁹⁾, the water soluble fraction and origin part on *tlc* in Fig. 2 are supposed to consist of phosphorylated product of NK-049-OH mainly. Identification of the microorganism and details of phosphorylation of NK-049-OH will be reported elsewhere.

From these results, a possible metabolic pathway of NK-049 in paddy soils is proposed as shown in Fig. 3. One of the processes is demethylation of methoxy group as known in the case of chlomethoxylin,¹⁰⁾ chloroneb¹¹⁾

and methoxychlor.¹²⁾ Oxidation of 3- or 3'-methyl group is another main process as in the case of metabolism of methylchlor.¹³⁾ Reduction of carbonyl group is an interesting process, because such soil microorganism as *Pseudomonas putida*¹⁴⁾ or a *Hydrogenomonas* sp.¹⁵⁾ cannot grow on benzophenone but they can use benzhydrol as a sole carbon source.

Most metabolites of NK-049 in paddy soils were found commonly in rice plant. However, oxidized metabolites of NK-049-OH such as 3'-carboxy-4-hydroxy-3-methylbenzophenone, 3-carboxy-4-hydroxy-3'-hydroxymethylbenzophenone, and 3,3'-dicarboxy-4-hydroxybenzophenone etc., which were identified in the excreta of rats treated with NK-049, were not observed. The liberation of $^{14}\text{CO}_2$ from carbonyl labeled ^{14}C -NK-049 or ^{14}C -NK-049-OH results in complete degradation of benzophenone structure. This liberation of $^{14}\text{CO}_2$ from ^{14}C -NK-049 was also observed in the photodegradation in water by UV irradiation.¹⁶⁾ These degradation processes to liberate $^{14}\text{CO}_2$ still remain to be elucidated.

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要 約

3,3'-ジメチル-4-メトキシベンゾフェノン (メトキシフェノン, NK-049) の水田土壤中および土壌微生物による代謝

黒 濱 晃, 黒川隆史, 山口 勇, 見里朝正

3,3'-Dimethyl-4-methoxybenzophenone (methoxyphenone, NK-049) の水田土壤における命運と、土壌微生物による代謝をカルボニル位に ^{14}C で標識した NK-049 を用いて検討した。NK-049 は湛水下静置条件(還元状態)ではすみやかに消失し、半減期は約 10 日であった。主生成物は 3,3'-dimethyl-4-hydroxybenzophenone (NK-049-OH) と $^{14}\text{CO}_2$ であり、3-,3'-位のメチル基の酸化生成物とカルボニル基の還元生成物も *in situ* により検出された。NK-049-OH の量は 2 週後に処理放射能の 43.0% (水戸土壤), 70.8% (鴻巣土壤) であった。鴻巣土壤では 6 週後までに顕著な $^{14}\text{CO}_2$ (55.0%) の生成を認めたが、水戸土壤では 0.7% にすぎなかった。前者では NK-049-OH から NK-049 の場合とほとんど同等の $^{14}\text{CO}_2$ の生成が認められた。湛水下振盪条件(酸化状態)では、NK-049 からの $^{14}\text{CO}_2$ の生成は静置条件とほぼ同じであったが、NK-049-OH の蓄積はみられなかった。単離した微生物による代謝物は、3,3'-dimethyl-4-methoxybenzhydrol を除いては土壤中の生成物と共通であった。