Tetrahedron Letters,Vol.28,No.16,pp 1795-1798,1987   0040-4039/87 $3.00 + .00
Printed in Great Britain   Pergamon Journals Ltd.

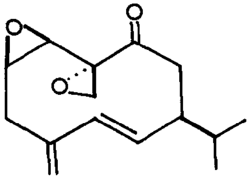
WHAT IS THE CORRECT STRUCTURE FOR PERIPLANONE A?

Yoshikazu Shizuri, Shu Yamaguchi, Yukimasa Terada,+ and Shosuke Yamamura*
Department of Chemistry, Faculty of Science and Technology, Keio University,
Hiyoshi, Yokohama, Japan
+ Faculty of Pharmacy, Meijo University, Tempaku-ku, Nagoya, Japan

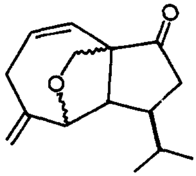
Summary: The stereostructures of periplanone A and its rearrangement product have been elucidated on the basis of molecular mechanics calculations together with ^{1}H NMR spectral data.

Two sex pheromones of the American cockroach Periplaneta americana, periplanone A and periplanone B, which have an independently biological activity, have been isolated by Persoons *et al.*[1] Of them, the stereostructure of periplanone B has been unambiguously determined as 1.[2] Furthermore, the structure (2) of periplanone A has been proposed by Persoons *et al.*, on the basis of its spectral data, particularly ^{1}H NMR spectrum, together with a plausible structure (3) of its rearrangement product.[3] Quite recently, however, Hauptmann *et al.* have reported on the isolation and structure of an epoxygermacrone (4), a common precursor of both periplanone A and periplanone B, and named it periplanone A,[4] although its spectral data are completely different from those of Persoons' periplanone A. Their publication prompted us to describe the correct structures of Persoons' periplanone A and its rearrangement product.

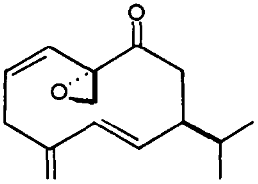
As described in the preceding paper on periplanone A, the tentative structure (2)[3] for periplanone A can not be explained by its IR and ^{1}H NMR spectral data. In the light of



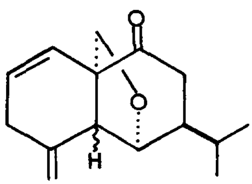
1



2

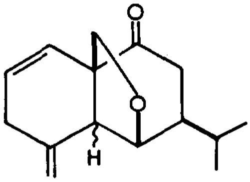


4



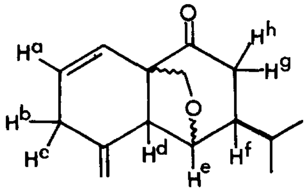
I (α-H)

III (β-H)



II (3) (β-H)

IV (α-H)



molecular mechanics calculations, therefore, we reexamined the ^1H NMR spectral data (chemical shifts and coupling constants)[3] of periplanone A and its rearrangement product, indicating that they are quite similar to each other in their structures. Clearly, the structure of periplanone A, which is quite unstable as compared with the rearrangement product, seems to be represented by one of the two possible structures [I and II (3)], while the latter must have III or IV.

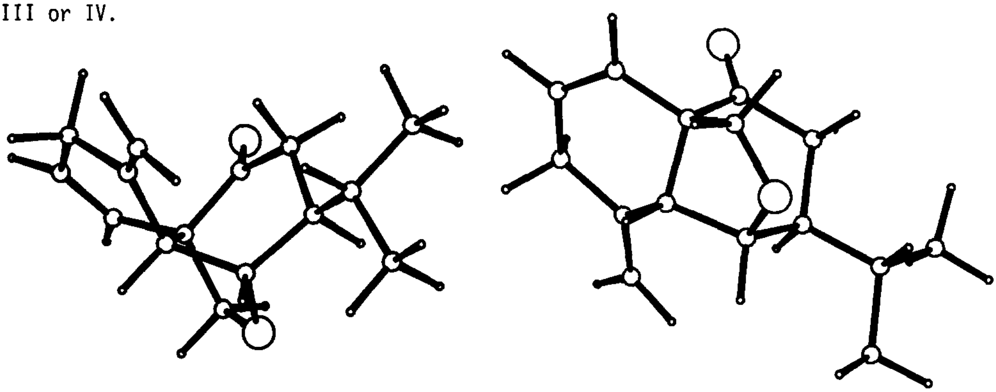


Fig. 1. I (CT: S.E., 39.1897 Kcal/mol) II (CC: S.E., 34.6895 Kcal/mol)

As judged from molecular mechanics calculations,[5] the cis decalone (I) mainly adopts two conformations [CT (S.E., 39.1897 Kcal/mol); CC (S.E., 40.8246 Kcal/mol); relative ratio at 25 °C: CT : CC = 94.1 : 5.9], of which the chair - twist boat (CT) conformer is mainly present, as seen in Fig. 1. On the other hand, II adopts only one chair - chair (CC) conformation (see Fig. 1). On the basis of these conformations, the coupling constants of I and II were calculated and cited in Table 1 together with the observed ones of periplanone A.[3]

Table 1. The observed coupling constants of periplanone A and the calculated ones of I and II

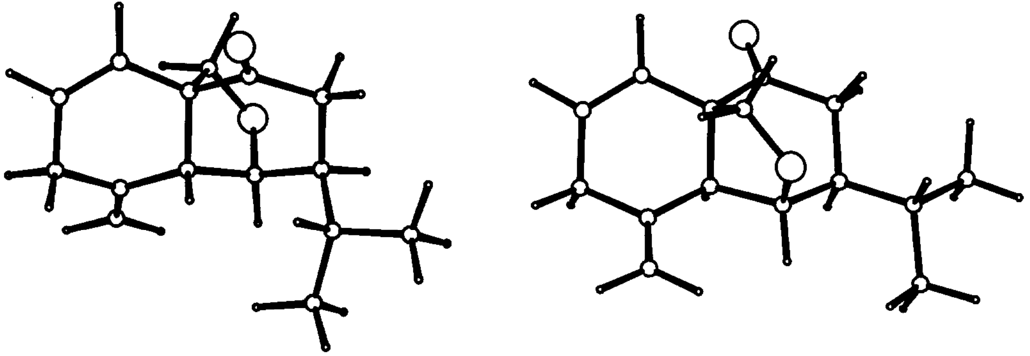
Assignment	Periplanone A (Hz)	I (Hz)*	II (Hz)*
H^a- H^b	------+	6.2 5.3	5.7 4.7
H^a- H^c	------+	2.7 1.6	3.0 2.0
H^d- H^e	ca. 4.5	5.4 4.8	5.9 5.2
H^e- H^f	------++	2.6 1.0	3.0 1.1
H^f- H^g	10.5	11.9 11.1	11.9 11.3
H^f- H^h	7.5	6.7 5.8	6.8 6.1

* Of a pair of the two calculated J-values, the upper one is based on Karplus equation, and the remaining one is based on Haasnoot equation.[6]

\+ Not observed.

++ J-Value seems to be quite small.

Furthermore, molecular mechanics calculations of the two trans decalones (III and IV) were also carried out, indicating that both compounds adopt CC conformation in more than 98% as compared with other ones (see Fig. 2). Then, the calculated coupling constants in III and IV are compared with the observed ones in the rearrangement product of periplanone A (see Table 2).[3]



IV (S.E., 32.5367 Kcal/mol)

Fig. 2. III (S.E., 34.0753 Kcal/mol)

Table. 2. The observed coupling constants of the rearrangement product and the calculated ones of III and IV

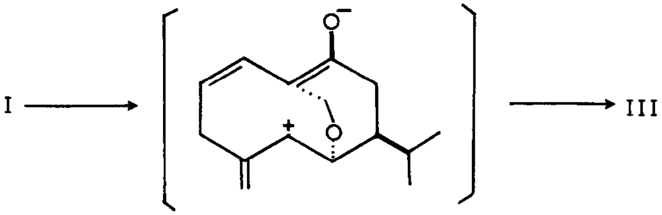
Assignment	The rearrangement product (Hz)	III (Hz)*	IV (Hz)*
H^a- H^b	ca. 4	6.5 5.5	6.6 5.7
H^a- H^c	ca. 2	2.5 1.5	2.5 1.4
H^d- H^e	--------+	2.1 0.47	2.1 0.48
H^e- H^f	3.5	4.5 3.7	3.3 1.2
H^f- H^g	8.5	7.8 6.9	11.9 11.3
H^f- H^h	3.5	2.2 1.2	6.7 6.1

* Of a pair of the two calculated J-values, the upper one is based on Karplus equation, and the remaining one is based on Haasnoot equation.[6]

\+ J-Value seems to be quite small.

As seen in Table 1, it is difficult to decide I or II for periplanone A, because of their similarity in the corresponding J-values. In Table 2, however, some remarkable differences are observed in the three coupling constants (H^e- H^f, H^f- H^g, and H^f- H^h). These J-values in III are compatible with the observed ones. In addition, remarkable differences between periplanone A and its rearrangement product are observed in their coupling constants (H^f-H^g,

H^f- H^h). These findings strongly support a relationship between I and III, and do not agree with a relationship between II and IV, because both II and IV are expected to have almost the same values in the coupling constants (H^f- H^g, H^f- H^h). In conclusion, the stereostructures of periplanone A and its rearrangement product must be represented by I and III, respectively. As seen from the molecular model, clearly, periplanone A (I) seems to be quite unstable (S.E., 39.1897 Kcal/mol), and must be readily converted into III (S.E., 34.0753 Kcal/mol) (see Scheme 1).



Scheme 1. Rearrangement of I to III

From a biogenetic point of view, the stereostructure of periplanone A (I) is quite reasonable. Further synthetic study on periplanone A and related compounds is in progress.

Calculations were performed at Nagoya University Computation Center. This research has been supported in part by grants from the Ministry of Education, Science and Culture.

References

1. C. J. Persoons, F. J. Ritter, and W. J. Lichtendonk, Proc. Kon. Ned. Akad. Wetensch., Amsterdam, C77, 201 (1974).
2. C. J. Persoons, P. E. J. Verwiel, F. J. Ritter, E. Talman, P. E. J. Nooyen, and W. J. Nooyen, Tetrahedron Lett., 1976, 2055; W. C. Still, J. Am. Chem. Soc., 101, 2493 (1979); M. A. Adams, K. Nakanishi, W. C. Still, E. V. Arnold, and C. J. Persoons, ibid., 101, 2495 (1979).
3. C. J. Persoons, P. E. J. Vermiel, F. J. Ritter, and W. J. Nooyen, J. Chem. Ecol., 8, 439 (1982).
4. H. Hauptmann, G. Muhlbauer, and H. Sass, Tetrahedron Lett., 27, 6189 (1986).
5. Program MM2: N. L. Allinger, J. Am. Chem. Soc., 99, 8127 (1977); QCPE #395.
6. C. A. G. Haasnoot, F. A. A. M. de Leeuw, and C. Altona, Tetrahedron, 36, 2783 (1980).

(Received in Japan 17 January 1987)