

Riassunto. Misure di diffrazione ai Raggi-X sui polipeptidi sintetici (Pro-Leu-Gly)_n e (Pro-Phe-Gly)_n permettono di suggerire una struttura originata dall'avvolgimento di una singola catena a formare una tripla elica.

Il confronto tra i dati ottenuti dagli autori e quelli riportati in letteratura indica che la presenza di prolina in posizione 1 è necessaria ma non sufficiente e che inoltre è importante la natura del residuo in posizione 2.

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Sex Pheromones of the Armyworm Moth, *Spodoptera exempta* (Wlk.)

The armyworm, *Spodoptera exempta* (Wlk.) (Lepidoptera, Noctuidae) is a serious pest of cereals and grasses which occurs in Africa, India, Malaysia, Indonesia and Australia. A synthetic sex pheromone would provide a valuable aid to its control. We have found that virgin female *S. exempta* produce two compounds which are potent olfactory stimulants for the male moth. They have been identified as (Z)-9-tetradecen-1-yl acetate (I) and (Z)-9,(E)-12-tetradecadien-1-yl acetate (II) and have been shown to attract male moths under laboratory conditions.

As only a small number of moths was available, gas chromatography (GC) combined with electroantennogram (EAG) recording¹ was used for the identification of the pheromones. Extracts of 1-day-old virgin female and male moths were prepared after a 3 h darkness treatment. The last 3 to 4 abdominal segments were clipped and extracted with dichloromethane for 15 min at room temperature without maceration; the solvent was removed by pipette and concentrated to 1 tip equivalent/ μ l.

Both male and female moth preparations were made for EAG recording. The extracts were chromatographed on polar and non-polar packed GC columns and the column effluent split 75% to the flame ionisation detector and 25% to the test insect's antenna; GC peaks and EAG responses were recorded simultaneously. The female moth did not respond to any components of either male or female extract (c.f.²). Male moths responded only to female extract: two responses were obtained to the effluent from a polar column, but from a non-polar column the 2 olfactory stimulants (designated S(i) and S(ii)) emerged as a single peak (Table I). The amounts of the 2 compounds in a female tip equivalent were 4 ng S(i) and approximately 0.2 ng S(ii).

As preliminary examination of their GC behaviour suggested that S(i) and S(ii) were acetates of C₁₄ unsaturated alcohols, they were compared directly with synthetic samples of the known sex pheromones of other *Spodoptera* species which are all compounds of this type³⁻⁶ (Table II). The results indicated that S(i) was a tetradecenyl acetate and S(ii) was a tetradecadienyl acetate in which the two double bonds were methylene interrupted. In an attempt to establish the positions and configurations of the double bonds in the two compounds, female tip extract (0.5 μ l), a range of tetradecenyl acetate isomers ((Z)- and (E)-7, -8, -9, -10, -11 and -12) and all 4 stereoisomers of 9,12-tetradecadienyl acetate were run through the GC-EAG link on support-coated open tubular columns (50 ft Carbowax 20M, Apiezon L and DEGS run isothermally at 150, 165 and 141 °C respectively, with a helium flow of 4 ml/min). All synthetic samples were chromatographed at a loading of 2 ng. Only (E)-10-tetradecenyl acetate and (Z)-9-tetradecenyl acetate (I) co-chromatographed with S(i), and only the (Z)-9 isomer elicited an EAG response at this loading. Only

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Table I. GC retention temperatures of the olfactory stimulants S(i) and S(ii) in female moth extract and corresponding male antennal responses

Sample	Retention temperature (°C) Column A	EAG response (mV)	Retention temperature (°C) Column B	EAG response (mV)
Dodecanyl acetate	155.0		147.6	
Tetradecanyl acetate	172.5		164.6	
Hexadecanyl acetate	191.4		182.8	
S(i) 4 ng	175.8	1.3	163.0	1.7
S(ii) ca. 0.2 ng	183.0	0.4		

Column A: 2½% Carbowax 20 M on Chromosorb G AW DCMS, temperature programmed at 4°C/min from 120–200°C with N₂ flow 25 ml/min. Column B: SE 30 (other conditions as for Column A).

Table II. GC retention temperatures of the *S. exempta* olfactory stimulants S(i) and S(ii) and of known *Spodoptera* spp. sex pheromones

Sample	Retention temperature (°C) Column A	Retention temperature (°C) Column C
Tetradecanyl acetate	172.9	133.0
(Z)-9-Tetradecenyl acetate	176.3	137.8
(Z)-9, (E)-12-Tetradecadienyl acetate	183.2	144.9
(Z)-9, (E)-11-Tetradecadienyl acetate	189.0	145.5
Olfactory stimulant S(i)	176.2	137.5
S(ii)	183.4	144.8

Column C: EGSS-X (other conditions as for Column A in Table I).

Table III. Comparison of male moth antennal responses to natural and synthetic olfactory stimulants

Sample	EAG response (mV)	
	Run 1	Run 2
Female tip extract containing S(i) 4 ng	1.0	1.1
S(ii) ca. 0.2 ng	0.4	0.4
(Z)-9-Tetradecenyl acetate, 4 ng	1.0	1.0
(Z)-9, (E)-12-Tetradecadienyl acetate, 0.2 ng	0.6	0.4

All samples were chromatographed on Column C (Table II). Weights quoted are for the amount of sample injected onto the GC column.

(Z)-9, (E)-12-tetradecadienyl acetate (II) co-chromatographed with S(ii) on all 3 columns, and this was the only diene isomer which caused an antennal response.

The potencies of compounds (I) and (II) were shown to be comparable with those of the natural olfactory stimulants by recording EAG responses of the same male moth to female extract and to corresponding amounts of compounds (I) and (II) (Table III). In a laboratory bioassay involving attraction of male moths into a trap⁷, a mixture of (I) (50 ng) and (II) (2.5 ng) attracted 40–60% of the test moths. It was concluded that these 2 compounds constitute the female sex pheromone of *S. exempta*, although field trials are needed to confirm this and to determine the exact functions of the 2 components.

Pheromones (I) and (II) are also produced by female *S. eridania*⁴ but in a different ratio from that found in *S. exempta*. The diene (II) has been found in *S. litura*⁶ in combination with a conjugated diene, and in *S. exigua*⁵; it has also been reported to be attractive to male *S. d. olichos*⁸. The mono-ene (I) has been isolated from *S. frugiperda*³ and forms part of the pheromone complex of *S. littoralis*².

Zusammenfassung. Es wurden mit gas-chromatographischer Elektroantennogramm-Methode (Z)-9-tetradecenyl-1-acetat und (Z)-9, (E)-12-tetradecadienyl-1-acetat als die Sexuallockstoffe weiblicher *Spodoptera exempta* (Wlk.) identifiziert.

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How Homologous are the α and β Subunits of C-Phycocyanin?

In recent years it has been demonstrated that C-phyocyanins are composed of two types of subunits (α and β) which always occur in a 1:1 ratio. The nature of these subunits – they are both single polypeptide chains – was clearly established by analysis of their amino terminals, molecular weights and amino acid composition^{1–7}. As soon as the results of the amino acid analyses of those subunits were available, a considerable homology between the two chains was anticipated owing to the fact that their amino acid compositions, though not identical, show remarkable analogies, e.g. the high content of glycine and alanine. This holds for the C-phyocyanins of all types of blue green algae which have so far been investigated in this respect^{4–7}. However, a

high degree of homology was not found when large chromophore-containing peptides of both chains from

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