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Some pyridyl terpenoid ether analogs of juvenile hormone were synthesized and tested for activity against stored-product insects. Compounds with a longer alkyl side chain were more active.

Recently Soli *et al.* synthesized new juvenile hormone (JH) analogs by combining geranyl chloride with several pyridin-3-ol derivatives and showed them to be highly active against some insects such as *Tenebrio molitor*, *Galleria mellonella* and *Culex pipiens*.¹⁾ Several years ago we reported that a molecular chain length of 17~18 atoms was optimal for the activity as an insect growth regulator.^{2,3)} We therefore wanted to lengthen the carbon chain of the terpenoid side of the pyridyl terpenoid ether so as to find more active JH mimics, especially against stored-product insects. The synthetic aspect of the work is recorded here, while a part of the biological results has already been published by us.⁴⁾

The parent compound reported by Soli *et al.* was 6,7-epoxy-3,7-dimethyloct-2-enyl 2-ethyl-5-pyridyl ether **1**.¹⁾ For the lengthening of the carbon chain, or in other words for the preparation of homologs of geranyl halide, we adopted two procedures as described below and obtained five new JH mimics **2a**~**2e**.

In the first route we used methyl geranate **3** as the starting material. The chain-lengthening step was carried out by the application of organocopper chemistry as it was in the case of our previous synthesis of JH analogs³⁾ and resulted in the synthesis of JH mimic **2a** with a length of 18 atoms. Methyl geranate **3** was oxidized with *m*-chloroperbenzoic acid to give

2a R₁=n-Bu R₂=Me (2E,6E)

b	n-Pr	Me
c	n-Bu	Me (mixture)
d	n-Pr	Et
e	n-Bu	Et

[†] Synthesis of Compounds with Juvenile Hormone Activity. XXIII. Part XXII, T. Takigawa, M. Tominaga, K. Mori and M. Matsui, *Agric. Biol. Chem.*, **43**, 1591 (1979). The experimental part of this work was taken from the B. Sc. theses of M. Komatsu (1978, Present address: Otsuka Pharmaceutical Company, Tokushima) and Y. Ichikawa (1979). Present address of T. Takigawa: Department of Chemistry, Indiana University, Bloomington, Indiana. Address correspondence to K. M.

the terminal epoxide **4**. This was heated at 180~200°C in the presence of alumina to give an allylic alcohol **5a**. The corresponding acetate **5b** was treated with lithium di(*n*-propyl)cuprate in ether to give methyl 3,7-dimethylundeca-2,6-dienoate **6** in 70% yield. This reaction is known to give (*E*)-alkene as the major product^{3,5,6)} and in the present case

gave (2*E*, 6*E*)-isomer **6**. Reduction of **6** with lithium aluminum hydride afforded an alcohol **7**. The corresponding bromide **8** was coupled with 2-ethylpyridin-5-ol in the presence of potassium hydroxide in *N,N*-dimethylformamide to give **9a**. The final epoxidation with *m*-chloroperbenzoic acid yielded the desired product **2a**. This route has the merit of providing a product with (2*E*, 6*E*)-diene system. It is well-known that the *E*-geometry of the central double bond at C-6 of JH, which corresponds to the double bond at C-2 of our alcohol **7**, is quite important for high JH activity. However, a disadvantage of this route lies in its relatively complicated experimental procedure.

The second route is based on our previous non-stereoselective synthesis of JH I and II.⁷⁾ This route enabled us to prepare four pyridyl epoxyterpenoid ethers **2b**~**2e** in a relatively short period, although as mixtures of geometrical isomers. Reaction of a ketone **10** with vinylmagnesium bromide gave a vinyl alcohol **11**. This was treated with hydrobromic

acid to give a bromide **12**. Alkylation of ethyl acetoacetate or ethyl 3-oxopentanoate with **12** gave a substituted β -keto ester **13**. Saponification and decarboxylation of **13** was effected with aqueous barium hydroxide to give a ketone **14**. Vinylmagnesium bromide converted the ketone **14** to an alcohol **15**, which gave a bromide **16** upon treatment with hydrobromic acid. The coupling of the bromide **16** with 2-ethylpyridin-5-ol yielded a pyridyl ether **9b**~**9e**. Epoxidation of **9b**~**9e** with *m*-chloroperbenzoic acid gave the desired products **2b**~**2e**. The whole sequence proceeded without difficulty.

The susceptibility of stored-product insects to these pyridyl ethers was determined at the U.S. Grain Marketing Research Laboratory. The results obtained with compounds **1**, **2a** and **9a** have already been published with experimental details.⁴⁾ We employed Indian meal moth (*Plodia interpunctella*), confused flour beetle (*Tribolium confusum*) and rice weevil (*Sitophilus oryzae*) as test insects. The insects were exposed to JH mimics admixed

TABLE I. ID₉₅ VALUES FOR JH MIMICS^a

Compound	Indian meal moth	ID ₉₅ values (ppm) for	
		Confused flour beetle	Rice weevil
1	~1	~5	>100
2a	0.04	2.2	49.3
2b	<1	20	~100
2c	<0.1	2	50
2d	<1	30	~100
2e	<1	2	25
9a	0.3	20.3	>100
9b	40	>100	>100
9c	<1	20	>100
9d	<1	~100	~100
9e	<1	24	65

^a ID₉₅ is expressed as the ppm per weight of grain necessary to obtain 95% inhibition of progeny development.

with diet. The ID₉₅ was then expressed as the ppm per weight of grain necessary to obtain 95% inhibition of progeny development. Table I shows that compounds **2a**, **2c** and **2e** are highly active against all three test species and they are comparable in their activities to methoprene, the well-known commercially available insect growth regulator.^{8,9} The data in Table I indicate the following order of activity with regard to the size of R₁ and R₂: (a) R₁: Me < *n*-Pr < *n*-Bu (b) R₂: Me < Et. This is in accord with our previous findings on the structure-activity relationship among other JH analogs.³⁾

EXPERIMENTAL

IR spectra were determined as films on a Jasco IRA-1 spectrometer. NMR spectra were recorded on a Hitachi R-24A spectrometer at 60 MHz in CCl₄ with TMS as an internal standard, unless otherwise stated.

Methyl 6,7-epoxy-3,7-dimethyloct-2-enoate (4). A solution of *m*-chloroperbenzoic acid (45.3 g) in dichloromethane (960 ml) was added dropwise during 40 min to a stirred and ice-cooled solution of **3** (44.2 g) in dichloromethane (200 ml) at 10°C. The mixture was stirred for 2 hr at 0~10°C, washed with sodium bicarbonate solution, 10% sodium bisulfite solution, sodium bicarbonate solution and brine, dried over magnesium sulfate and concentrated *in vacuo*. The residue was distilled to give 42.3 g (90.3%) of **4**, bp 102~103°C (1.7 mmHg); *n*_D²¹ 1.4618;

IR $\nu_{\max}$ cm⁻¹: 1730 (s), 1650 (s), 1230 (s), 1160 (s); NMR δ 1.20 (3H, s), 1.22 (3H, s), 1.68 (2H, q, *J*=6 Hz), 2.14 (3H, s), ~2.10~2.42 (2H, m), 2.52 (1H, t, *J*=6 Hz), 3.60 (3H, s), 5.63 (1H, s).

Methyl 6-hydroxy-3,7-dimethylocta-2,7-dienoate (5a). Woelm neutral alumina (activity grade I, 2 g) was added to **4** (10 g) and the mixture was heated at 180~200°C for 1.5 hr under argon. By repeating the pyrolysis on this scale, 113 g of crude **5** was obtained from 115 g of **4**. This was chromatographed over neutral alumina (grade II, 2 kg). The fractions containing **5** was combined and concentrated *in vacuo*. The residue was distilled to give 49.6 g (43.1%) of **5**, bp 115~116°C (0.9 mmHg), *n*_D²⁰ 1.4842; IR $\nu_{\max}$ cm⁻¹: 3400 (m), 3040 (w), 2940 (s), 1720 (s), 1650 (s), 1440 (m), 1230 (s), 1150 (s), 1030 (m), 900 (m); NMR δ 1.71 (3H, s), 2.12 (3H, s), 3.60 (3H, s), 3.95 (1H, m), 4.86 (2H, d, *J*=6 Hz), 5.63 (1H, s).

Methyl 6-acetoxy-3,7-dimethylocta-2,7-dienoate (5b). Acetic anhydride (148 ml) was added to a solution of **5a** (48 g) in dry pyridine and the mixture was left to stand overnight at room temperature. It was then poured into ice-water and extracted with ether. The ether solution was washed with water, sodium bicarbonate solution, cupric sulfate solution, water and brine, dried over magnesium sulfate and concentrated *in vacuo*. The residue was distilled to give 53 g (91%) of **5b**, bp 106~109°C (0.3 mmHg); *n*_D²² 1.4609; IR $\nu_{\max}$ cm⁻¹: 3080 (w), 2940 (s), 1740 (s), 1720 (s), 1650 (sh), 1640 (s), 1430 (s), 1370 (s), 1230 (s), 1150 (s), 1020 (m), 900 (m); NMR δ 1.72 (3H, s), 1.98 (3H, s), 2.14 (3H, s), 3.58 (3H, s), 4.75~5.20 (2H, m), 5.56 (1H, s); *Anal.* Found: C, 64.88; H, 8.43. Calcd. for C₁₃H₂₀O₄: C, 64.98; H, 8.39%.

Methyl (2E, 6E)-3,7-dimethylundeca-2,6-dienoate (6). A solution of *n*-propyllithium (75.6 mmol) in ether (84 ml) was added dropwise to a stirred and cooled suspension of cuprous iodide (7.2 g, 37.8 mmol) in ether (120 ml) at -12°C under argon. The initially formed yellow-brown precipitates dissolved completely to give a dark brown solution. After the addition the mixture was stirred at -12~-20°C for 30 min. Then a solution of **5b** (3 g) in ether (18 ml) was added dropwise at -20~-10°C. The mixture was stirred for 40 min at -15~-10°C and then poured into ice-ammonium chloride solution. The mixture was filtered through Celite. The ether layer was separated and the aqueous layer was extracted with ether. The ether solution was washed with water and brine, dried over magnesium sulfate and concentrated *in vacuo*. The residue was distilled to give 2.1 g (75%) of **6**, bp 134~137°C (9 mmHg); *n*_D¹⁹ 1.4691; IR $\nu_{\max}$ cm⁻¹: 2950 (s), 2920 (s), 1720 (vs), 1640 (s), 1430 (s), 1225 (vs), 1140 (vs); NMR δ : 0.90 (3H, m), ~1.30 (4H, br. m), 1.58 (3H, s), 2.10 (3H, s), 3.55 (3H, s), 5.00 (1H, br), 5.02 (1H, s); GLC (Column, 5% LAC 2R-446 on Diasolid, 1.5 m × 3 mm at 150°C; Carrier gas, N₂, 1.1 kg/cm²); *t*_R 10.0 min (84.4%).

(2*E*, 6*E*)-3,7-Dimethylundeca-2,6-dien-1-ol (**7**). A solution of **6** (4 g) in ether (8 ml) was added to a stirred and ice-cooled suspension of lithium aluminum hydride (1.2 g) in ether (40 ml). The mixture was stirred and heated under reflux for 30 min, and cooled. The excess metal hydride was decomposed by the addition of water (0.6 ml), 10% sodium hydroxide solution (0.6 ml) and water (1.8 ml). The mixture was filtered and the filter cake was washed with ether. The ether solution was concentrated *in vacuo* and the residue was chromatographed over silica gel. Elution with *n*-hexane-ether gave **7**. This was distilled to give 1.3 g (37%) of pure **7**, bp 135~136°C (8 mmHg); n_D^{20} 1.4741; IR $\nu_{\max}$ cm⁻¹: 3320 (m), 2960 (s), 2920 (s), 2860 (s), 1665 (m), 1450 (m), 1380 (m), 1000 (m); NMR δ 0.90 (3H, m), 1.54 (3H, s), 1.64 (3H, s), 4.02 (2H, d, $J=6$ Hz), ~4.9~5.5 (2H, m); *Anal.* Found: C, 78.82; H, 12.22. Calcd. for C₁₃H₂₄O: C, 79.53; H, 12.32%.

(2*E*, 6*E*)-3,7-Dimethylundeca-2,6-dienyl bromide (**8**). A solution of phosphorus tribromide (0.5 g) in ether (8 ml) was added dropwise to a stirred and cooled (ice-salt) solution of **7** (1.0 g) in ether (30 ml). After the addition the mixture was stirred for 1 hr at room temperature, poured into ice-water and extracted with ether. The ether solution was washed with sodium bicarbonate solution, water and brine, dried over magnesium sulfate and concentrated *in vacuo* to give 1.2 g of **8**; IR $\nu_{\max}$ cm⁻¹: 2960 (s), 2920 (s), 2860 (s), 1655 (m), 1450 (m), 1385 (m), 1205 (s). This was employed for the next step without further purification.

(2*E*, 6*E*)-3,7-Dimethylundeca-2,6-dienyl 2-ethyl-5-pyridyl ether (**9a**). Powdered potassium hydroxide (0.132 g) was added to a solution of 2-ethylpyridin-5-ol (0.258 g) in *N,N*-dimethylformamide (10 ml) and the mixture was stirred for 1 hr. Then **8** (0.5 g) was added to the solution and the mixture was stirred overnight at room temperature. The mixture was poured into ice-water and extracted with ether. The ether solution was washed with water, dried over sodium sulfate and concentrated *in vacuo* to give an oil (0.5 g). This was chromatographed over silica gel. Elution with benzene-ethyl acetate gave 0.4 g (74%) of **9a**, n_D^{20} 1.5098; IR $\nu_{\max}$ cm⁻¹: 2960 (s), 2940 (s), 2860 (s), 1670 (w), 1600 (w), 1580 (m), 1505 (s), 1495 (s), 1400 (m), 1300 (s), 1280 (s), 1255 (s), 1220 (m), 1025 (m), 1000 (m), 840 (m); NMR δ 0.89 (3H, deformed t, $J=\sim 6$ Hz), 1.22 (3H, t, $J=7$ Hz), 1.56 (3H, s), 1.72 (3H, s), 2.66 (2H, q, $J=7$ Hz), 4.44 (2H, d, $J=6$ Hz), 5.00 (1H, m), 5.36 (1H, m), 6.88 (2H, br. s), 8.00 (1H, br. s); *Anal.* Found: C, 78.84; H, 10.57; N, 4.39. Calcd. for C₂₀H₃₁ON: C, 79.67; H, 10.37; N, 4.65%.

(2*E*, 6*E*)-6,7-Epoxy-3,7-dimethylundec-2-enyl 2-ethyl-5-pyridyl ether (**2a**). A solution of *m*-chloroperbenzoic acid (85%, 145 mg) in dichloromethane (10 ml) was added to a stirred and ice-cooled solution of **9a** (200 mg) in dichloromethane (10 ml). The mixture was stirred for 2 hr at 0~5°C. Then it was thoroughly washed with sodium

bicarbonate solution, dried over sodium sulfate and concentrated *in vacuo*. The residue was chromatographed over silica gel. Elution with benzene-ethyl acetate afforded 100 mg (48%) of **2a**, n_D^{20} 1.5042; IR $\nu_{\max}$ cm⁻¹: 2980 (s), 2940 (s), 2880 (s), 1670 (w), 1600 (w), 1570 (s), 1500 (s), 1490 (s), 1470 (s), 1395 (s), 1290 (s), 1280 (s), 1250 (s), 1130 (w), 1060 (w), 1025 (m), 1000 (m), 840 (m); NMR δ 0.90 (3H, deformed t, $J=6$ Hz), 1.13 (3H, t, $J=6$ Hz), 1.16 (3H, s), 1.36 (4H, br. s), 1.74 (3H, s), 2.66 (2H, q, $J=6$ Hz), 4.46 (2H, d, $J=6$ Hz), 5.42 (1H, t, $J=6$ Hz), 6.88 (2H, d, $J=2$ Hz), 8.02 (1H, br. s). *Anal.* Found: C, 74.65; H, 9.75; N, 4.74. Calcd. for C₂₀H₃₁O₂N: C, 75.67; H, 9.84; N, 4.41%.

3-Methylhept-1-en-3-ol (**11c**). A solution of vinylmagnesium bromide was prepared from vinyl bromide (69.6 g) and magnesium (15 g) in tetrahydrofuran (300 ml). A solution of methyl *n*-butyl ketone (25 g) in tetrahydrofuran (25 ml) was added to the Grignard reagent with stirring. After the addition the mixture was stirred and heated under reflux for 1 hr. The mixture was added to ice-ammonium chloride solution and extracted with ether. The ether extract was washed with sodium bicarbonate solution and brine, dried with magnesium sulfate and concentrated *in vacuo*. The residue was distilled to give 27.1 g (85%) of **11b**, bp 75~80°C (46 mmHg); n_D^{20} 1.4323; IR $\nu_{\max}$ cm⁻¹: 3400 (m), 3120 (w), 2960 (s), 2940 (s), 2880 (m), 1650 (w), 1000 (m), 920 (s); NMR δ 0.90 (3H, distorted t, $J=6$ Hz), 1.20 (3H, s), 4.8~6.1 (3H, m); *Anal.* Found: C, 74.21; H, 12.34. Calcd. for C₈H₁₆O: C, 75.00; H, 12.50%.

3-Methylhex-1-en-3-ol (**11b**). In the same manner as described above 34.4 g of methyl *n*-propyl ketone gave 37.5 g (80.6%) of **11b**, bp 62~65°C (50 mmHg); $n_D^{21.8}$ 1.4230; IR $\nu_{\max}$ cm⁻¹: 3380 (m), 3080 (w), 1640 (w), 995 (s), 920 (s); NMR δ 0.92 (3H, distorted t, $J=7$ Hz), 1.20 (3H, s), 1.30~1.55 (4H, m), 2.28 (1H, s, -OH), 4.8~6.1 (3H, m).

3-Methylhept-2-enyl bromide (**12c**). The alcohol **11c** (51.6 g) was added dropwise to stirred and ice-cooled 47% hydrobromic acid (270 ml) at 0~10°C. After stirring for 1 hr, the mixture was extracted with petroleum ether. The extract was washed with water, sodium bicarbonate solution and brine, dried over calcium chloride and concentrated *in vacuo*. The residue was distilled to give 67.3 g (87.6%) of **12c**, bp 97~100°C (34 mmHg), n_D^{20} 1.4828; IR $\nu_{\max}$ cm⁻¹: 2940 (s), 2920 (s), 2840 (m), 1650 (m), 1200 (s); NMR δ 0.92 (3H, distorted t, $J=6$ Hz), 1.32 (4H, m), 1.70 (3H, s), 2.00 (2H, d, $J=10$ Hz), 5.48 (1H, t, $J=10$ Hz); *Anal.* Found: C, 50.49; H, 7.88. Calcd. for C₈H₁₅Br: C, 50.26; H, 7.85%.

3-Methylhex-2-enyl bromide (**12b**). In the same manner as above 36.7 g of **11b** yielded 42.8 g (79.5%) of **12b**, bp 80~83.5°C (35.5 mmHg); $n_D^{21.8}$ 1.4290; IR $\nu_{\max}$ cm⁻¹: 2960 (s), 2920 (s), 2860 (s), 1660 (m), 1210 (s); NMR δ 0.90 (3H, deformed t, $J=6$ Hz), 1.2~1.7 (2H, m), 1.70 (3H, s)

1.9~2.4 (2H, m), 3.90 (2H, d, $J=8$ Hz), 5.47 (1H, t, $J=7$ Hz).

3-Ethoxycarbonyl-6-methyldec-5-en-2-one (13c). A solution of sodium ethoxide in ethanol was prepared from sodium (8.3 g) and ethanol (500 ml). This was diluted with benzene (300 ml) and the inner temperature was cooled to 10°C. Ethyl acetoacetate (47 g) was added to the mixture and the soln was stirred for 1 hr. Then **12c** (66 g) was added and the mixture was stirred and heated under reflux for 1 hr. Then it was diluted with water and extracted with ether. The ether solution was washed with brine, dried over magnesium sulfate and concentrated *in vacuo*. The residue was distilled to give 61.3 g (83.3%) of **13c**, bp 138~142°C (6.5 mmHg); n_D^{20} 1.4490; IR $\nu_{\max}$ cm^{-1} : 1755 (s), 1730 (s), 1160 (m); NMR δ 0.92 (3H, distorted t, $J=6$ Hz), 1.23 (3H, t, $J=7$ Hz), 1.60 (3H, s), 2.10 (3H, s), 2.42 (2H, t, $J=7$ Hz), 3.24 (1H, t, $J=7$ Hz), 4.05 (2H, q, $J=7$ Hz), 4.94 (1H, t, $J=6$ Hz). *Anal.* Found: C, 69.60; H, 10.01. Calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_3$: C, 69.71; H, 10.37%.

3-Ethoxycarbonyl-6-methylnon-5-en-2-one (13b). In the same manner as above **12b** (40 g) and ethyl acetoacetate (32.6 g) gave 41.9 g (77.8%) of **13b**, bp 118~124°C (6.0 mmHg); n_D^{20} 1.4490; NMR δ 0.90 (3H, deformed t, $J=6$ Hz), 1.24 (3H, t, $J=7$ Hz), 1.60 (3H, s), 2.10 (3H, s), 2.42 (2H, t, $J=7$ Hz), 3.26 (1H, t, $J=7$ Hz), 4.10 (2H, t, $J=7$ Hz), 4.96 (1H, t, $J=7$ Hz). The IR spectrum was similar to that of **13c**.

4-Ethoxycarbonyl-7-methyldec-6-en-3-one (13d). In the same manner **12d** (22 g) and ethyl 3-oxopentanoate (19.1 g) yielded 21.0 g (79.7%) of **13d**, bp 131~134°C (5.5 mmHg), n_D^{20} 1.4573. The IR and NMR spectra were in accord with the structure.

4-Ethoxycarbonyl-7-methylundec-6-en-3-one (13e). In the same manner **12e** (28 g) and ethyl 3-oxopentanoate (23.0 g) gave 27.2 g (72.5%) of **13e**, bp 138~142°C (4 mmHg), n_D^{20} 1.4510. The IR and NMR spectra were in accord with the structure.

6-Methyldec-5-en-2-one (14c). A mixture of **13c** (60 g), barium hydroxide octahydrate (116.0 g), 95% ethanol (136 ml) and water (475 ml) was stirred and heated overnight under reflux under nitrogen atmosphere. This was poured into ice and dilute hydrochloric acid and extracted with ether. The ether solution was washed with sodium bicarbonate solution and brine, dried over magnesium sulfate and concentrated *in vacuo*. The residue was distilled to give 30.2 g (71.8%) of **14c**, bp 95~121°C (7 mmHg), n_D^{20} 1.4446; IR $\nu_{\max}$ cm^{-1} : 2960 (s), 2920 (s), 2860 (m), 1720 (s), 1450 (m), 1380 (m), 1360 (m), 1160 (m); NMR δ 0.90 (3H, deformed t, $J=6$ Hz), 1.30 (4H, m), 1.58 (3H, s), 2.02 (3H, s), ~1.70~2.10, 2.28 (2H, m), 4.98 (1H, t, $J=6$ Hz); *Anal.* Found: C, 78.11; H, 12.05. Calcd. for $\text{C}_{11}\text{H}_{20}\text{O}$: C, 78.57; H, 11.90%.

6-Methylnon-5-en-2-one (14b). In the same manner as above **13b** (41.0 g) yielded 21.1 g (78.1%) of **14b**, bp 77~78°C (7.5 mmHg), n_D^{22} 1.4450; *Anal.* Found: C, 77.15; H, 11.56. Calcd. for $\text{C}_{10}\text{H}_{18}\text{O}$: C, 77.92; H, 11.69%. The IR and NMR spectra were in accord with the structure.

7-Methyldec-6-en-3-one (14d). In the same manner **13d** (20 g) gave 10.6 g (70%) of **14d**, bp 81~83°C (3.5 mmHg), n_D^{20} 1.4502; IR $\nu_{\max}$ cm^{-1} : 2940 (s), 2920 (s), 2860 (m), 1715 (s), 1460 (m), 1420 (m), 1380 (m), 1360 (m), 1110 (m); NMR δ 0.85 (3H, deformed t, $J=7$ Hz), 0.99 (3H, t, $J=7$ Hz), ~1.2~1.5 (2H, m), 1.58 (3H, s), ~1.80~2.10 (4H, m), 2.28 (3H, s), ~2.10~2.60 (4H, m), 5.04 (1H, t, $J=6$ Hz).

7-Methylundec-6-en-3-one (14e). In the same manner **13e** (27 g) gave 16.0 g (85%) of **14e**, bp 105~110°C (7 mmHg), n_D^{20} 1.4479; *Anal.* Found: C, 78.80; H, 12.13. Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}$: C, 79.12; H, 12.09%. The IR and NMR spectra were in accord with the structure.

3,7-Dimethyldeca-1,6-dien-3-ol (15b). This was prepared in the same manner as described for the preparation of **11c** and **14b** (23.7 g) gave 20.3 g (86%) of **15b**, bp 96~105°C (1.7~2.0 mmHg), n_D^{20} 1.4625; IR $\nu_{\max}$ cm^{-1} : 3370 (m), 3070 (w), 2940 (s), 2920 (s), 2860 (m), 1640 (w), 1450 (m), 1380 (m), 1120 (m), 995 (m), 920 (s); NMR δ 0.88 (3H, deformed t, $J=6$ Hz), 1.22 (3H, s), 1.30~1.51 (4H, m), 1.57 (3H, s), 1.71~2.24 (5H, m), 4.82~6.14 (4H, m); *Anal.* Found: C, 78.42; H, 12.00. Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}$: C, 79.12; H, 12.09%.

3,7-Dimethylundeca-1,6-dien-3-ol (15c). In the same manner as above **14c** (29 g) gave 25.6 g (80%) of **15c**, bp 104.5~107.5°C (2 mmHg), n_D^{20} 1.4631; *Anal.* Found: C, 78.73; H, 12.17. Calcd. for $\text{C}_{13}\text{H}_{23}\text{O}$: C, 79.59; H, 12.24%. The IR and NMR spectra were in accord with the structure.

3-Ethyl-7-methyldeca-1,6-dien-3-ol (15d). In the same manner as above **14d** (10.0 g) gave 10.2 g (86.4%) of **15d**, bp 102~104°C (4 mmHg); $n_D^{20.5}$ 1.4646; *Anal.* Found: C, 79.24; H, 12.30. Calcd. for $\text{C}_{13}\text{H}_{25}\text{O}$: C, 79.19; H, 12.69%. The IR and NMR spectra were in accord with the structure.

3-Ethyl-7-methylundeca-1,6-dien-3-ol (15e). In the same manner as above **14e** (15 g) gave 14.35 g (93%) of **15e**, bp 102~106°C (3 mmHg), n_D^{20} 1.4653; *Anal.* Found: C, 79.47; H, 12.54. Calcd. for $\text{C}_{14}\text{H}_{27}\text{O}$: C, 79.62; H, 12.80%. The IR and NMR spectra were in accord with the structure.

3,7-Dimethyldeca-2,6-dienyl bromide (16b). This was prepared in the same manner as described for **12c**, and **15b** (10 g) afforded 8.5 g (69.6%) of **16b**, bp 98~110°C (1.4 mmHg); n_D^{20} 1.4930; IR $\nu_{\max}$ cm^{-1} : 2940 (s), 2920 (s), 2860

(s), 1650 (m), 1450 (s), 1380 (s), 1200 (s); *Anal.* Found: C, 59.31; H, 8.85. Calcd. for $C_{12}H_{21}Br$: C, 58.80; H, 8.58%. Due to the presence of geometrical isomers, the high field region of its NMR spectrum was quite complicated but 2H-doublet at δ 3.92 (CH_2Br , $J=8$ Hz) and 3H-olefinic protons at δ 4.8~5.7 supported the structure.

3,7-Dimethylundeca-2,6-dienyl bromide (16c). In the same manner as above **15c** (10.0 g) gave 10.0 g (77.5%) of **16c**, bp 116°C (1 mmHg); n_D^{20} 1.4935. The IR and NMR spectra were in accord with the structure.

3-Ethyl-7-methyldeca-2,6-dienyl bromide (16d). In the same manner as above **15d** (8.0 g) gave 5.36 g (50.6%) of **16d**, bp 80~90°C (0.25 mmHg), n_D^{20} 1.4913. The IR and NMR spectra were consistent with the structure.

3-Ethyl-7-methylundeca-2,6-dienyl bromide (16e). In the same manner as above **15e** (8 g) gave 5.7 g (55.1%) of **16e**, bp 90~100°C (0.27 mmHg), n_D^{20} 1.4821. The IR and NMR spectra were consistent with the structure.

3,7-Dimethylundeca-2,6-dienyl 2-ethyl-5-pyridyl ether (9c). Powdered potassium hydroxide (85%, 0.455 g) was added to a solution of 2-ethylpyridin-5-ol (1.05 g) in *N,N*-dimethylformamide (40 ml) and the mixture was stirred for 1 hr. Then **16c** (2 g) was added to the solution and the mixture was stirred overnight at room temperature. The mixture was poured into ice-water and extracted with ether. The ether solution was washed with water, dried over sodium sulfate and concentrated *in vacuo*. The residue (2.5 g) was chromatographed over silica gel. Elution with benzene gave 1.12 g (48.2%) of **9c**, bp 125~130°C (bath temperature, 0.08 mmHg), n_D^{20} 1.5058; IR, ν_{max} cm^{-1} : 2940 (s), 2920 (s), 2860 (s), 1660 (w), 1595 (w), 1565 (s), 1490 (s), 1480 (s), 1450 (s), 1380 (m), 1285 (s), 1270 (s), 1250 (s), 1240 (s), 1020 (m), 995 (m), 830 (m); NMR δ 0.88 (3H, distorted t, $J=7$ Hz), 1.20 (3H, t, $J=7$ Hz), 1.54 (3H, s), 1.68 (3H, s), $\sim 1.5\sim 1.8$ (4H), 2.65 (2H, q, $J=7$ Hz), 4.45 (2H, d, $J=6$ Hz), 5.02 (1H), 5.39 (1H, t, $J=7$ Hz), 6.88 (2H), 8.02 (1H); *Anal.* Found: C, 79.35; H, 10.54; N, 4.48. Calcd. for $C_{20}H_{31}ON$: C, 79.73; H, 10.30; N, 4.65%.

3,7-Dimethyldeca-2,6-dienyl 2-ethyl-5-pyridyl ether (9b). In the same manner as described above, **16b** (2.0 g) gave 1.25 g (52.9%) of **9b**, bp 138~142°C (bath temperature, 0.4 mmHg), n_D^{20} 1.5062. The IR and NMR spectra were in accord with the structure.

3-Ethyl-7-methyldeca-2,6-dienyl 2-ethyl-5-pyridyl ether (9c). In the same manner as described above **16c** (2.0 g) gave 580 mg (27.4%) of **9c**, n_D^{20} 1.5081; MS (m/e): 302 (M^+). Due to the presence of geometrical isomers, the high field region of its NMR spectrum was quite complicated, but in the low field region, signals were observable which supported the assigned structure: δ 2.68

(2H, q, $J=7$ Hz), 4.48 (2H, d, $J=6$ Hz), 5.08 (1H, m), 5.40 (1H, t, $J=6$ Hz), 6.92 (2H, s), 8.08 (1H, br. s).

3-Ethyl-7-methylundeca-2,6-dienyl 2-ethyl-5-pyridyl ether (9d). In the same manner as described above **16d** (2.0 g) gave 800 mg (36.2%) of **9d**, n_D^{20} 1.5061; MS (m/e): 316 (M^+). The IR and NMR spectra were in accord with the structure.

6,7-Epoxy-3,7-dimethylundec-2-enyl 2-ethyl-5-pyridyl ether (2c). A solution of *m*-chloroperbenzoic acid (85%, 366 mg) in dichloromethane (10 ml) was added dropwise to a solution of **9c** (500 mg) in dichloromethane (10 ml) with stirring and ice-cooling. The mixture was stirred for 2 hr, washed with sodium carbonate solution, dried over magnesium sulfate and concentrated *in vacuo*. The residue was purified by preparative TLC (Kieselgel G; benzene-ethyl acetate = 5:1) to give 137 mg of pure **2c**, n_D^{21} 1.5025; IR, ν_{max} cm^{-1} : 2960 (s), 2920 (s), 2860 (s), 1665 (w), 1595 (w), 1570 (s), 1495 (s), 1485 (s), 1470 (s), 1390 (m), 1290 (s), 1270 (s), 1250 (s), 1210 (m), 1130 (w), 1050 (w), 1020 (m), 1000 (m), 910 (w), 870 (w), 840 (m); NMR δ 0.90 (3H, deformed t, $J=7$ Hz), 1.18 (3H, s), 1.24 (3H, t, $J=7$ Hz), $\sim 1.1\sim 1.6$ (8H), 1.75 (3H, s), $\sim 1.9\sim 2.5$ (3H, m), 2.70 (2H, q, $J=7$ Hz), 4.50 (2H, d, $J=6$ Hz), 5.50 (1H, t, $J=6$ Hz), 6.98 (2H, s), 8.12 (1H, br. s); MS (m/e): 318 (M^+).

6,7-Epoxy-3,7-dimethyldec-2-enyl 2-ethyl-5-pyridyl ether (2b). In the same manner as above, **9b** (500 mg) gave 100 mg of **2b**, n_D^{20} 1.5039; MS (m/e): 304 (M^+). The IR spectrum was very similar to that of **2c** and the NMR spectrum supported the structure.

6,7-Epoxy-3-ethyl-7-methyldec-2-enyl 2-ethyl-5-pyridyl ether (2d). In the same manner as above, **9d** (200 mg) gave 90 mg of **2d**, n_D^{20} 1.5031; MS (m/e): 318 (M^+). The IR spectrum was in accord with the assigned structure. Due to the presence of geometrical isomers, the high field region of the NMR spectrum was rather complicated, but in the low field region, signals were observable which supported the assigned structure: δ 2.72 (2H, q, $J=7$ Hz), 4.55 (2H, d, $J=6$ Hz), 5.52 (1H, t, $J=6$ Hz), 7.00 (2H, s), 8.18 (1H, br. s).

6,7-Epoxy-3-ethyl-7-methylundec-2-enyl 2-ethyl-5-pyridyl ether (2e). In the same manner as above, **9e** (200 mg) gave 90 mg of **2e**, n_D^{20} 1.5008; MS (m/e): 332 (M^+). The IR and NMR spectra were in accord with the structure.

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