^{14}C-LABELLING OF PRALLETHRIN SF, *(4S)*-1-OXO-2-PROPARGYL-3-METHYLCYCLOPENT-2-EN-4-YL *(1R)-CIS-* AND *(1R)-TRANS*-CHRYSANTHEMATES

Hiroshi Kanamaru, Kazuo Kawahara, Takeshi Kamada, Akira Yoshitake and Iwao Nakatsuka
Takarazuka Research Center, Sumitomo Chemical Co., Ltd.,
2-1, Takatsukasa 4-chome, Takarazuka-shi, Hyogo Prefecture, 665, Japan.

SUMMARY

Both of the components of prallethrin SF [*(4S)*-1-oxo-2-propargyl-3-methylcyclopent-2-en-4-yl *(1R)-cis,trans*-chrysanthemate], a novel potent insecticidal pyrethroid, were labelled with carbon-14 at the cyclopentenyl-2 position for use in metabolic studies. Carbonation of 2-lithio-5-methylfuran (4) with carbon-14 dioxide (3) gave 5-methyl-2-[carboxyl-^{14}C]furoic acid (5). Reduction of 5 with lithium aluminium hydride followed by oxidation with manganese dioxide afforded 5-methyl[carbonyl-^{14}C]-furfural (7). Modified Grignard reaction of 7 with propargyl bromide and magnesium in the presence of mercuric chloride yielded 1-(5-methyl-2-furyl)[1-^{14}C]but-3-yn-1-ol (8). Molecular rearrangement of 8 followed by isomerization afforded 2-propargyl-3-methyl[2-^{14}C]cyclopent-2-en-4-ol-1-one (9) in 30% yield from barium [^{14}C]carbonate (2). Direct optical resolution of 9 by preparative HPLC with a chiral-phase column gave (+)-*(4S)* and (-)-*(4R)* isomers (10 and 11) quantitatively. Condensation of 10 with *(1R)-cis-* or *(1R)-trans*-chrysanthemoyl chloride (12a or 12b) yielded *(4S),(1R)-cis-* or *(4S),(1R)-trans*-[cyclopentenyl-2-^{14}C]prallethrin (1a or 1b). Both overall radiochemical yields of 1a and 1b were about 9% from 2.

Key Words: Carbon-14, Prallethrin, 2-Propargyl-3-methylcyclopent-2-en-4-ol-1-one, Optically Active

INTRODUCTION

Prallethrin SF is a novel potent synthetic pyrethroid which provides wide and high insecticidal activity of relatively low mammalian toxicity compared to carbamates, organophosphates and organochlorines[1],[2],[3]. This agent is

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composed of two optically active esters, namely, the esters of *(1R)-cis-* and *(1R)-trans*-chrysanthemic acids with *(4S)*-2-propargyl-3-methylcyclopent-2-en-4-ol-1-one, one of chiral rethrolones. Therefore, it is necessary to prepare both of the esters labelled with carbon-14 at either the acid moieties or the alcohol moiety for studies of its metabolic and enviornmental fate. To date, the metabolic studies of this pyrethroid in mammals have been exclusively carried out by the use of both esters labelled at the acid moieties due to the ease of their preparation[4]. In order to further investigate, it became necessary to synthesize both esters labelled at the alcohol moiety. In this paper, we wish to report the syntheses of two components of prallethrin SF via a new efficient preparation of chiral [^{14}C]rethrolones.

RESULTS AND DISCUSSION

The procedures for the syntheses of *(4S),(1R)-cis-* and *(4S),(1R)-trans*-[cyclopentenyl-2-^{14}C]prallethrins (1a and 1b) are illustrated in Figure 1. In the present work, there were two major problems to be solved; i) incorporation of carbon-14 in the rethrolone, and ii) optical resolution of the labelled rethrolone. Yamamoto and Casida[5] accomplished the ^{14}C-labelling of allethrolone, a typical rethrolone, for the preparation of [^{14}C]allethrin by using cyclization of a 1,4-diketone derivative. Their method, however, seemed to be unsuitable for our present purpose due to its low yield (6%) and tedious processes for the ^{14}C-labelled 1,4-diketone, the key intermediate. Recently, Saito and Yamachika[6] reported a new method for the preparation of non-radioactive rethrolones. In their report, 2-furylcarbinols were rearranged to cyclopent-2-en-4-ol-1-ones, which were then isomerized to the desired rethrolones in good yields. We chose this method for the ^{14}C-labelling of the rethrolone because of its simplicity.

An important intermediate, 1-(5-methyl-2-furyl)[1-^{14}C]but-3-yn-1-ol (8), was synthesized according to the series of the following reactions. ^{14}C-Carbonation of 2-lithio-5-methylfuran (4), which was prepared by the method of Ramanathan and Levine[7], gave 5-methyl-2-[carboxyl-^{14}C]furoic acid (5) in 88% yield from barium [^{14}C]carbonate (2). Direct conversion of various acids

to aldehydes with sodium bis(2-methoxyethoxy)aluminium hydride[8] or lithium aluminium hydride[9] has been reported, but application of these methods to the acid 5 resulted in poor yields of 5-methyl[carbonyl-^{14}C]furfural (7) in our hands. Therefore, it was tried to convert 5 indirectly to 7 via 5-methyl[α-^{14}C]-furfuryl alcohol (6). The acid 5 was reduced with lithium aluminium hydride according to the method of Divald[9] to give the alcohol 6 quantitatively.

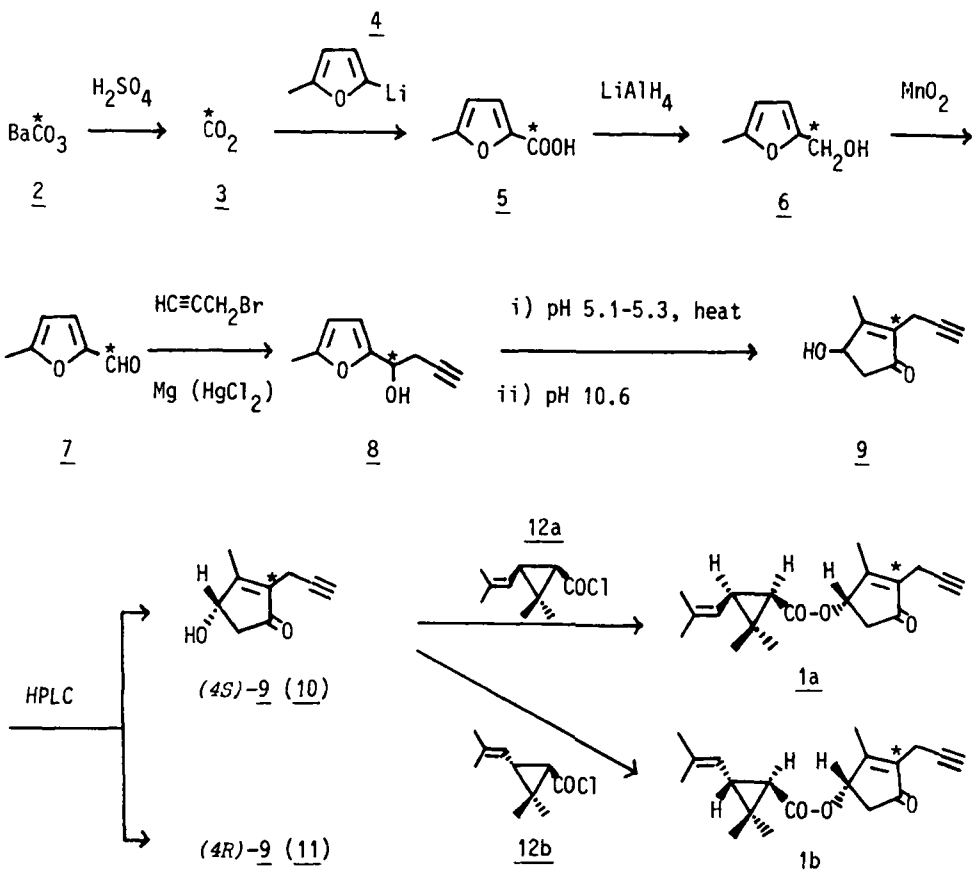

Figure 1 Scheme for the synthese of *(4S),(1R)-cis-* and *(4S),(1R)-trans-*[cyclopentenyl-2-^{14}C]prallethrins

Oxidation of 6 by the use of well-known oxidants such as chromium trioxide-pyridine[10] or dichromates[11] led to only a low yield of the aldehyde 7 due to side-reaction. Manganese dioxide was found to be the most suitable oxidant for this reaction. Thus, the alcohol 6 was treated with an excess amount of manganese dioxide in refluxing dichloromethane to give the aldehyde 7 in 97%

yield. Modified Grignard reaction of 7 with propargyl bromide and magnesium in the presence of mercuric chloride afforded the desired carbinol 8 with the purity of 80%.

Conversion of the carbinol 8 into the key rethrolone, 2-propargyl-3-methyl-[2-^{14}C]cyclopent-2-en-4-ol-1-one (9), was successfully carried out according to the method of Saito and Yamachika[6]. Thus, the carbinol 8 was heated at 100°C for 43 hr in acetate buffer (pH 5.1 - 5.3), and then the resulting product was treated with acetate-phosphate buffer (pH 10.55 - 10.60) at room temperature for 6 hr to give the labelled rethrolone 9. The yield of 9 was 30% from 2 after purification by column chromatography.

Optical resolution of non-radioactive allethrolone has been achieved by fractional recrystallization of its proper diastereomeric derivatives such as the semicarbazone[12] or the salt of acid phthalate[13] These methods, however, seemed to be unpractical for the resolution of the labelled compound because of their complicated procedures and low yields especially in a small-scale preparation. Therefore, we tried to resolve the rethrolone 9 directly by application of a preparative HPLC method with a chiral-phase column. A chiral column, N-[*(R)*-1-(1-naphthyl)ethylamidocarbonyl]-*(S)*-valyl-3-aminopropyl silica (Sumipax OA-4100, Sumika Chemical Analysis Service, Ltd.)[14], was found to be most suitable for the enantiomeric separation of 9. By using this method, (+)-*(4S)* and (-)-*(4R)* isomers (10 and 11)were resolved quantitatively.

The (+)-*(4S)* rethrolone (10) was condensed with *(1R)-cis-* and *(1R)-trans-* chrysanthemoyl chlorides (12a and 12b) in the presence of pyridine to afford *(4S),(1R)-cis-* and *(4S),(1R)-trans-*[cyclopentenyl-2-^{14}C]prallethrins (1a and 1b), respectively, in satisfactory yields without any epimerization. The overall radiochemical yields of 1a and 1b were 8.6 and 9.1% from 2, respectively.

Further application of the new method described above also permitted the production of [2-^{14}C]allethrolone in a goog yield (41% from 2), which will be reported elsewhere.

EXPERIMENTAL

Radio-gas chromatography (RGC) was carried out on a Yanaco G-180 gas chromatograph (Yanagimoto Co., Ltd., Japan) equipped with a RD-4 gas-flow GM-

counter (Aloka, Japan). A glass column (2 m x 3 mm ID) packed with 5% Silicone XE-60 on Chromosorb W AW DMCS (60 - 80 mesh) was used for the analyses of 5-methyl[α-^{14}C]furfuryl alcohol (6) and 5-methyl[carbonyl-^{14}C]furfural (7). Operating condition: column temperature 80°C, carrier gas He (30 ml/min), detectors FID (H_2 50 ml/min) and RD (oxidation temperature 600°C, counting gas n-C_3H_8 50 ml/min) [retention times: 10.1 (6) and 9.3 min (7)]. The same column was used for the analysis of 1-(5-methyl-2-furyl)[1-^{14}C]but-3-yn-1-ol (8) at 110°C [retention time: 8.2 min]. A column (1 m x 3 mm ID) packed with 3% Polyphenyl Ether 7 Rings on Chromosorb W HP (80 - 100 mesh) was used for the analysis of 2-propargyl-3methyl[2-^{14}C]cyclopent-2-en-4-ol-1-one (9). Operating condition: column temperature 140°C, carrier gas He (24 ml/min) [retention time: 12.4 min]. Optically active [^{14}C]prallethrins (1a and 1b) were analyzed on a glass column (3 m x 3 mm ID) packed with 5% Silicone OV-101 on Chromosorb W AW DMCS (60 - 80 mesh). Operating condition: column temperature 180°C, carrier gas He (90 ml/min) [retention times: 25.5 (1a) and 26.7 min (1b)].

Radio-high performance liquid chromatography (RHPLC) was conducted at room temperature on a LC-3A high performance liquid chromatograph (Shimadzu Co., Ltd., Japan) equipped with a SPD-2A UV-detector (240 nm, Shimadzu Co.) and a RLC-551 Radioanalyzer (Aloka). A stainless steel column (25 cm x 4 mm ID) packed with Sumipax OA-4100 (5 μm, Sumika Chemical Analysis Service, Ltd., Japan) was used for the analyses of *(4S)*-2-propargyl-3-methyl[2-^{14}C]cyclopent-2-en-4-ol-1-one (10) and the antipode (11). Operating condition: mobile phase n-hexane/1,2-dichloroethane/ethanol = 100/20/1 (v/v/v), flow rate 1.0 ml/min [retention times: 41.4 (10) and 44.2 min (11)]. Optically active [^{14}C]prallethrins (1a and 1b) were analyzed on two HPLC columns. One was packed with Sumipax OA-2000 (5 μm, 25 cm x 4 mm ID; Sumika Chemical Analysis Service, Ltd.) and operated under the following condition: mobile phase n-hexane/chloroform = 50/3 (v/v), flow rate 1.0 ml/min [retention times: 32.5 (1a) and 35.2 min (1b)]. The other was packed with Lichrosorb RP-18 (10 μm, 30 cm x 4 mm ID; Merck & Co., Inc., N.J., U.S.A.) and operated under the condition: mobile phase methanol/water = 7/3 (v/v), flow rate 1.0 ml/min [retention times: 17.5 (1a) and 19.7 min (1b)].

Radio-thin layer chromatography (RTLC) was carried out on a Silica Gel 60

F_{254} plate (Merck), and the radioactivity on the plate was determined by a Thin Layer Chromatogram Scanner 101U (Aloka).

Radioactivity was measured by a Model TRI-CARB 460 liquid scintillation counter (Packard Instrument Co., Il., U.S.A.; measuring time 5 min).

5-Methyl-2-[carboxyl-^{14}C]furoic acid (5) -- To a solution of 2-methylfuran (862 mg, 10.5 mmol) in anhydrous ether (15 ml) was added a solution of n-butyllithium in n-hexane (1.88 M, 5.60 ml, 10.5 mmol), and the mixture was refluxed for 3 hr under dry nitrogen atmosphere to prepare 2-lithio-5-methylfuran (4). After cooling, the reaction flask was connected to a vacuum manifold, and the mixture was frozen in a liquid nitrogen bath. To the frozen mixture was introduced carbon-14 dioxide (3) which was liberated from barium [^{14}C]carbonate (2) (157 mCi, 22.1 mCi/mmol, 7.10 mmol) with concentrated sulfuric acid. The mixture was then stirred in a dry ice-acetone bath (-78°C) for 30 min. After decomposition with wet ether and water, the aqueous layer was separated, cooled in an ice bath, acidified (pH 1 - 2) with hydrochloric acid, saturated with sodium chloride, and extracted with ether. The extract was dried over anhydrous sodium sulfate and evaporated to give yellow needles of 5-methyl-2-[carboxyl-^{14}C]furoic acid (5) (138 mCi); the purity 95% on RTLC [benzene/ethyl acetate = 1/1 (v/v), R_f 0.09]; IR (ν_{max}, cm^{-1}, nujol): 1675 (C=O); NMR (δ, ppm, $CDCl_3$): 2.40 (3H, s, $\underline{CH}_3$), 6.13 (1H, d, J=4 Hz, furyl H), 7.20 (1H, d, J=4 Hz, furyl H), 11.79 (1H,

5-Methyl[α-^{14}C]furfuryl alcohol (6) -- To a stirring solution of 5-methyl-2-[carboxyl-^{14}C]furoic acid (5) (138 mCi, 6.24 mmol) in anhydrous ether (40 ml) was added portionwise lithium aluminium hydride (947 mg, 25.0 mmol), and the mixture was refluxed for 1 hr under dry nitrogen atmosphere. After cooling, the mixture was decomposed with wet ether (20 ml) and water (10 ml), filtered, and the precipitate was washed with ether. The combined filtrates (about 250 ml) were washed with saturated sodium chloride solution (50 ml) and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 5-methyl[α-^{14}C]furfuryl alcohol (6) (139 mCi) as a yellow oil; the purity 99% on RGC and RTLC [benzene/ethyl acetate = 1/1 (v/v), R_f 0.42]; NMR (δ, ppm, $CDCl_3$): 2.29 (3H, s, $\underline{CH}_3$), 4.49 (3H, s + s, $\underline{CH}_2\underline{OH}$), 5.83 (1H, d, J=3 Hz, furyl H), 6.07 (1H, d, J= 3 Hz, furyl H).

5-Methyl[carbonyl-^{14}C]furfural (7) -- A mixture of 5-methyl[α-^{14}C]furfuryl alcohol (6) (135 mCi, 6.09 mmol) and manganese dioxide (2.01 g, 23.1 mmol) in dichloromethane (30 ml) was refluxed for 1 hr. After addition of the same amount of manganese dioxide, the mixture was refluxed for additional 1 hr to complete the oxidation. The mixture was then cooled, filtered, and the insoluble material was washed with dichloromethane. The filtrate was washed with 5% sodium carbonate and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated under atmospheric pressure to give 5-methyl-[carbonyl-^{14}C]furfural (7) (131 mCi); the purity 97% on RGC and RTLC [dichloromethane, R_f 0.41]; IR (ν_{max}, cm^{-1}, liquid film): 1665 (C=O); NMR (δ, ppm, $CDCl_3$): 2.38 (3H, s, CH_3), 6.20 (1H, d, J=4 Hz, furyl H), 7.13 (1H, d, J=4 Hz, furyl H), 9.41 (1H, s, CHO).

1-(5-Methyl-2-furyl)[1-^{14}C]but-3-yn-1-ol (8) -- To a stirring mixture of magnesium turnings (220 mg, 9.05 mg-atom) and mercuric chloride (a catalytic amount) in anhydrous ether-tetrahydrofuran (3/1 v/v, 4 ml) was added dropwise a solution of 5-methyl[carbonyl-^{14}C]furfural (7) (131 mCi, 5.92 mmol) and propargyl bromide in anhydrous ether-tetrahydrofuran (3/1 v/v, 4 ml) to keep gentle reflux during the addition (about 25 min). The mixture was refluxed for a further 10 min. After cooling in an ice bath, the mixture was decomposed with 20% ammonium chloride and filtered through a Celite pad. The filtrate was saturated with sodium chloride and extracted with ether. The extract was washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate and evaporated to give crude 1-(5-methyl-2-furyl)[1-^{14}C]but-3-yn-1-ol (8) (127 mCi); the purity 80% on RGC and RTLC [chloroform, R_f 0.16]; IR (ν_{max}, cm^{-1}, liquid film): 3400 and 3280 (OH), 2120 (C≡C); NMR (δ, ppm, $CDCl_3$): 2.01 (1H, t, J=3 Hz, C≡CH), 2.24 (3H, s, CH_3), 2.66 - 2.86 (3H, m, ≡C-CH_2 and OH), 4.72 (1H, t, J=7 Hz, furfuryl-α H), 5.84 (1H, d-d, J=3 and 1 Hz, furyl H), 6.09 (1H, d, J=3 Hz, furyl H).

2-Propargyl-3-methyl[2-^{14}C]cyclopent-2-en-4-ol-1-one (9) -- A mixture of crude 1-(5-methyl-2-furyl)[1-^{14}C]but-3-yn-1-ol (8) (127 mCi, 5.77 mmol) in 2.5 mM sodium acetate buffer (132 ml, pH 5.1 - 5.3 at 100°C) was refluxed for 43 hr

under nitrogen stream. After cooling to room temperature, the mixture was washed with toluene (50 ml). The aqueous layer was made alkaline (pH 10.55 - 10.60) by addition of dipotassium hydrogen phosphate (172 mg, 1.27 mmol) and diluted sodium hydroxide solution, and stirred at room temperature for 6 hr. After neutralization, the mixture was saturated with sodium chloride and extracted with ethyl acetate several times. The extracts were combined, washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. Evaporation of the solvent gave an oily residue, which was chromatographed on silica gel with dichloromethane-acetone (92/8, v/v). The main fraction was evaporated to afford 2-propargyl-3-methyl[2-^{14}C]cyclopent-2-en-4-ol-1-one (9) (46.4 mCi); the purity 99% on RGC, RHPLC and RTLC [ether, R_f 0.23; dichloromethane/acetone = 20/1 (v/v), R_f 0.04]; IR (ν_{max}, cm^{-1}, liquid film): 1695 (C=O), 2120 (C≡C); NMR (δ, ppm, $CDCl_3$): 1.99 (1H, t, J=3 Hz, C≡CH), 2.22 (3H, s, CH_3), 2.40 (1H, d, J=3 Hz, ring H), 2.66 (1H, d, J=6 Hz, ring H), 3.08 (2H, d, J=3 Hz, CH_2-C≡C), 3.77 (1H, bs, OH), 4.71 (1H, d-m, J=6 Hz, CH-OH).

Optical resolution of 2-propargyl-3-methyl[2-^{14}C]cyclopent-2-en-4-ol-1-one (9) by using a chiral-phase HPLC column -- A solution of the racemic [^{14}C]rethrolone 9 (46.4 mCi, 315 mg, 2.10 mmol) in n-hexane-ethanol (3/1 v/v, 6.3 ml) was injected by portions (100 µl) to the preparative HPLC [column Sumipax OA-4100 (5 µm, 25 cm x 2 cm ID), mobile phase n-hexane/chloroform/ethanol = 500/50/8 (v/v/v), flow rate 8.0 ml/min, detector UV (240 nm)]. Fractions containing the (+)-*(4S)* isomer (10) (retention time 67 min) and the (-)-*(4R)* isomer (11) (retention time 81 min) were collected individually and evaporated to give 10 (21.1 mCi) and 11 (21.7 mCi), respectively. The optical purities of 10 and 11 were both more than 99% on RHPLC.

(4S)-1-Oxo-2-propargyl-3-methyl[2-^{14}C]cyclopent-2-en-4-yl *(1R)-cis*-chrysanthemate [*(4S),(1R)-cis*-[cyclopentenyl-2-^{14}C]prallethrin] (1a) -- A solution of *(1R)-cis*-chrysanthemic acid (240 mg, 1.42 mmol; the optical purity 99.5%) and oxalyl chloride (1.80 g, 14.2 mmol) in n-pentane (6 ml) was stirred at room temperature for 1.5 hr and evaporated to give a yellow oil of *(1R)-cis*-chrysanthemoyl chloride (12a), which was taken up in anhydrous toluene (2 ml). To a mixture of

the *(4S)* rethrolone 10 (7.31 mCi, 0.331 mmol) in anhydrous benzene (1 ml) were added the solution of 12a and a solution of pyridine (57 mg, 0.73 mmol) in anhydrous toluene (1 ml), and the mixture was stirred at room temperature for 1.5 hr under dry nitrogen stream. After dilution with 2% hydrochloric acid, the mixture was extracted with benzene. The extract was washed with 2% aqueous ammonia, water and saturated sodium chloride solution, successively, and dried over anhydrous sodium sulfate. Evaporation of the solvent gave an oily residue, which was chromatographed on silica gel with dichloromethane. The main fraction was evaporated to give *(4S),(1R)-cis*-[cyclopentenyl-2-^{14}C]prallethrin (1a) (4.50 mCi); the purity 98% on RGC, RHPLC and RTLC [dichloromethane/acetone = 50/1 (v/v), R_f 0.21; n-hexane/ethyl acetate = 10/1 (v/v), R_f 0.18; benzene/ether = 1/1 (v/v), R_f 0.65]; NMR (δ, ppm, $CDCl_3$): 1.22 (3H, s, cyclopropyl CH_3), 1.26 (3H, s, cyclopropyl CH_3), 1.70 (3H, s, $C=C(CH_3)_2$), 1.76 (3H, s, $C=C(CH_3)_2$), 1.86 - 2.02 (2H, m, cyclopropyl H), 2.15 (3H, bs, cyclopentenyl CH_3), 2.34 (1H, t, J=2 Hz, $C\equiv CH$), 2.79 (1H, d-d, J=6 and 2 Hz, cyclopentenyl CH_2), 3.15 (2H, d, J=2 Hz, $CH_2C\equiv CH$), 5.31 (1H, d-m, J=7 Hz, vinyl H), 5.67 (1H, d-m, CO-O-CH).

(4S)-1-Oxo-2-propargyl-3-methyl[2-^{14}C]cyclopent-2-en-4-yl *(1R)-trans*-chrysanthemate [*(4S),(1R)-trans*-[cyclopentenyl-2-^{14}C]prallethrin] (1b) -- By the similar method described above, the *(4S)* rethrolone 10 (7.31 mCi, 0.331 mmol) was condensed with *(1R)-trans*-chrysanthemoyl chloride (12b) (1.42 mmol, the optical purity 99.2%) to give *(4S),(1R)-trans*-[cyclopentenyl-2-^{14}C]prallethrin (1b) (4.81 mCi); the purity 98% on RGC, RHPLC and RTLC; NMR (δ, ppm, $CDCl_3$): 1.15 (3H, s, cyclopropyl CH_3), 1.31 (3H, d, J=2 Hz, cyclopropyl CH_3), 1.71 (6H, s, $C=C(CH_3)_2$), 1.90 - 2.04 (2H, m, cyclopropyl H), 2.14 (3H, bs, cyclopentenyl CH_3), 2.34 (1H, d-d, J=6 and 2 Hz, $CH_2C\equiv CH$), 2.80 (1H, d-d, J=7 and 3 Hz, cyclopentenyl CH_2), 3.14 (2H, d, J=2 Hz, $CH_2C\equiv CH$), 4.86 (1H, d-m, J=7 Hz, vinyl H), 5.64 (1H, t-m, J=7 Hz).

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