^{14}C-LABELLING OF OPTICALLY ACTIVE FENVALERATE, α-CYANO-3-PHENOXY-BENZYL (S)-2-(4-CHLOROPHENYL)-3-METHYLBUTYRATE (I)

Akira Yoshitake, Hiroshi Kanamaru, Fumiaki Shono and Iwao Nakatsuka
Institute for Biological Science, Sumitomo Chemical Co., Ltd., 2-1, 4-Chome, Takatsukasa, Takarazuka-shi 665, Japan

SUMMARY

(S)-Fenvalerate [α-cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate], a novel insecticide, was labelled with carbon-14 individually at the carbonyl (1a), the cyano (1b) and the alcoholic methyne (1c) carbons for use in metabolic studies. Isopropylation of 4-chlorophenylacetonitrile-^{14}C with isopropyl bromide followed by hydrolysis gave racemic 2-(4-chlorophenyl)-3-methylbutyric-1-^{14}C acid, which on optical resolution with (-)-1-phenylethylamine gave the (S)-acid. Esterification of the (S)-acid with α-cyano-3-phenoxybenzyl bromide gave 1a in 18% yield from potassium cyanide-^{14}C. Esterification of α-cyano-^{14}C-3-phenoxybenzyl alcohol with (S)-2-(4-chlorophenyl)-3-methylbutanoyl chloride (9) gave 1b in 65% yield. Condensation of 3-phenoxybenzaldehyde-(carbonyl-^{14}C), prepared from 3-phenoxybenzoic-^{14}C acid, with 9 and sodium cyanide gave 1c in 54% yield from barium carbonate-^{14}C.

Key Words: Carbon-14, Fenvalerate, Insecticide, Optically Active

INTRODUCTION

Fenvalerate [α-cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate] is a novel insecticide possessing a great potential for control of insect pests in agriculture due to its outstanding insecticidal activity, moderate mammalian toxicity and adequate stability in the field[1]. While fenvalerate is a mixture of optical isomers, so called (S)-fenvalerate (1), which is the ester of (S)-2-(4-chlorophenyl)-3-methylbutyric acid and racemic α-cyano-3-phenoxybenzyl alcohol (Table 1), has been revealed to be insecticidally more active than the

0362-4803/81/030391-12$01.00 Received September 26, 1979

Table 1 Absolute Configurations of Fenvalerates

Compound	Configuration	
	Acid	Alcohol
Fenvalerate	RS	RS
Fenvalerate Aα	S	S
Fenvalerate Aβ	S	R
(S)-Fenvalerate (Aα /Aβ = 1/1 mixture)	S	RS

corresponding antipode[2,3].

In this report we describe the synthesis of (S)-fenvalerate labelled with carbon-14 individually at the carbonyl, the cyano and the alcoholic methyne carbons for use in metabolic studies.

DISCUSSION

Figure 1 illustrates the procedure for the synthesis of (S)-fenvalerate-(carbonyl-^{14}C)(1a). ^{14}C-Cyanation of 4-chlorobenzyl chloride with potassium cyanide-^{14}C in dimethylformamide-water (1/1 v/v) gave 4-chlorophenylacetonitrile-^{14}C (2) in 80% yield.

In general, hydrocarbons with a sufficiently acidic hydrogen can be alkylated with bases and alkylating halides in non-aqueous media. Treatment of 4-chlorophenylacetonitrile in toluene with sodium hydride followed by alkylation with isopropyl bromide gave 2-(4-chlorophenyl)-3-methylbutyronitrile (3) in a good yield[4]. Application of this method with some modifications for a small-scale preparation, however, gave unsatisfactory results. The yield of 3 was 60% at the highest mainly because of by-production of the dialkylated nitrile.

An alternative method[5] describes isopropylation of 2 with isopropyl halides using aqueous bases and quaternary ammonium compounds as a phase transfer catalyst [6]. The reaction was investigated for the present synthesis and a good result obtained. Thus, 4-chlorophenylacetonitrile-^{14}C was allowed to react with a slightly excess of isopropyl bromide and 46% sodium hydroxide aqueous solution containing a catalitic amount of benzyltriethylammonium chloride to give 2-(4-

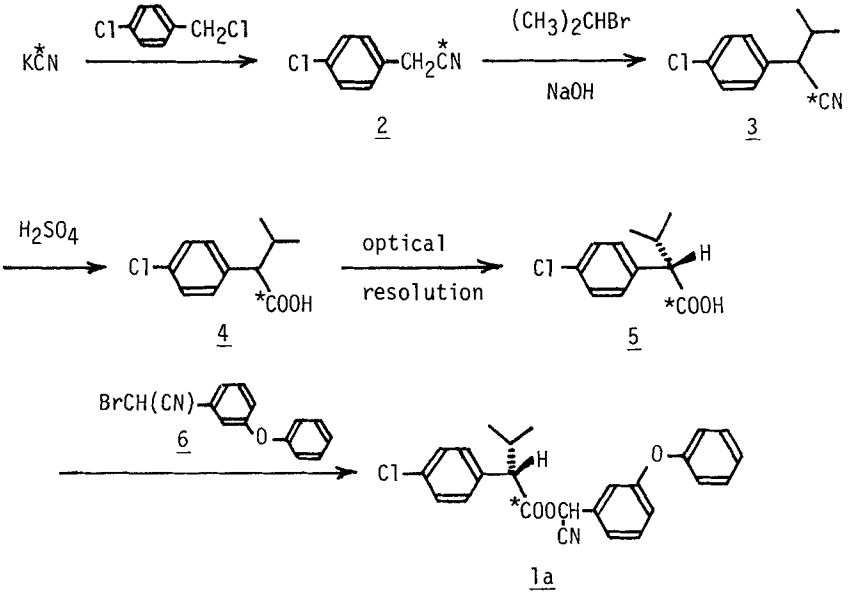

Fig. 1 Scheme for the synthesis of (S)-fenvalerate-(carbonyl-^{14}C)

chlorophenyl)-3-methylbutyronitrile-1-^{14}C (3) in 80% yield.

Hydrolysis of 3 with 64% sulfuric acid led to 2-(4-chlorophenyl)-3-methylbutyric-1-^{14}C acid (4) in a quantitative yield. Optical resolution of the racemic acid (4) was carried out by the diastereomeric salt formation with (-)-1-phenylethylamine[3,7]. Treatment of 4 with (-)-1-phenylethylamine in 80% ethanol gave a crystalline salt which was fractionally recrystallized from the same solvent. The crystalline salt of (S)-enantiomer thus obtained was decomposed with diluted hydrochloric acid to afford (S)-2-(4-chlorophenyl)-3-methylbutyric-1-^{14}C acid (5) radiochemically in 30% yield, which showed an optical purity of 97% with $[\alpha]_D$= 47.1°.

For the synthesis of fenvalerate using the butyric acid (4), the following methods are known so far: i) esterification of 4 with α-cyano-3-phenoxybenzyl bromide[8,9], ii) esterification of the acid chloride of 4 with α-cyano-3-phenoxybenzyl alcohol[1], and iii) direct condensation of the acid chloride of 4 with 3-phenoxybenzaldehyde and sodium cyanide[10]. The first method was chosen for the preparation of (S)-fenvalerate-(carbonyl-^{14}C) (1a), because it was considered

that the method not only shortens the synthetic steps but also lessens the chance of racemization of the product as compared to others. The (S)-butyric acid (5) was allowed to react with α-cyano-3-phenoxybenzyl bromide in a two-phase system of methylchloroform-water (3/2 v/v) containing potassium carbonate and tetra-*n*-butylammonium bromide to give quantitatively a crude product of 1a. The product was chromatographed on silica gel and eluted with hexane-benzene to give fractionated eluates. Fenvalerate Aα and Aβ can be analyzed by gaschromatography (GC) and have the retention times of 24.6 and 22.2 min, respectively. GC-Analyses of the eluates revealed that each contained radioactive fenvalerate Aα and Aβ in a different ratio; the former eluates containing a larger amount of Aβ than Aα. The fact indicates that diastereomeric Aα and Aβ were slightly separated by the column chromatography. Therefore, in order to prepare 1a the fractionated eluates needed to be properly collected in the manner to obtain the 1/1 ratio of Aα and Aβ. In this manner, (S)-fenvalerate-(carbonyl-^{14}C) was obtained in the overall yield of 18% from potassium cyanide-^{14}C; the optical purity being 97%.

It is known that the one-step reaction (the third method described above) requires a much excess of sodium cyanide though an improved yield of fenvalerate is expected. Therefore, the second method, which includes stepwise reactions *via* the cyanohydrin of 3-phenoxybenzaldehyde (7), was applied to the synthesis of (S)-fenvalerate-(cyano-^{14}C)(1b) in consideration of the radiochemical yield based on potassium cyanide-^{14}C. The procedures are shown in Figure 2.

Hydrogen cyanide-^{14}C generated from potassium cyanide-^{14}C by acetic acid was allowed to react with 7 to afford α-cyano-^{14}C-3-phenoxybenzyl alcohol (8) in 80% yield. Since the product was not so stable, it was used without any purification for the following reaction. Esterification of 8 with (S)-2-(4-chlorophenyl)-3-methylbutanoyl chloride (9) in pyridine led to (S)-fenvalerate-(cyano-^{14}C) (1b) in 64% yield after purification by column chromatography. The optical purity of the final product was 97%.

The synthetic route to (S)-fenvalerate-(methyne-^{14}C)(1c) is shown in Figure 3. ^{14}C-Carbonation of 3-phenoxyphenylmagnesium bromide with carbon-^{14}C

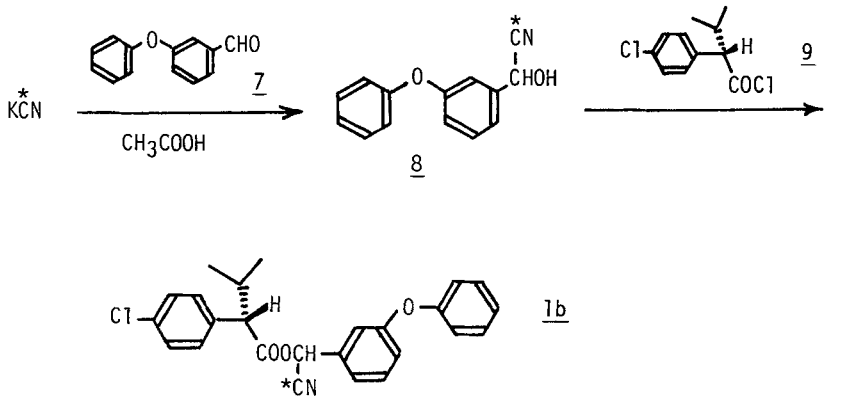

Fig. 2 Scheme for the synthesis of (S)-fenvalerate-(cyano-^{14}C)

dioxide followed by reduction with lithium aluminum hydride gave 3-phenoxybenzyl-^{14}C alcohol (11) in 85% yield. Air oxidation[11] of 11 in dimethylsulfoxide yielded 3-phenoxybenzaldehyde-^{14}C (12) in 70% yield.

Conversion of 12 to (S)-fenvalerate-(methyne-^{14}C)(1c) was achieved according to the third method described above. The aldehyde (12) was allowed to react with (S)-2-(4-chlorophenyl)-3-methylbutanoyl chloride (9) and an excess of sodium cyanide in a two-phase system of heptane-water using benzyltriethylammonium chloride as a phase transfer catalyst; giving 1c in 90% yield after purification by column chromatography; the optical purity being 97%.

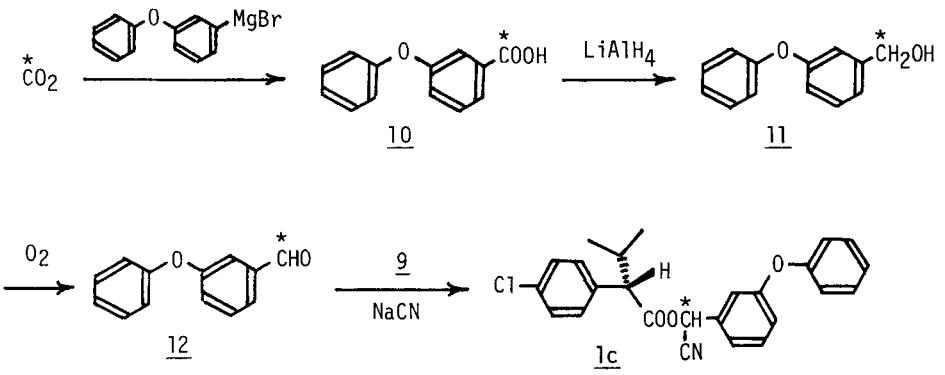

Fig. 3 Scheme for the synthesis of (S)-fenvalerate-(methyne-^{14}C)

EXPERIMENTAL

Radio-gaschromatography (RGC) was carried out on a Yanako G-80 gaschromatograph (Yanagimoto Co., Ltd., Japan) equipped with a RD-4 gas-flow GM-counter (Nihon Musen Co., Ltd., Japan). A glass column (2 m, 3 mm I.D.) packed with 3% Silicone OV-17 on Chromosorb was used for the analyses of 4-chlorophenylacetonitrile-^{14}C and 2-(4-chlorophenyl)-3-methylbutyronitrile-^{14}C. Operating condition: column temperature 140°, carrier gas He (26 ml/min), detector FID (H_2 50 ml/min), oxidation temperature 600°, counting gas propane (50 ml/min). Retention times: 4-chlorophenylacetonitrile 8.4 min, 2-(4-chlorophenyl)-3-methylbutyronitrile 14.7 min. A glass column (1.5 m, 3 mm I.D.) packed with 3% Silicone SE-52 on Chromosorb was used for the analysis of 3-phenoxybenzaldehyde-^{14}C; column temperature 150°, carrier gas He (40 ml/min); retention time 11.0 min. (S)-Fenvalerate-^{14}C was analyzed on a glass column (3 m, 3 mm I.D.) packed with 10% Silicone DC QF-1 on Chromosorb; column temperature 245°, carrier gas He (100 ml/min); retention times: fenvalerate Aα 24.6 min, Aβ 22.2 min. Optical rotations were measured with a DIP 181 polarimeter (Japan Spectroscopic Co., Ltd.) in chloroform.

4-Chlorophenylacetonitrile-1-^{14}C (2) - To a solution of potassium cyanide-^{14}C (150 mCi, 531 mg, 8.2 mmol) in water (9 ml) was added dropwise at room temperature a solution of 4-chlorobenzyl chloride (1.32 g, 8.2 mmol) in dimethylformamide, and the mixture stirred at 95-100° for 3.5 hr. After cooling, the mixture was diluted with water and extracted with ether. The extract was washed with water, dried over sodium sulfate, evaporated under reduced pressure, and the residue chromatographed on silica gel with hexane-ether (92/8 v/v). Evaporation of the main fractions gave 4-chlorophenylacetonitrile-1-^{14}C (120 mCi, 987 mg); the purity 99% on RGC and radio-thinlayerchromatogram (RTLC)(silica gel, hexane/ether=3/1, R_f-value=0.15); IR νmax ($CHCl_3$): 2250 cm^{-1} (CN).

2-(4-Chlorophenyl)-3-methylbutyronitrile-1-^{14}C (3) - A mixture of 4-chlorophenylacetonitrile-1-^{14}C (120 mCi, 987 mg, 6.5 mmol), isopropyl bromide (1.31 g, 11 mmol), sodium hydroxide (1.88 g) and benzyltriethylammonium chloride (90 mg) in

water (2.2 ml) was stirred at 50-60° for 4 hr. After adding isopropyl bromide (0.15 g, 1.3 mmol) and benzyltriethylammonium chloride (40 mg), the mixture was stirred at the same temperature for an additional 1 hr. The mixture was diluted with ice-water and extracted with ether. The extract was washed with water, dried, and the solvent removed on a rotary evaporator. Column chromatography of the residue on silica gel with hexane-ether (97/3 v/v) gave 2-(4-chlorophenyl)-3-methylbutyronitrile-1-^{14}C (95.8 mCi, 1.01 g); the purity 99% on RGC and RTLC (silica gel, hexane/ether=5/1, R_f-value=0.27); IR νmax ($CHCl_3$): 2250 cm^{-1}(CN); NMR (δ, $CDCl_3$): 0.95 (3H, d, J=3 Hz, CH_3), 1.05 (3H, d, J=3 Hz, CH_3), 1.80-2.45 (1H, m, -C<u>H</u>$(CH_3)_2$), 3.60 (1H, d, J=6Hz, methyne H), 7.10-7.40 (4H, broad s, aromatic H); mass spectrum (m/e): 195 and 193 (M^+), 101, 103 (base peak).

<u>2-(4-Chlorophenyl)-3-methylbutyric-1-^{14}C Acid (4)</u> - A mixture of 2-(4-chlorophenyl)-3-methylbutyronitrile-1-^{14}C (95.8 mCi, 1.01 g, 5.2 mmol) and 64% sulfuric acid (7 ml) was heated at 150-155° for 8.5 hr. The resulting mixture was cooled, diluted with ice-water and extracted with ether. The ethereal solution was then extracted with 5% sodium hydroxide solution. The aqueous extract was washed with ether, acidified with concentrated hydrochloric acid and re-extracted with ether. The extract was washed with water, dried, and evaporated to give 2-(4-chlorophenyl)-3-methylbutyric-1-^{14}C acid (94.4 mCi, 1.09 g) as colorless crystals; the purity 99% on RTLC (silica gel, chloroform/methanol=3/2, R_f-value =0.56); IR νmax (nujol): 1705 cm^{-1} (CO); NMR (δ, $CDCl_3$): 0.70 (3H, d, J=4 Hz, CH_3), 1.07 (3H, d, J=4 Hz, CH_3), 2.00-2.54 (1H, m, -C<u>H</u>$(CH_3)_2$), 3.13 (1H, d, J=8 Hz, methyne H), 7.10-7.40 (4H, broad s, aromatic H); mass spectrum (m/e): 214 and 212 (M^+), 169, 167 (base peak).

<u>(S)-2-(4-Chlorophenyl)-3-methylbutyric-1-^{14}C Acid (5)</u> - To a stirred solution of 2-(4-chlorophenyl)-3-methylbutyric-1-^{14}C acid (94.4 mCi, 1.09 g, 5.1 mmol) in 80% ethanol (9 ml) was added dropwise a solution of (-)-1-phenylethylamine (400 mg, 3.3 mmol) in the same solvent (9 ml), and white precipitates appeared shortly thereafter. The mixture diluted with 80% ethanol (4.5 ml) was refluxed until

a clear solution was obtained. The solution was cooled and allowed to stand for 1 hr, and colorless crystals produced. The crystals collected by filtration were recrystallized from the same solvent (20 ml). A mixture of the crystals and 5% hydrochloric acid (15 ml) was stirred at room temperature for 10 min, and extracted with ether. The extract was washed with water, dried and evaporated to give (S)-2-(4-chlorophenyl)-3-methylbutyric-1-^{14}C acid (28.3 mCi, 327 mg); $[\alpha]_D^{20}$ +47.1° (c=1.11)[7]; the purity 99% on RTLC.

α-Cyano-3-phenoxybenzyl (S)-2-(4-Chlorophenyl)-3-methylbutyrate-1-^{14}C, (S)-Fenvalerate-(carbonyl-^{14}C)(1a) - A mixture of (S)-2-(4-chlorophenyl)-3-methylbutyric-1-^{14}C acid (28.3 mCi, 327 mg, 1.5 mmol), α-cyano-3-phenoxybenzyl bromide (450 mg, 1.6 mmol)[8], potassium carbonate (115 mg, 0.83 mmol) and tetra-*n*-butylammonium bromide (68 mg, 0.22 mmol) in methylchloroform (6 ml) and water (4 ml) was stirred at 60-65° for 5 hr. After cooling, the mixture was diluted with water, extracted with methylchloroform, and the extract washed successively with 5% potassium carbonate solution, 5% hydrochloric acid and water. Evaporation of the dried extract under reduced pressure gave an oily residue. Column chromatography of the residue on silica gel with hexane-benzene (13/7 v/v) gave α-cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate-1-^{14}C (26.9 mCi, 614 mg, 18.4 mCi/mmol); the purity 99% on RGC and RTLC (silica gel, benzene, hexane/ether=2/1, chloroform/methanol=9/1, R_f-values=0.38, 0.45, 0.78, respectively); $[\alpha]_D^{20}$ -9.33° (c=1.46)[12]; IR νmax ($CHCl_3$): 2300 cm^{-1}(CN), 1745 cm^{-1}(CO); NMR (δ, $CDCl_3$): 0.68 and 0.70 (3H, each d, J=6 Hz, CH_3), 0.94 and 1.04 (3H, each d, J=6 Hz, CH_3), 1.95-2.55 (1H, m, -CH$(CH_3)_2$), 3.21 (1H, d, J=10 Hz, -COCH=), 6.29 and 6.32 (1H, each s, -CH(CN)-O-), 6.86-7.60 (13H, m, aromatic H); mass spectrum (m/e): 421 and 419 (M^+). The product was identical in every respect with the unlabelled authentic sample[12].

α-Cyano-^{14}C-3-phenoxybenzyl Alcohol (8) - To a mixture of potassium cyanide-^{14}C (50.8 mCi, 85 mg, 1.3 mmol), 3-phenoxybenzaldehyde[13] (200 mg, 1.0 mmol) in ethanol (6 ml) was added dropwise a solution of acetic acid (0.6 ml) in ethanol

(3 ml) and resulting mixture stirred at room temperature for 6.5 hr. The mixture was diluted with water and extracted with ether. The extract was washed with water, dried and evaporated under reduced pressure to give α-cyano-^{14}C-3-phenoxybenzyl alcohol (40.0 mCi) as a pale yellow oil, which was applied to the following reaction without any purification.

α-Cyano-^{14}C-3-phenoxybenzyl (S)-2-(4-Chlorophenyl)-3-methylbutyrate, (S)-Fenvalerate-(cyano-^{14}C)(1b) - To a solution of α-cyano-^{14}C-3-phenoxybenzyl alcohol (40.0 mCi, about 1 mmol) and pyridine (0.3 ml) in anhydrous toluene (3 ml) was added dropwise a solution of (S)-2-(4-chlorophenyl)-3-methylbutanoyl chloride[12] (364 mg, 1.5 mmol, $[\alpha]_D^{20}$ +53.0° c=5.80) in anhydrous toluene (12 ml) at -5-0° in a period of 30 min, and the mixture allowed to stand at room temperature overnight. The resulting mixture was diluted with water and extracted with benzene. The extract was washed successively with 5% sodium hydroxide solution, 3% hydrochloric acid and water, dried, and evaporated. The residue (34.6 mCi) was diluted with unlabelled authentic (S)-fenvalerate (0.5 g, 1.2 mmol), subjected to column chromatography on silica gel and eluted with hexane-benzene (3/1 v/v). Evaporation of the main fractions gave α-cyano-^{14}C-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate (25.9 mCi, 692 mg, 15.7 mCi/mmol) as a colorless oil; the purity 99% on RGC and RTLC; $[\alpha]_D^{20}$ -9.30 (c=1.40). The final product was identical in every respect with the unlabelled authentic sample[12].

3-Phenoxybenzoic-(carbonyl-^{14}C) Acid (10) - A solution of 3-phenoxybromobenzene (2.80 g, 11 mmol) in anhydrous tetrahydrofuran (6 ml) was added dropwise to a stirred mixture of magnesium turnings (290 mg, 12 mmol) in anhydrous tetrahydrofuran (17 ml) with gentle reflux during 20 min. After complete addition, the mixture was refluxed for further 30 min and cooled. The reaction flask was connected to a vacuum manifold, and the mixture frozen in a liquid nitrogen bath. To the frozen mixture was introduced carbon-^{14}C dioxide which was liberated from barium carbonate-^{14}C (49.9 mCi, 294 mg, 1.5 mmol). The mixture was then warmed to -15° and stirred for 1 hr. After decomposition with 20% ammonium chloride solution, the mixture was acidified with 5% hydrochloric acid and extracted with

ether. The ethereal solution was extracted with 5% sodium carbonate solution, and the extract acidified with concentrated hydrochloric acid. The resulting mixture was re-extracted with ether. The extract was washed with water, dried and evaporated to give 3-phenoxybenzoic-(carbonyl-^{14}C) acid (44.0 mCi, 287 mg) as colorless needles; the purity 99% on RTLC (silica gel, chloroform/methanol=9/1, R_f-value=0.43); IR νmax ($CHCl_3$): 1695 cm^{-1} (CO).

3-Phenoxybenzyl-α-^{14}C Alcohol (11) - To a stirred solution of 3-phenoxybenzoic-(carbonyl-^{14}C) acid (44.0 mCi, 278 mg, 1.3 mmol) in anhydrous ether (40 ml) was added portionwise lithium aluminum hydride (300 mg) at -5-0°, and the mixture stirred at the same temperature for 1 hr. After addition of ice-water and 10% hydrochloric acid below 0°, the resulting mixture was extracted with ether. The extract was washed with water, dried and evaporated to give 3-phenoxybenzyl-α-^{14}C alcohol (43.6 mCi, 257 mg) as a colorless oil; the purity 99% on RTLC (silica gel, chloroform/methanol=9/1, R_f-value=0.44). The product was used for the following reaction without any purification.

3-Phenoxybenzaldehyde-(carbonyl-^{14}C)(12) - A solution of 3-phenoxybenzyl-α-^{14}C alcohol (43.6 mCi, 257 mg, 1.3 mmol) in dimethylsulfoxide (20 ml) was stirred at 180° with air passing through the solution for 13 hr. The solution was cooled, diluted with water, and extracted with ether. The extract was washed with water, dried and evaporated under reduced pressure. The oily residue was purified by column chromatography on silica gel and eluted with chloroform. Removal of the solvent gave 3-phenoxybenzaldehyde-(carbonyl-^{14}C)(30.5 mCi, 178 mg) as a colorless oil; the purity 99% on RGC and RTLC (silica gel, chloroform, R_f-value-0.33); IR νmax ($CHCl_3$): 1700 cm^{-1}(CO); NMR (δ, $CDCl_3$): 6.85-7.70 (9H, m, aromatic H), 9.89 (1H, s, -CHO); mass spectrum (m/e): 198 (M^+, base peak), 197, 181, 169.

α-Cyano-3-phenoxybenzyl-α-^{14}C (S)-2-(4-Chlorophenyl)-3-methylbutyrate, (S)-Fenvalerate-(methyne-^{14}C)(1c) - To a stirred solution of 3-phenoxybenzaldehyde-(carbonyl-^{14}C)(30.5 mCi, 178 mg, 0.90 mmol) and (S)-2-(4-chlorophenyl)-3-methylbutanoyl chloride (374 mg, 1.5 mmol, $[\alpha]_D$ see above) in heptane (10 ml) was added

dropwise, at room temperature, a solution of sodium cyanide (98 mg, 2.0 mmol) and benzyltriethylammonium chloride (8 mg) in water (4 ml), and the mixture stirred at the same temperature for 16 hr. To the mixture was added additional sodium cyanide (74 mg, 1.5 mmol) and (S)-2-(4-chlorophenyl)-3-methylbutanoyl chloride (230 mg, 1.0 mmol), and the mixture continued to be stirred for 8 hr. The resulting mixture was extracted with benzene and the extract washed successively with 5% sodium carbonate solution, 5% sodium bisulfite solution and water. Evaporation of the extract gave an oily residue which was diluted with the unlabelled authentic (S)-fenvalerate (250 mg, 0.6 mmol). Column chromatography of the product on silica gel with hexane-ether (9/1 v/v) followed by removal of the solvent gave α-cyano-3-phenoxybenzyl-α-^{14}C (S)-2-(4-chlorophenyl)-3-methylbutyrate (27.1 mCi, 562 mg, 20.2 mCi/mmol) as a colorless oil; the purity 99% on RGC and RTLC; $[\alpha]_D^{20}$ -9.34° (c=1.45). The product was identical in every respect with the unlabelled authentic sample[12].

ACKNOWLEDGEMENT

The authors wish to thank Drs. N.Itaya, N. Ohno and Mr. M. Horiba for helpful discussions and providing the unlabelled authentic materials used in this work.

REFERENCES

1. Ohno N., Fujimoto K., Okuno Y., Mizutani T., Hirano M., Itaya N., Honda T. and Yoshioka H. - Pestic. Sci. 7: 241 (1976)
2. Nakayama I., Ohno N., Aketa K., Suzuki Y., Kato T. and Yoshioka H. - Advances in Pesticide Science, Part 2, Pergamon Press, New York, 1979, p. 174
3. Miyakado M., Ohno N., Okuno Y., Hirano M., Fujimoto K. and Yoshioka H. - Agr. Biol. Chem. 39: 267 (1975)
4. Shell Internationale Research Maatschappij B.V. - Neth. Appl. 6,408,190 (1965)
5. Ohno N., Umemura T. and Watanabe T. - Japan Kokai 76 63,145 (1976)
6. Dockx J. - Synthesis: 441 (1973)

7. Miyakado M., Ohno n. and Horiuchi A. - Japan Kokai 75 25,544 (1975)
8. Ohno N., Ume Y. and Tsushima K. - Japan Kokai 76 43,740 (1976)
9. Wood D. A. - Ger. Offen. 2,651, 341 (1977)
10. Sheldon R. A., Been P., Wood D. A. and Mason R. F. - Ger. Offen. 2,708,590 (1977)
11. Yoshitake A., Makari Y., Kawahara K. and Endo M. - J. Label. Comp. 9: 537 (1973)
12. Hirano M., Ohno I., Ohno N. and Mine A. - Japan Kokai 78 24,019 (1978)
13. Angyal S. J. - Organic Reactions 8: 197