

SEX PHEROMONES OF THE AMERICAN COCKROACH, PERIPLANETA AMERICANA:

A TENTATIVE STRUCTURE OF PERIPLANONE-B

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The identification of the sex pheromone of the American cockroach, Periplaneta americana, is a long-standing problem¹⁻⁵. In a previous communication⁶ we described the isolation and partial identification of two sexual excitants for this insect. Independently, Chen⁷ also demonstrated the presence of two sex pheromones in P. americana. Some of the chemical properties of one of them, namely periplanone-B, are described in a recent survey of pheromone research in the Netherlands⁸. In this report we present spectral data of the compound, and select one of six possible structures as being the most likely on the basis of these data and of biogenetic considerations. The compound was isolated and purified according to techniques described in our previous papers^{6,8}. The amount of material available for analysis could be augmented by extracting not only filter paper on which virgin females had been kept, but also the alimentary tracts of many thousands of insects³. The purification procedure was improved and shortened by the introduction of high pressure liquid chromatography⁹. The amount of purified material finally available was about 200 µg.

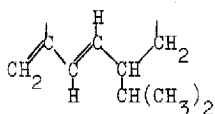
The mass spectrum (LKB 9000 GC/MS) of periplanone-B shows the highest mass at m/e 248.¹⁰ Peak matching gave m/e values of 248.139 and 248.134. Together with the other spectroscopic data, this matching leads to the molecular formula C₁₅H₂₀O₃ (m/e calculated = 248.141). Other prominent peaks in the mass spectrum are present at m/e 204, 187, 111, 91, 43 and 41 (base peak). The molecular formula was concluded to be C₁₅H₂₀O₃ as the signals in the NMR-spectrum (Varian HR 300) amount to a maximum of 21 hydrogens.

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
The mass spectrum of hydrogenated¹¹ periplanone-B shows peaks at $m/e = 250$ ($C_{15}H_{22}O_3$) and $m/e = 234$ ($C_{15}H_{24}O_3 - H_2O$) suggesting the presence of two double bonds. Actually, the presence of a conjugated diene $H_2C=C=C-CH$ (trans) is in accordance with the signals of four olefinic hydrogen atoms in the NMR spectrum (solvent CS_2) at $\delta = 4.87(s)$, $\delta = 5.02(s)$, $\delta = 5.91$ (d. 16 Hz) and $\delta = 5.78$ (dd. 16 and 10 Hz), with IR bands at 1600 and 1650 cm^{-1} , and with a UV absorption (hexane) at $\lambda_{max} = 226$ nm. Saturation of the proton at $\delta 5.78$ showed that it is coupled to a multiplet at $\delta 2.06$, which is part of an AB-type system ($\delta 2.04$ dd. 5.5 Hz and (-) 11.5 Hz; $\delta 2.06$ d. 5.5 Hz and further splittings).

In turn, saturation of this two-proton AB-multiplet, causes the triplet-like signal at $\delta 2.55$ (with $J = 10$ Hz and (-) 11.5 Hz) to collapse into a singlet. Therefore, a CH_2 ($\delta 2.04$ and 2.55) must be attached to the allylic CH ($\delta 2.06$).

That the compound contains an isopropyl group could be shown by saturation of the one-proton multiplet at $\delta 1.56$, which caused the methyl doublets at $\delta 0.87$ and 0.89 to collapse into singlets. The even-multiplet pattern of the signal at $\delta 1.56$ indicates that the isopropyl group is attached to a methine group. Since the allylic CH group appears to be the only possible site of attachment, the following partial structure results:



Computer simulations of the NMR pattern of this system are in good agreement with the observed spectrum.

The AB pattern at $\delta 2.63$ and $\delta 2.84$ ($J = 6$ Hz) is attributed to an *exo*-epoxide group , because the other plausible explanation, namely a CH-CH group without any further vicinal couplings, is found to be impossible when the other structural elements present are taken into account (see also below).

The strong IR absorption near 1700 cm^{-1} constitutes evidence for a non-conjugated ketone.

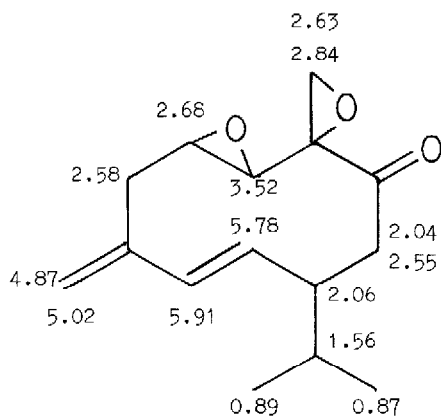
The one-proton doublet at $\delta 3.52$ (d. 4 Hz) accounts for the third oxygen atom, which forms part of the epoxide group in $-CH-CH-CH_2-$. Evidence for the proton sequence in this partial structure was obtained by saturation of the one-proton doublet at $\delta 3.52$, which resulted in simplifi-

cation of the one-proton multiplet at δ 2.68 (ddd. 8 Hz, 6 Hz and 4 Hz). The signal at δ 2.68 is strongly coupled to a CH_2 signal at δ 2.58 ($J_{\text{gem}} = -12$ Hz). Spectrum simulation of this ABCX system (for the CS_2 as well as the CDCl_3 solution of the compound, the spectra of which have quite different patterns) confirmed the $\text{CH}-\text{CH}_2$ couplings. The vicinal coupling constant of 4 Hz indicates that the epoxide has the cis-configuration.

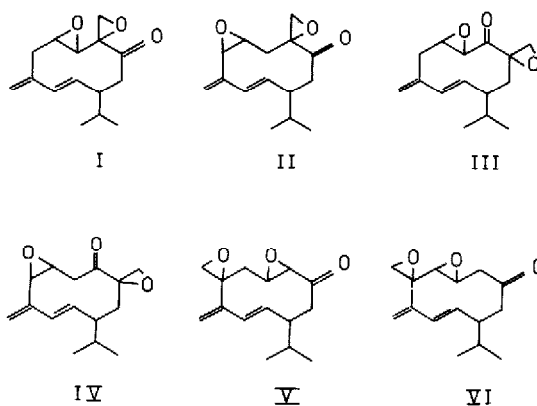
Combination of the four partial structures described above leads to six possible structures (apart from stereochemical differences), all of which possess a ten-membered alicyclic ring. Only two (I and II) have a germacrane-type skeleton, which obeys the head-to-tail isoprene rule. Two of the other structures (III and IV) are also composed of three isoprene units, but beside a head-to-tail they also contain a tail-to-tail junction. The remaining two structures (V and VI) are not isoprenoid.

The chemical shifts expected for $\text{CH}_2-\text{CH}-\text{CH}(\text{CH}_3)_2$ in structures III and IV, and for $\text{CH}_2-\text{CH}-\text{CH}$ in V, are about 0.5 ppm lower than those found for periplanone-B. Structures III, IV and V can therefore be considered less probable. As regards the remaining structures (I, II and VI), chemical shift expectations for the $\text{CH}_2-\text{CH}-\text{CH}$ protons slightly favour structure I.

Biogenetic considerations and the reported activity of another germacrane derivative (germacrene-D) towards *Periplaneta americana*¹²⁾ are in favour of I and II, structure I being slightly preferred on the basis of chemical shift criteria, as mentioned above. In conclusion, it appears that, among the six structures given, formula I seems to be the most plausible for the sex pheromone periplanone-B. Conclusive proof will have to be provided by synthesis.



Assignment of protons in I.



Acknowledgement

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References and footnotes

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7. In a completely independent investigation, S.M.L. Chen reached the same conclusion: Chen, S.M.L., Chapter III. Thesis Columbia University, New York, 1974.
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9. Du Pont 830 Liquid Chromatograph. Three 25 cm x 5 mm i.d. columns; Merckosorb Si60 5 μ with about 30,000 theoretical plates/m. Effluent: hexane - 2% ethyl acetate, 2.5 ml/min.
10. The mass spectrum of a compound independently isolated by Chen proved to be in agreement with our own data. K. Nakanishi, personal communication.
11. Hydrogenation was carried out on a 1/4" DC 200 column (2 m, 5%), with Pd as the catalyst, placed in the top of the column.
12. S. Tahara, M. Yoshida, J. Muzitani, C. Katamura and S. Takahashi, *Agr. Biol. Chem.* 39 (7) 1517 (1975).