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SYNTHESIS OF BOTH THE ENANTIOMERS OF HAUPTMANN'S PERIPLANONE-A AND CLARIFICATION OF THE STRUCTURE OF PERSOONS'S PERIPLANONE-A†

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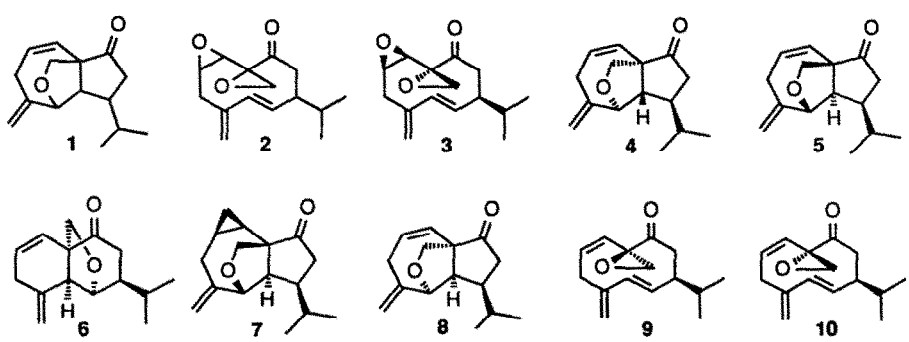
Abstract: The naturally occurring (-)-enantiomer of Hauptmann's periplanone-A and its stereoisomers were synthesized. Thermal rearrangement of Hauptmann's (-)-periplanone-A by GLC gave Persoons's periplanone-A, the structure of which was determined through an X-ray crystallographic analysis of the corresponding alcohol.

Introduction

In 1974 Persoons *et al.* isolated two potent sex pheromone components of the American cockroach (*Periplaneta americana*)[1a] and named them periplanone-A and periplanone-B.[1b] Spectroscopic analyses of these pheromone components led them to propose tentative structures **1**[2] and **2**[3], respectively. The confirmation of the proposed structure **2** for periplanone-B and the establishment of its stereochemistry as **3** were achieved by Still's synthetic studies.[4] Other synthetic works[5] on (±)-**3** or the natural enantiomer (-)-**3** also confirmed the structure, including its absolute configuration. On the other hand, the structure of periplanone-A has remained obscure. In 1987 Shizuri *et al.* synthesized (±)-**4**[6] and (±)-**5**[7], two of the four possible diastereomers of **1**. However, their spectral data were different from those of periplanone-A. They therefore reexamined the spectral data reported by Persoons *et al.*, and proposed **6** as the most plausible structure for this pheromone.[8] Quite recently they reported a synthesis of (±)-**6**.[9] However, ^{1}H NMR spectrum of their synthetic sample was not identical with that reported for periplanone-A.[2,9] Another proposal for the structure of periplanone-A was made by Macdonald *et al.*[10] Through their synthesis of (±)-**7**, they assigned **8** to the



† Pheromone Synthesis, Part 124. Part 123, S. Kuwahara and K. Mori, *Tetrahedron*, the preceding paper.

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pheromone isolated by Persoons *et al.* Moreover, they assumed that the *cis*-fused hydroazulenone **8** might be an artifact derived from **9**. Their synthetic (±)-**9** was evaluated to be highly bioactive, so the germacrone **9** was proposed to be the genuine pheromone. However, this proposal was later rejected by the bioassay using pure synthetic (±)-**9**, which showed only a weak bioactivity.[11,12] Meanwhile, Hauptmann *et al.* isolated **10** from the American cockroach and showed synthetic (±)-**10** to have a high sex pheromone activity.[13] They called their pheromone (**10**) periplanone-A. The spectral data of **10** were, however, completely different from those reported for periplanone-A by Persoons *et al.* Therefore, Hauptmann's periplanone-A could not be identical with Persoons's periplanone-A. Nishino *et al.* also isolated Hauptmann's periplanone-A from the American cockroach.[14] However, Persoons's periplanone-A was not reisolated by both Hauptmann *et al.* and Nishino *et al.*

From the discussion described above, two problems to be solved were pointed out: (1) the relationship between Hauptmann's periplanone-A and Persoons's periplanone-A, and (2) the structure of Persoons's periplanone-A. We thought that the key to solve the former problem should exist in the differet isolation procedures used by each of the research groups. Persoons *et al.*[2] purified periplanone-A finally by GLC, while Hauptmann *et al.*[13] and Nishino *et al.*[14] did not expose their samples to such high temperatures. This made us assume Persoons's periplanone-A to be a thermal decomposition product of Hauptmann's periplanone-A. The same speculation was made also by Nishino *et al.*[14] and Hauptmann *et al.*[15] Thus, we planned to decompose Hauptmann's periplanone-A actually by GLC using the same stationary phase as that used by Persoons *et al.* The first thing we should do was therefore to secure a considerable amount of Hauptmann's periplanone-A. Our works along this line finally enabled us to give unambiguous solutions to the problems pointed out above.

Synthesis of Both the Enantiomers of Hauptmann's Periplanone-A

The relative stereochemistry of Hauptmann's periplanone-A **10** seemed to be sure through the syntheses of (±)-**10**[11,12] and (±)-**9**[10], although the spectroscopic proofs were not sufficient.[13] Its absolute configuration, however, has not been confirmed. We therefore decided to synthesize both the enantiomers of **10** and evaluate their bioactivities in order to establish the absolute configuration. Our synthetic plan is shown in Fig.1. As described in the preceding paper concerning the synthesis of (-)-periplanone-B, a separable mixture of (*Z*)-**13** and (*E*)-**13** is obtained in 8 steps from (-)-**11** *via* **12**. The anionic oxy-Cope rearrangement of (*Z*)-**13** has been

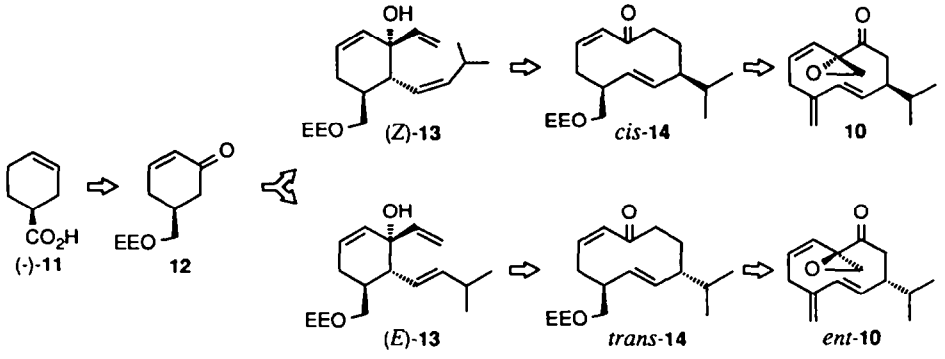
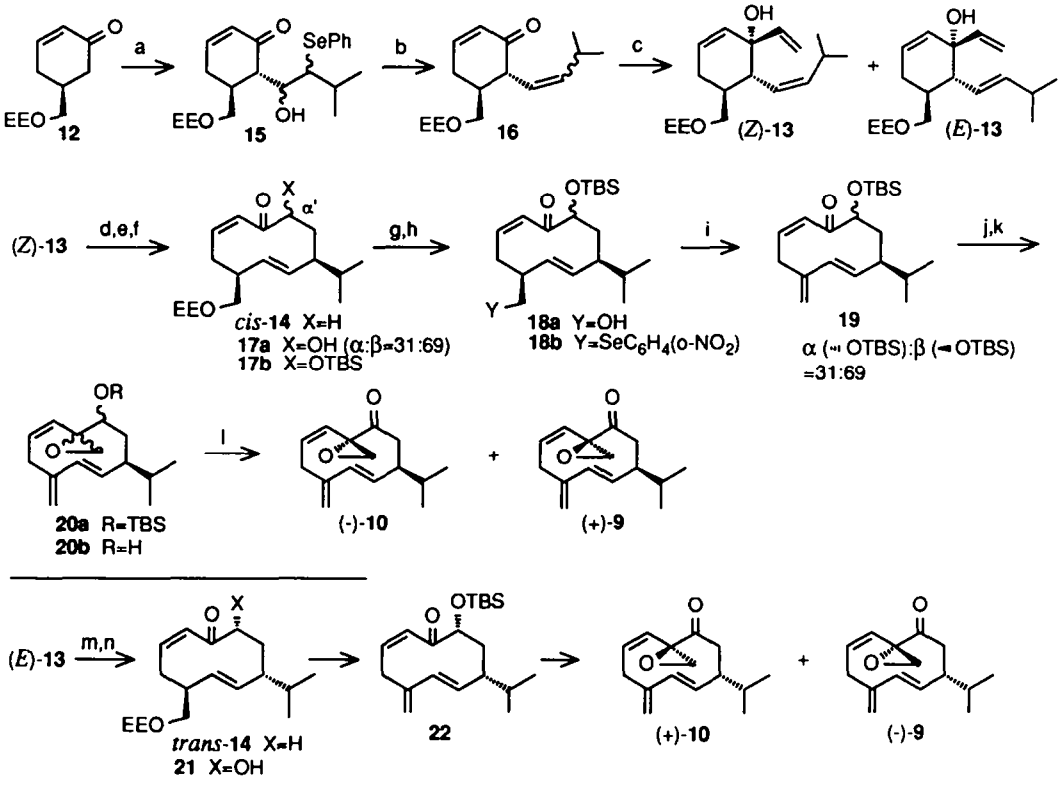


Fig. 1. Synthetic plan for Hauptmann's periplanone-A and its enantiomer.

shown to give *cis*-**14**,[5] while (*E*)-**13** should be converted into *trans*-**14**. These two diastereomeric enones, *cis*-**14** and *trans*-**14**, seemed to be convertible into the target molecules, **10** and its antipode *ent*-**10**, respectively.

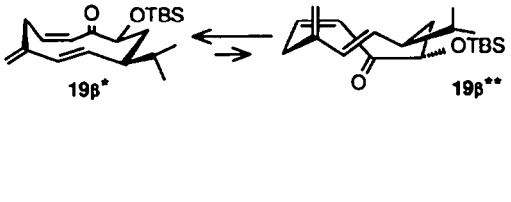
Our synthetic scheme is shown in Fig.2. The lithium enolate of **12** generated by LDA in THF was subjected to the aldol reaction with α-phenylselenoisovaleraldehyde[5] to give **15** as a diastereomeric mixture in 96% yield. Stereospecific elimination of PhSeOH from the aldol **15** by Reich's method[16] gave **16** as a mixture of geometrical isomers. GLC analysis of the mixture revealed that the ratio of (*Z*)-**16** to (*E*)-**16** was 62:38. Addition of vinyllithium to **16** gave (*Z*)-**13** and (*E*)-**13** in 42% and 27% isolated yield from **15**, respectively. The former was converted into *cis*-**14** by treatment with KH, while the latter yielded *trans*-**14**. In the case of *cis*-**14**, the corresponding lithium enolate was unstable. However, its potassium enolate was quite stable and could be trapped with TMSCl. Oxidation of the resulting TMS enol ether with *m*CPBA followed by treatment with $(n\text{-Bu})_4$NF yielded **17a** as a mixture of α'-epimers. The ratio of the α-alcohol to the β-alcohol was 31:69



Reagents: a) LDA, α-phenylselenoisovaleraldehyde, THF, -78°C (96%); b) MsCl, Et_3N, CH_2Cl_2; c) vinyllithium, ether (42% and 27% in two steps); d) KH, 18-crown-6, DME (86%); e) i) $KN(TMS)_2$, TMSCl, THF; ii) mCPBA, n-hexane-CH_2Cl_2; iii) $(n\text{-Bu})_4$NF, THF; f) TBSCl, imidazole, DMF (75% in four steps); g) PPTS, EtOH; h) o-$(NO_2)C_6H_4SeCN$, $(n\text{-Bu})_3P$, THF; i) H_2O_2 aq, THF (68% in three steps); j) ICH_2Cl, MeLi, ether; k) $(n\text{-Bu})_4$NF, THF; l) CrO_3·2Py, CH_2Cl_2 (38% and 33% in three steps); m) KH, 18-crown-6, THF (80%); n) $LiN(TMS)_2$, MoOPH, THF (86%).

Fig. 2. Synthesis of Hauptmann's periplanone-A and its stereoisomers.

as determined by 300MHz ^{1}H NMR. Although the alcohols were separable by SiO_2 column chromatography, they proved to be rather unstable toward both SiO_2 and Al_2O_3. Therefore the alcohols **17a** were used for the next step without separation. Treatment of the corresponding TBS ether **17b** with PPTS in EtOH was followed by a conventional organoselenium method to give **19** *via* **18a** and **18b**. During these three steps, the ratio (α:β=31:69) was maintained. In contrast to *cis*-**14**, *trans*-**14** derived from(*E*)-**13** could be oxidized directly by treating the corresponding lithium enolate with MoO_5·HMPA·Py to give **21** as a single stereoisomer. The alcohol **21** was converted into **22** in the same manner as described for **17a**. The mixture of alcohols, **19α** and **19β**, was treated successively with $LiCH_2Cl$,[17] $(n\text{-}Bu)_4NF$, and CrO_3·2Py to yield (-)-**10** (as needles, m.p. 42-44°C; 38% from **19**) and (+)-**9** (33% from **19**) *via* **20a** and **20b**.[18] The same treatment of **22**, the enantiomer of **19β**, gave (+)-**10** and (-)-**9** in 23% and 45% yield, respectively. These stereoselectivities were contrary to our expectation. The *cis*-substituted ten-membered ring enone (±)-**19β** had been shown in Still's synthesis of (±)-periplanone-B[4a] to have the preferred conformation as depicted in **19β***. Therefore, we thought that the



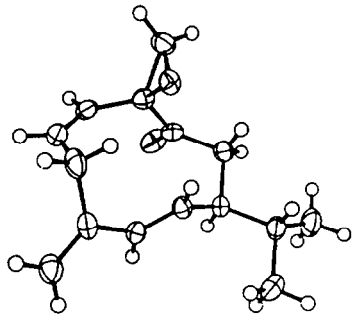


Fig. 3. X-ray structure of (-)-**10**.

peripheral insertion of methylene group to the carbonyl group should give an epoxide with desired relative configuration for **10** as the major epimer. Of course, the enantiomeric enone **22** should have afforded (+)-**10** predominantly. The results obtained above seem to suggest that the peripheral attack of chloromethyl anion to the major conformer **19β*** was retarded by the pseudoequatorial TBSO-group, resulting in the preferential reaction *via* the minor but less hindered conformer **19β****. In addition, from the comparison of the ratios of (-)-**10** to (+)-**9** and (+)-**10** to (-)-**9**, the stereoselectivity of the conversion of **19α** into (-)-**10** was estimated to be quite high. In order to confirm the stereochemistry of (-)-**10**, its X-ray crystallographic analysis was carried out.[19] As shown by the ORTEP drawing (Fig.3), the relative structure proposed by Hauptmann *et al.*[13] was confirmed to be correct. Bioactivity of our synthetic samples was evaluated by observing the wing-raising behavior of the male American cockroaches.[20] The levorotatory enantiomer of Hauptmann's periplanone-A (-)-**10** showed the activity at 10^{-5} μg, while (+)-**10** was 1,000 times less active than (-)-**10**. Therefore, the naturally occurring enantiomer of Hauptmann's periplanone-A was shown to be (-)-**10**. The low bioactivity of (+)-**10** seems to be ascribable to the contamination of a minute amount of (-)-**10**, which was brought about by the incomplete separation of (*Z*)-**13** and (*E*)-**13**. Macdonald's epoxy ketone (+)-**9**[10] was active at 10^{-1} μg. We have recently reported another synthesis of (-)-**10** starting from (+)-**11**.[21] The present synthesis described above was somewhat better than the previous synthesis in stereoselectivity. By these syntheses, about 250 mg of (-)-**10** was secured.

Clarification of the Structure of Persoons's Periplanone-A and Its Relationship to Hauptmann's Periplanone-A

According to our speculation that Persoons's periplanone-A was a thermal decomposition product of Hauptmann's periplanone-A, we first tried the GC-MS analysis of (-)-**10** at 180°C using a short column (1m x 3mm) packed with 3% OV-17.[22] The gas chromatogram showed mainly two peaks (Fig.4a). Although the mass spectrum of the major peak **A** was that of Hauptmann's periplanone-A itself, the minor peak **B** gave the mass spectrum (Fig.4b) which was very similar to that published for Persoons's periplanone-A.[2a] In order to isolate the decomposition product, the thermolysis of a total amount of 80 mg of (-)-**10** was carried out at a

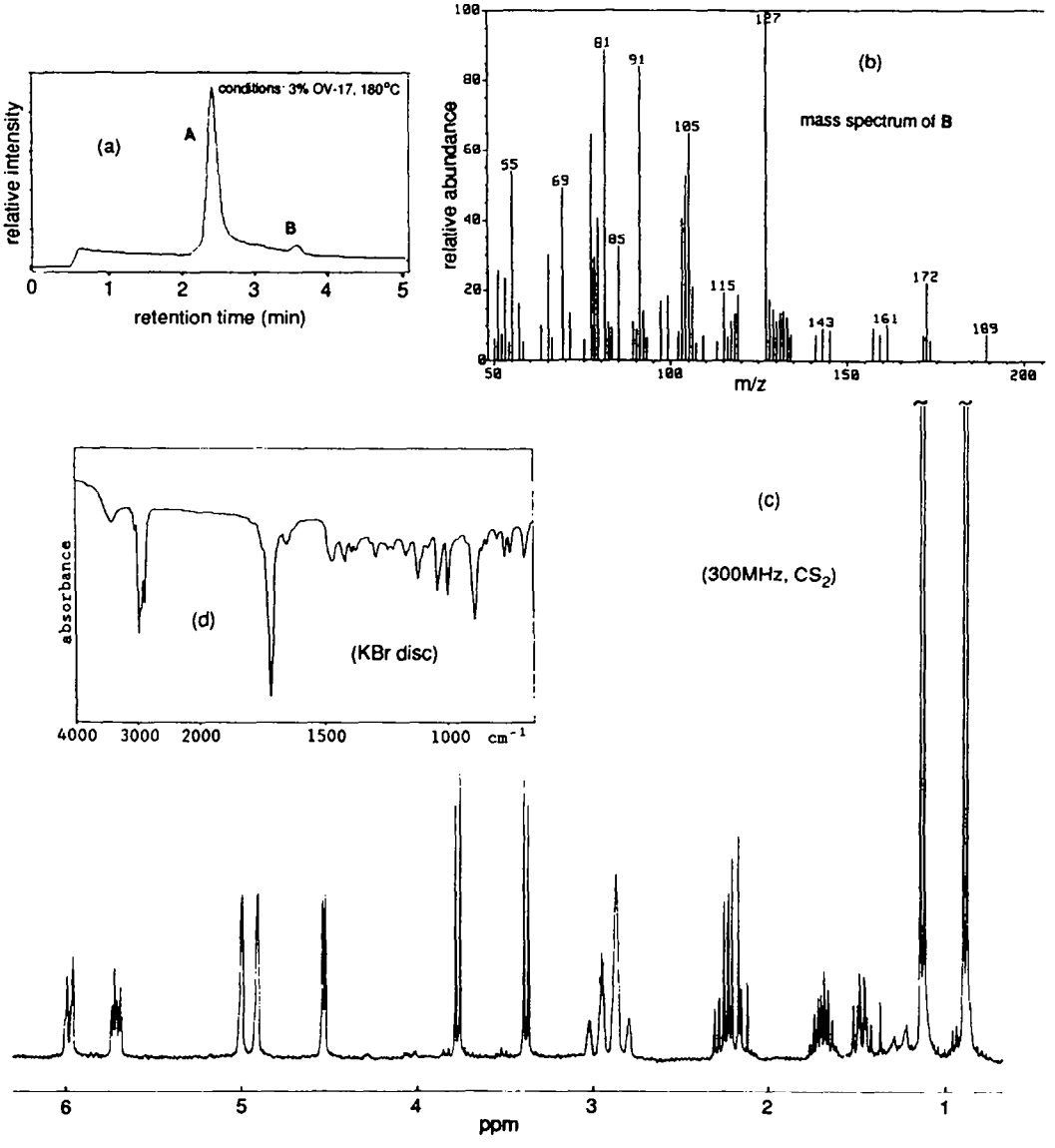


Fig. 4. (a) GLC analysis of (-)-**10** and (b) Mass, (c) ^{1}H NMR and (d) IR spectra of the thermal decomposition product of (-)-**10**.

higher temperature (220°C) using a preparative GLC column (3% OV-17, 2m X 6mm). Under these conditions, the decomposition was achieved quite efficiently. After TLC purification, the major decomposition product was isolated in 71% yield. Its ^{1}H NMR spectrum (Fig.4c) was identical with that published for Persoons's periplanone-A,[2] although Persoons's sample was contaminated with PA 22-VII (**23**), the stable rearrangement product of Persoons's periplanone-A.[2,23] Furthermore, its IR spectrum (Fig.4d) was exactly the same as that published for Persoons's periplanone-A.[24] Therefore, the major product obtained by the thermolysis of Hauptmann's periplanone-A (-)-**10** must surely be Persoons's periplanone-A.

The next task was the structure elucidation of Persoons's periplanone-A obtained above. In order to determine the structure unambiguously, we wanted to prepare a crystalline derivative of Persoons's periplanone-A and carry out its X-ray crystallographic analysis. Fortunately, Persoons's periplanone-A gave a crystalline alcohol (m.p. 77-78°C) in 80% yield on reduction with $NaBH_4$ in MeOH. Its X-ray structure is shown in Fig.5. Thus, the structure of the alcohol was established as **24**.[25] The Swern oxidation of the alcohol **24** regenerated Persoons's periplanone-A. Accordingly, Persoons's periplanone-A was determined to have the structure **6** (Fig.6), which was also supported by detailed ^{1}H NMR analyses of **6** and **24**.[25] As mentioned before, Shizuri *et al.*[8] proposed **6** for the structure of Persoons's periplanone-A from the reexamination of the spectral data presented by Persoons *et al.*, and recently claimed the synthesis of (±)-**6**, of which ^{1}H NMR spectrum was, however, different from that reported for Persoons's periplanone-A. Our unambiguous result implies that the compound synthesized by them was not (±)-**6**, although their structural proposal was correct.

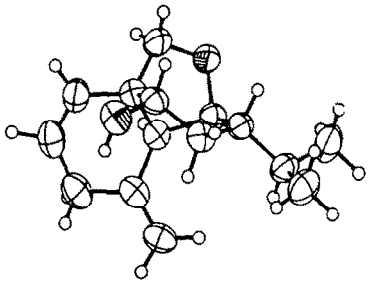


Fig. 5. X-ray structure of **24**.

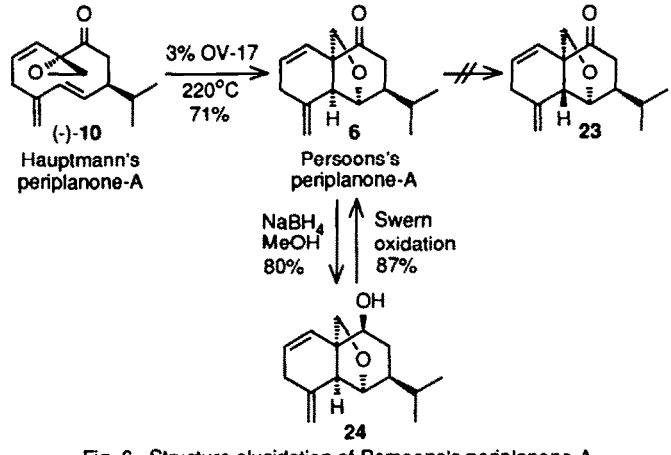


Fig. 6. Structure elucidation of Persoons's periplanone-A

To complete our study on Persoons's periplanone-A **6**, we examined its pheromone activity.[20] Persoons's periplanone-A obtained by TLC purification of the crude thermolysis product was bioactive at 10^{-3} μg. However, pure **6** obtained by the Swern oxidation of pure crystalline **24** was inactive even at 10 μg. The bioactivity of **6** observed by Persoons *et al.* therefore seems to be ascribable to the contamination of a minute amount of the highly active pheromone(s), periplanone-B and/or Hauptmann's periplanone-A. As to the stability of **6**, it was quite stable contrary to Persoons's observstion that **6** was unstable (half-life, 2 weeks at 0°C) and gradually changed into PA 22-VII (**23**).[2] Some unknown impurities contained in their sample must have accelerated this conversion.

Conclusion

We could establish the structure of Hauptmann's periplanone-A unambiguously to be (-)-**10** by the synthesis of both the enantiomers of **10** and their bioassays, coupled with the X-ray crystallographic analysis of (-)-**10**. Persoons's periplanone-A was a biologically inactive artifact derived from Hauptmann's periplanone-A (-)-**10**.[26] The structure of Persoons's periplanone-A **6** was determined unambiguously through the X-ray crystallographic analysis of the corresponding alcohol **24**. A lesson learned through whole of the works related to Persoons's periplanone-A is that one should employ as mild conditions as possible in isolating an unstable and extremely bioactive compound to avoid possible decomposition. Production of an artifact may demand tremendous amount of rewardless efforts by others to restore the proper order out of the chaos. It should be added that our study as described here necessitated the revision of the nomenclature of the American cockroach pheromones, and Persoons's periplanone-A is now called isoperiplanone-A.[27]

EXPERIMENTAL

All m.ps were not corrected. IR spectra were measured as films for oils or as KBr discs for solids on a Jasco IRA-102 spectrometer. ^{1}H NMR spectra were measured with TMS as an internal standard at 100MHz in $CDCl_3$ on a JEOL JNM FX-100 spectrometer unless otherwise stated. Optical rotations were measured on a Jasco DIP 140 polarimeter. Mass spectra were recorded at 70eV on a JEOL DX-303 spectrometer. GLC analyses and thermolysis were performed on a Yanaco G-180 gas chromatograph. Merck Kieselgel 60 Art. 7734 was used for SiO_2 column chromatography.

(5S,6S,1'RS,2'RS)-5-[(1-Ethoxyethoxy)methyl]-6-(1'-hydroxy-3'-methyl-2'-phenylselenobutyl)-2-cyclohexen-1-one **15**. In the same manner as described for **14b** in the preceding paper exept that the reaction mixture was quenched with AcOH (1.5 ml) at -78°C without raising the reaction temp, **12** (4.10 g) yielded 8.69 g (96%) of **15**.

(5S,6R)-5-[(1-Ethoxyethoxy)methyl]-6-(3'-methyl-1'-butenyl)-2-cyclohexen-1-one **16**. In the same manner as described for **7b** in the preceding paper, **15** (8.50 g) gave 5.21 g (quant) of **16**, GLC (Column, 5% FFAP, 2m x 3mm at 100°C +3°C/min; Carrier gas, N_2, 0.85kg/cm^2) Rt 30.4min [62%, (*Z*)-isomer], 31.5min [38%, (*E*)-isomer]. This was employed for the next step without further purification.

(1S,5S,6R,1'Z)- and (1S,5S,6R,1'E)-5-[(1-Ethoxyethoxy)methyl]-6-(3'-methyl-1'-butenyl)-1-vinyl-2-cyclohexen-1-ol (*Z*)-**13** and (*E*)-**13**. In the same manner as described for **6a** in the preceding paper, **16** (5.06 g) yielded 2.35 g (42% from **15**) of (*Z*)-**13** and 1.51 g (27% from **15**) of (*E*)-**13** after SiO_2 column chromatography (Merck Kieselgel 60 Art. 9385, *n*-hexane-ether). The physical properties of (*Z*)-**13** were identical with those described in the preceding paper. The minor isomer (*E*)-**13** showed the following properties: n_D^{23} 1.4756; $[\alpha]_D^{23}$ +147° (c=1.06, *n*-hexane); ν_{max} 3475 (m), 3090 (w), 3030 (m), 2970 (s), 2910 (s), 2875 (s), 1655 (w), 1630 (w), 1460 (m), 1380 (m), 1335 (m), 1130 (s), 1100 (s), 1055 (s), 975 (s), 925 (s), 880 (m), 735 (m), 720 (m) cm^{-1}; δ 1.01 (6H, d, J=7.0Hz), 1.20 (3H, t, J=7.0Hz), 1.27 (3H, d, J=5.5Hz), 1.59 (1H, s, OH), 1.70-2.50 (5H, m), 3.05-3.80 (4H, m), 4.50-4.75 (1H, m), 5.10 (1H, dd, J=7.6, 16.0Hz), 5.12 (1H, dd, J=1.8, 10.1Hz), 5.15 (1H, dd, J=1.8, 17.7Hz), 5.48 (1H, br.d, J=10.0Hz), 5.57 (1H, dd, J=6.4, 16.0Hz), 5.79 (1H, dt, J=10.0, 3.1Hz), 5.89 (1H, dd, J=10.1, 17.7Hz). (Found: m/z 294.2267. Calc for $C_{18}H_{30}O_3$: 294.2195).

(2Z,5S,6E,8R)-5-[(1-Ethoxyethoxy)methyl]-8-isopropyl-2,6-cyclodecadien-1-one trans-**14**. KH (20% in mineral oil, 8.5 g) was washed three times with *n*-pentane under Ar and suspended in dry THF (35 ml). To the stirred mixture was added dropwise a soln of (*E*)-**13** (2.34 g) in dry THF (45 ml). After the addition, 18-crown-6 (10.9 g) was added in a single portion and the stirring was continued for 1h at room temp. The mixture was cooled to -78°C and diluted with *n*-hexane (50 ml). MeOH (1.7 ml) was added dropwise to the vigorously stirred mixture. The mixture was diluted with sat NH_4Cl aq and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (120 g, *n*-hexane-ether) to give 1.87 g (80%) of *trans*-**14**, n_D^{21} 1.4866; $[\alpha]_D^{16}$ +50.6° (c=1.37, *n*-hexane); ν_{max} 2970 (s), 2880 (s), 1685 (s), 1620 (m), 1450 (m), 1400 (m), 1380 (m), 1340 (m), 1210 (m), 1135 (s), 1095 (s), 1060 (s), 980 (m), 930 (m), 840 (m), 740 (m), 680 (m) cm^{-1}; δ 0.85 (3H, d, J=6.5Hz), 0.89 (3H, d, J=6.5Hz), 1.20 (3H, t, J=7.5Hz), 1.30 (3H, d, J=5.5Hz), 1.35-1.90 (4H, m), 1.90-2.70 (5H, m), 3.20-3.85 (4H, m), 4.50-5.25 (3H, m), 5.77 (1H, dt, J=12.0, 8.1Hz), 6.32 (1H, d, J=12.0Hz). (Found: m/z 294.2155. Calc for $C_{18}H_{30}O_3$: 294.2195).

(2Z,5S,6E,8S)-10-t-Butyldimethylsilyloxy-5-[(1-ethoxyethoxy)methyl]-8-isopropyl-2,6-cyclodecadien-1-one **17b**. KH (35% in mineral oil, 0.17 g) was washed three times with *n*-pentane under Ar and suspended in dry THF (40 ml). To the mixture was added $HN(TMS)_2$ (0.33 ml) at room temp. After stirring for 70min, a soln of *cis*-**14**[5] (0.255 g) in dry THF (5 ml) was added dropwise to the mixture at -78°C. The mixture was stirred for 1h. TMSCl (0.26 ml) was then added to the mixture and the stirring was continued for 20min at -78°C. The reaction mixture was diluted with *n*-hexane (20 ml) and washed with sat $NaHCO_3$ aq. To the *n*-hexane soln were added $NaHCO_3$ (1 g) and a soln of *m*CPBA (0.4 g) in CH_2Cl_2 (5 ml) under ice-cooling. After stirring for 10min, the reaction mixture was quenched by the addition of sat Na_2SO_3 aq and extracted with ether. The extract was washed with sat $NaHCO_3$ aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in THF (3 ml) and (n-Bu)$_4$NF (1M in THF, 3

ml) was added to the soln. After stirring for 10min, the mixture was diluted with ether and washed with brine. The ether soln was dried ($MgSO_4$) and concentrated *in vacuo* to give 0.450 g of crude **17a**, which was then dissolved in DMF (2.5 ml). To the soln were added imidazole (0.3 g) and TBSCl (0.4 g). The mixture was stirred overnight at room temp, diluted with sat $NaHCO_3$ aq and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (25 g, *n*-hexane-ether) to give 0.275 g (75% from *cis*-**14**) of **17b** as a mixture of epimers, n_D^{25} 1.4575; $[\alpha]_D^{25}$ +50.3° (c=1.48, *n*-hexane); TLC (Merck Kieselgel 60 Art. 5715, *n*-hexane-ether=2:1) Rf 0.54 (major) and 0.47 (minor); ν_{max} 2960 (s), 2930 (s), 2860 (m), 1685 (m), 1610 (m), 1460 (m), 1380 (m), 1250 (m), 1130 (s), 1080 (s), 850 (s), 835 (s), 775 (s) cm^{-1}. A portion of the epimeric mixture was separated by SiO_2 column chromatography to give β-epimer (major) and α-epimer (minor), which showed the following ^1H NMR spectra: δ(β-epimer) 0.03 (3H, s), 0.07 (3H, s), 0.70-0.95 (15H), 1.21 (3H, t, J=7.2Hz), 1.30 (3H, d, J=4.9Hz), 1.35-1.95 (3H, m), 2.30-3.00 (4H, m), 3.15-3.75 (4H, m), 3.80-4.05 (1H, m), 4.50-4.90 (1H, m), 4.67 (1H, q, J=5.4Hz), 5.06 (1H, dd, J=5.2, 16.7Hz), 5.65-6.05 (1H, m), 6.60 (1H, d, J=12.1Hz); δ(α-epimer) 0.10 (6H, br.s), 0.75-1.00 (15H), 1.20 (3H, t, J=7.2Hz), 1.29 (3H, d, J=5.2Hz), 1.35-1.65 (1H, m), 1.80-2.70 (6H, m), 3.20-3.80 (4H, m), 4.17 (1H, d, J=5.9Hz), 4.67 (1H, q, J=5.2Hz), 4.75-5.50 (2H, br), 5.82 (1H, dt, J=12.1, 8.3Hz), 6.50 (1H, d, J=12.1Hz). The ratio of α-epimer to β-epimer was determined to be 31:69 by comparing (300MHz, ^1H NMR) the intensities of the peaks (δ 4.17 and 3.80-4.05) due to -CH(OTBS)- of **17b**. The stereochemical assignment was confirmed by converting the β-epimer into the known compound **19β**.[4c] (Found: m/z 424.2934. Calc for $C_{24}H_{44}O_4Si$: 424.3009).

(2Z,6E,8S)-10-t-Butyldimethylsilyloxy-8-isopropyl-5-methylene-2,6-cyclodecadien-1-one **19**. A mixture of **17b** (0.198 g) and PPTS (0.021 g) in EtOH (4 ml) was stirred for 4.5h at 60°C. The mixture was poured into sat $NaHCO_3$ aq and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 0.159 g of crude **18a**, ν_{max} 3400 (m), 2950 (s), 2930 (s), 2860 (m), 1680 (m), 1610 (m), 1460 (m), 1250 (m), 1070 (s), 980 (m), 835 (s), 775 (m) cm^{-1}. The alcohol **18a** was dissolved in THF (3.5 ml). To the soln were added *o*-$(NO_2)C_6H_4SeCN$ (0.16 g) and $(n\text{-}Bu)_3P$ (0.175 ml). After stirring for 50min, the mixture was diluted with water and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 0.36 g of crude **18b**. The selenide **18b** was dissolved in THF (10 ml) and 35% H_2O_2 (1 ml) was added to the soln. After stirring for 1h, $NaHCO_3$ (0.5 g) was added to the mixture and the stirring was continued for 16h. The mixture was diluted with water and extracted with ether. The extract was washed with sat $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (20 g, *n*-hexane-ether) to give 0.106 g (68% from **17b**) of **19** as an epimeric mixture, n_D^{22} 1.4856; $[\alpha]_D^{22}$ -8.0° (c=1.21, *n*-hexane); ν_{max} 3080 (w), 3020 (w), 2960 (s), 2940 (s), 2860 (m), 1690 (s), 1605 (m), 1460 (m), 1385 (m), 1250 (m), 1075 (s), 975 (m), 835 (s), 775 (s) cm^{-1}; TLC (Merck Kieselgel 60 Art. 5715, *n*-hexane-ether=10:1) Rf 0.46 (major) and 0.34 (minor). A small portion of the epimeric mixture was separated by preparative TLC (Merck Kieselgel 60 Art. 5744, *n*-hexane-ether) to give **19α** and **19β**, which showed the following ^1H NMR spectra: δ(the major epimer **19β**) 0.06 (3H, s), 0.08 (3H, s), 0.70-0.95 (6H), 0.89 (9H, s), 1.35-2.10 (4H, m), 3.14 (2H, d, J=8.2Hz), 4.01 (1H, dd, J=5.0, 9.6Hz), 4.74-4.81 (1H, m), 4.88-4.96 (1H, m), 5.02 (1H, dd, J=9.1, 16.1Hz), 5.56 (1H, d, J=16.1Hz), 5.81 (1H, dt, J=11.9, 8.2Hz), 6.38 (1H, br.d, J=11.9Hz); δ(the minor epimer **19α**) 0.09 (6H, s), 0.75-0.96 (6H), 0.94 (9H, s), 1.30-1.70 (1H, m), 1.80-2.40 (3H, m), 2.68 (1H, dd, J=7.0, 11.7Hz), 3.48 (1H, dd, J=10.2, 11.7Hz), 4.19 (1H, d, J=6.3Hz), 4.76 (1H, br.s), 4.95 (1H, br.s), 5.07 (1H, dd, J=9.2, 16.0Hz), 5.69 (1H, ddd, J=7.0, 10.2, 11.9Hz), 5.79 (1H, d, J=16.0Hz), 6.26 (1H, d, J=11.9Hz). The ratio of **19α** to **19β** was determined to be 31:69 in the same manner as described for **17b**. The ^1H NMR spectrum of **19β** measured in CCl_4 was identical with that reported for (±)-**19β** by Still.[4c] (Found: m/z 334.2259. Calc for $C_{20}H_{34}O_2Si$: 334.2329).

(2Z,5S,6E,8R,10R)-5-[(1-Ethoxyethoxy)methyl]-10-hydroxy-8-isopropyl-2,6-cyclod ecadien-1-one **21**. A soln of $LiN(TMS)_2$ in THF was prepared by the addition of *n*-BuLi (1.49N in *n*-hexane, 1.3 ml) to a soln of $HN(TMS)_2$ (0.43 ml) in dry THF (4.3 ml). To this soln was added dropwise a soln of *trans*-**14** (0.470 g) in THF (4.7 ml) over a period of 30min at -78°C. After stirring for 30min, the reaction temp was raised to -20°C. To the soln was added MoO_5·HMPA·Py (1.41 g) in a single portion and the stirring was continued for 1h. The mixture was quenched with 10% Na_2SO_3 aq (7 ml) and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (20 g, *n*-hexane-ether) to give 0.367 g (74%) of **21** and 0.065 g of recovered *trans*-**14**. The product **21** showed the following physical properties: n_D^{22} 1.4820; $[\alpha]_D^{16}$ +6.1° (c=1.60, *n*-hexane); ν_{max} 3420 (m), 2990 (s), 2940 (s), 2890 (s), 1690 (s), 1615 (m), 1450 (m), 1400 (m), 1380 (m), 1130 (s), 1100 (s), 1050 (s), 980 (m), 930 (m), 780 (m) cm^{-1}; δ 0.83 (3H, d, J=6.5Hz), 0.86 (3H, d, J=6.5Hz), 1.18 (1.5H, t, J=7.2Hz), 1.19 (1.5H, t, J=7.2Hz), 1.28 (3H, d, J=5.3Hz), 1.35-2.30 (5H, m), 2.30-2.75 (2H, m), 3.09 (1H, d, J=4.5Hz, OH), 3.20-3.80 (4H, m), 3.80-4.10 (1H, m), 4.50-5.15 (3H, m), 5.92 (1H, dt, J=11.9, 8.7Hz), 6.61 (1H, d, J=11.9Hz). (Found: m/z 310.2072. Calc for $C_{18}H_{30}O_4$: 310.2144).

(2Z,6E,8R,10R)-10-t-Butyldimethylsilyloxy-8-isopropyl-5-methylene-2,6-cyclodecadien-1-one **22**. To a mixture of **21** (0.350 g) and imidazole (0.20 g) in DMF (2.5 ml) was added TBSCl (0.33 g). After stirring overnight, the mixture was diluted with sat $NaHCO_3$ aq and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 0.571 g of the corresponding TBS ether, ν_{max} 2980 (s), 2950 (s), 2880 (s), 1690 (m), 1610 (w), 1460 (m), 1380 (m), 1250 (s), 1130 (s), 1080 (s), 980 (m), 840 (s), 775 (s) cm^{-1}. This TBS ether was dissolved in EtOH (10 ml) and PPTS (0.06 g) was added to the soln. After stirring for 1.5h at 60°C, the mixture was diluted with sat $NaHCO_3$ aq and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to give an alcohol (0.387 g), ν_{max} 3450 (m), 3050 (w), 2990 (s), 2960 (s), 2890 (s), 1695 (s), 1615 (m), 1465 (m), 1405 (m), 1255 (s), 1180 (s), 980 (m), 850 (s), 840 (s), 780 (s) cm^{-1}. This alcohol was dissolved in THF (9 ml). To the soln were added *o*-$(NO_2)C_6H_4SeCN$ (0.52 g) and $(n\text{-}Bu)_3P$ (0.57 ml). After stirring for 50min, the mixture was diluted with water and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was triturated with ether. The ether soln was concentrated *in vacuo* to give the corresponding selenide (1.22 g). This selenide was dissolved in THF (25 ml) and 35% H_2O_2 aq (2.5 ml) was added to the soln. After stirring for 45min, $NaHCO_3$ (1.5 g) was added to the mixture and the stirring was continued overnight. The mixture was diluted with water and extracted with ether. The extract was washed with sat $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (30 g, *n*-hexane-ether) to give 0.246 g (65% from **21**) of **22**, n_D^{21} 1.4860; $[\alpha]_D^{24}$ -85.7° (c=1.12, *n*-hexane). (Found: m/z 334.2327. Calc for $C_{20}H_{34}O_2Si$: 334.2328). The IR and ^1H NMR spectra were

identical with those of **19β**.

(2R,3Z,7E,9S)- and (2S,3Z,7E,9S)-2,2-Epoxymethano-9-isopropyl-6-methylene-3,7-cyclodecadien-1-one (-)-**10** and (+)-**9**. To a stirred soln of **19** (α:β=31:69, 0.101 g) and ICH_2Cl (0.088 ml) in dry ether (2 ml) was added dropwise a soln of MeLi (1.10N in ether, 1.1 ml) at -78°C. After stirring for 5min, the cooling bath was removed and the stirring was continued for 1h. The mixture was diluted with *n*-hexane and washed with water and brine. The *n*-hexane soln was dried (Na_2SO_4) and concentrated *in vacuo* to give **20a** as an oil, which was dissolved in THF (0.4 ml). To the soln was added $(n\text{-}Bu)_4NF$ (1M in THF, 0.9 ml). After stirring for 15min, the mixture was diluted with ether. The mixture was washed with water and brine, dried (Na_2SO_4) and concentrated *in vacuo* to give **20b** as an oil. The Collins reagent was prepared by the addition of CrO_3 (0.42 g) to a soln of Py (0.67 g) in dry CH_2Cl_2 (6.7 ml) followed by stirring for 1h. To the mixture was added a soln of the oil **20b** in CH_2Cl_2 (2 ml). After stirring for 50min, the mixture was diluted with ether and filtered through a Celite pad. The filtrate was concentrated *in vacuo* to give a mixture of (-)-**10** and (+)-**9**. These epimers were separated by preparative TLC (Merck Kieselgel 60 Art. 5744, *n*-hexane-ether) to give 26.4 mg (38% from **19**) of (-)-**10** as crystals and 22.9 mg (33% from **19**) of (+)-**9** as an oil. The major epimer (-)-**10** was recrystallized from *n*-hexane to give pure (-)-**10** as needles, m.p. 42-44°C; $[\alpha]_D^{24}$ -574° (c=0.103, *n*-hexane); TLC (Merck Kieselgel 60 Art. 5715, *n*-hexane=2:1) Rf 0.45; ν_{max} 3100 (w), 3040 (w), 2980 (s), 2950 (sh), 2890 (m), 1705 (vs), 1650 (w), 1615 (m), 1470 (m), 1430 (w), 1385 (m), 1370 (m), 1310 (m), 1275 (m), 1165 (w), 1120 (m), 1190 (w), 1040 (m), 1020 (m), 980 (s), 945 (w), 905 (s), 895 (s), 850 (m), 820 (w), 750 (m), 735 (s), 720 (m) cm^{-1}; δ (500MHz, $CDCl_3$) 0.90 (3H, d, J=6.8Hz), 0.92 (3H, d, J=6.8Hz), 1.59-1.69 (1H, m), 2.09 (1H, dd, J=5.5, 9.6Hz), 2.11-2.18 (1H, m), 2.59 (1H, dd, J=7.3, 11.7Hz), 2.68 (1H, dd, J=9.6, 11.0Hz), 2.85 (1H, d, J=5.3Hz), 2.88 (1H, d, J=5.3Hz), 3.76 (1H, br.dd, J=9.8, 11.7Hz), 4.77-4.79 (1H, m), 4.94-4.96 (1H, m), 5.66 (1H, ddd, J=7.3, 9.8, 11.3Hz), 5.97 (1H, dd, J=1.0, 11.3Hz), 5.98 (1H, br.d, J=16.0Hz), 6.09 (1H, dd, J=10.5, 16.0Hz); MS: m/z 232 (M^+), 202, 189, 172, 159, 145, 131, 127, 117, 115, 105, 104, 91 (100%), 81, 77, 69, 65, 55. (Found: C, 77.29; H, 8.78. Calc for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%). The minor epimer (+)-**9** showed the following physical properties: n_D^{20} 1.5194; $[\alpha]_D^{25}$ +182° (c=0.206, *n*-hexane); TLC (the same conditions as described for (-)-**10**) Rf 0.40; ν_{max} 3090 (w), 3040 (w), 2980 (s), 2950 (sh), 2890 (s), 1705 (vs), 1640 (w), 1615 (w), 1465 (m), 1390 (m), 1370 (m), 1320 (m), 1260 (m), 1160 (w), 1120 (m), 1060 (m), 1040 (m), 1020 (m), 970 (m), 945 (m), 890 (s), 850 (m), 800 (m), 735 (s) cm^{-1}; δ (300 MHz, $CDCl_3$) 0.91 (3H, d, J=6.7Hz), 0.96 (1H, d, J=6.7Hz), 1.63-1.73 (1H, m), 2.23-2.31 (1H, m), 2.50 (1H, dd, J=8.3, 10.9Hz), 2.56 (1H, dd, J=5.6, 10.9Hz), 2.887 (1H, d, J=6.0Hz), 2.893 (1H, d, J=8.1, 12.4Hz), 3.08 (1H, d, J=6.0Hz), 3.14 (1H, dd, J=8.8, 12.4Hz), 4.81 (1H, t, J=~1.5Hz), 4.94 (1H, s), 5.62 (1H, dd, J=9.1, 16.2Hz), 5.67 (1H, ddd, J=8.1, 8.8, 11.2Hz), 5.86 (1H, d, J=16.2Hz), 6.00 (1H, d, J=11.2Hz). (Found: m/z 232.1456. Calc for $C_{15}H_{20}O_2$: 232.1463).

(2S,3Z,7E,9R)- and (2R,3Z,7E,9R)-2,2-Epoxymethano-9-isopropyl-6-methylene-3,7-cyclodecadien-1-one (+)-**10** and (-)-**9**. In the same manner as described for (-)-**10** and (+)-**9**, **22** (0.230g) yielded 36.0mg (23%) of (+)-**10** and 72.1mg (45%) of (-)-**9**. (+)-**10**: m.p. 42-44°C; $[\alpha]_D^{25}$ +584° (c=0.125, *n*-hexane). (Found: m/z 232.1483. Calc for $C_{15}H_{20}O_2$: 232.1463). (-)-**9**: n_D^{20} 1.5186; $[\alpha]_D^{25}$ -168° (c=0.196, *n*-hexane). (Found: m/z 232.1457. Calc for $C_{15}H_{20}O_2$: 232.1463). The IR and ^1H NMR spectra of (+)-**10** and (-)-**9** were each identical with those of the corresponding enantiomers described above.

(1R,6S,7S,8S)-8-Isopropyl-5-methylene-12-oxatricyclo[5.3.2.0^{1,6}]dodec-2-en-10-one **6**. Hauptmann's periplanone-A (-)-**10** (34.7 mg) was dissolved in acetone (300 μl). About 30 μl portions of the soln were injected into a gas chromatograph (column, 3% OV-17, 2m X 6mm at 220°C; injection, 260°C; carrier gas, N_2, 45ml/min). The effluents were bubbled into *n*-hexane cooled with Dry Ice-acetone bath. The *n*-hexane soln was concentrate *in vacuo*. Preparative TLC (Merck Kieselgel 60 Art. 5744, *n*-hexane-ether) of the residue gave 24.7 mg (71%) of **6**, $[\alpha]_D^{25}$ -290° (c=0.096, *n*-hexane); ν_{max} (KBr) 3100 (w), 3050 (w), 2980 (s), 2940 (sh), 2880 (m), 1715 (vs), 1650 (w), 1460 (w), 1415 (w), 1385 (w), 1370 (w), 1290 (w), 1240 (w), 1220 (w), 1165 (w), 1120 (m), 1040 (m), 995 (m), 890 (w), 860 (w), 765 (w), 745 (w), 690 (w) cm^{-1}; δ (300MHz, CS_2) 0.88 (3H, d, J=6.5Hz), 1.13 (3H, d, J=6.5Hz), 1.47 (1H, dt, J=7.6, 11.0Hz), 1.59-1.79 (1H, m), 2.18 (1H, dd, J=11.0, 16.0Hz), 2.25 (1H, dd, J=7.6, 16.0Hz), 2.78-2.91 (1H, m, J_1=21.6Hz), 2.87 (1H, br), 2.92-3.05 (1H, m, J_1=21.6Hz), 3.38 (1H, d, J=7.6Hz), 3.77 (1H, d, J=7.6Hz), 4.53 (1H, d, J=4.7Hz), 4.91 (1H, br), 5.00 (1H, br), 5.70 (1H, dt, J=9.7, 3.7Hz), 5.96 (1H, br.d, J=9.7Hz). (Found: m/z 232.1475. Calc for $C_{15}H_{20}O_2$:232.1463).

(1S,6S,7S,8S,10S)-8-Isopropyl-5-methylene-12-oxatricyclo[5.3.2.0^{1,6}]dodec-2-en-10-ol **24**. $NaBH_4$ (ca. 5 mg) was added to a soln of **6** (24 mg) in MeOH (1 ml) at -10°C. After stirring for 3min, the mixture was diluted with water and extracted with ether. The extract was washed with water and brine, dried (Na_2SO_4) and concentrated *in vacuo*. Preparative TLC (Merck Kieselgel 60 Art. 5744, *n*-hexane-ether) of the residue gave 19.3 mg (80%) of **24** as crystals. Recrystallization of the product from *n*-hexane-ether yielded pure **24** as needles, m.p. 77-78°C; δ (500MHz, C_6D_6) 0.88 (3H, d, J=6.5Hz), 0.98 (3H, d, J=6.5Hz), 1.41 (1H, d, J=3.8Hz, OH), 1.50-1.85 (1H, m), 1.83 (1H, dt, J=14.3, 5.8Hz), 1.97 (1H, ddd, J=5.5, 7.5, 14.3Hz), 2.04-2.12 (1H, m), 2.59 (1H, br.s), 2.66-2.72 (1H, m, J_1=21.8Hz), 2.74-2.80 (1H, m, J_1=21.8Hz), 3.38 (1H, d, J=7.5Hz), 3.48 (1H, ddd, seemingly dt, J=3.8, 5.5, 5.8Hz), 3.57 (1H, d, J=7.5Hz), 4.68 (1H, dd, J=2.4, 4.4Hz), 4.75 (1H, br.s), 4.92 (1H, br.s), 5.40 (1H, dt, J=9.7, 2.1Hz), 5.57 (1H, dt, J=9.7, 3.6Hz); ^{13}C NMR (125MHz, C_6D_6): δ 22.30, 22.50, 29.28, 29.51, 33.85, 48.48, 48.59, 50.38, 73.80, 74.61, 77.41, 108.81, 127.02, 130.41, 142.23; Crystal data: $C_{15}H_{22}O_2$, formula weight 234.34; monoclinic, $P2_1$(#4); a=12.174(2), b=6.357(2), c=8.740(2)Å, β=106.63(1)°; V=647.3(2)Å^3; Z=2; D_{calc}=1.197, D_{obs}=1.200gcm^{-3}; F_{000}=256; λ(CuKα)=1.54178Å; μ(CuKα)=5.75 cm^{-1}; No. of reflections measured, total: 974, unique: 241; R, R_W=0.025, 0.025. The details of the X-ray crystallographic analysis will be published in the near future.[25]

The Swern oxidation of 24. To a stirred soln of oxalyl chloride (30 μl) in dry CH_2Cl_2 (1.2 ml) was added DMSO (49 μl) at -50~-60°C. After stirring for 2min at -10~-15°C, a soln of **24** (13.4 mg) in dry CH_2Cl_2 (0.7 ml) was added to the mixture and the stirring was continued for 15min. The reaction mixture was then cooled to -60°C and Et_3N (0.24 ml) was added to the mixture. After stirring for 5min, the cooling bath was removed and the stirring was continued for 10min. The mixture was diluted with water and extracted with CH_2Cl_2. The extract was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. Preparative TLC (Merck Kieselgel 60 Art. 5744, *n*-hexane-ether) yielded 11.5 mg (87%) of **6**. Its

^{1}H NMR spectrum was identical with that of the sample obtained by the thermolysis of (-)-**10**.

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