Die Konfiguration der 15,16-Methylengruppe lässt sich wegen des Fehlens der 13-Methylgruppe nicht über eine NMR-Signallagenberechnung von H-18 mit Inkrementen[9,10] durchführen.

Eine eindeutige Zuordnung der Stellung des Cyclopropanrings ist jedoch über **7** möglich. Das Vorhandensein des Dreirings folgt aus den für Cyclopropane charakteristischen Banden im nahen IR-Bereich (6080 und 4490 cm^{-1})[10]. Er ist α-ständig angeordnet, da die NMR-Signallage und die Aufspaltung des H-17α mit den entsprechenden Werten des 15α,16α-Methylentestosterons (δ H-17α 3,26 ppm, d, J = 2,5 Hz) gut übereinstimmen[10] und das 17α-Proton sich damit über der Ebene des Dreirings befinden muss. Das Massenspektrum liefert die richtige Molekülgrösse für **7**.

Das 15α,16α-Methylensteroid **6a** zeigte am Kaninchen bei subcutaner Applikation im Befruchtungshemmtest sowie bei subcutaner und oraler Applikation im Claubergtest gegenüber der entsprechenden nichtmethylenierten Verbindung deutlich erhöhte Wirkungen[11].

Summary. The synthesis and biological activities of 18-methyl-15α,16α-methylene-17α-ethinyl-19-nortestosterone **6a** are described.

R. Wiechert, D. Bittler and G.-A. Hoyer

Schering AG, Pharma-Forschung, Department Steroidchemie, Müllerstrasse 170–172, D–1 Berlin 65 (Deutschland), 4. September 1973.

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(Z-E)-7,11-hexadecadien-1-ol Acetate: The Sex Pheromone of the Angoumois Grain Moth, *Sitotroga cerealella*[1]

For many years entomologists have been interested in the chemicals produced by insects of one sex to attract insects of the other sex for mating. The possibility of using these insect sex pheromones to control insects is under intensive investigation. Often, however, practical research toward the control of a species with sex pheromones must await the isolation, identification, and synthesis of the sex pheromone of that species. The female of *Sitotroga cerealella* (Olivier), the Angoumois grain moth, one of the most destructive pests of stored grain, has previously been shown to release a chemical to attract males[2]. We report here the isolation, identification, and synthesis of this sex pheromone.

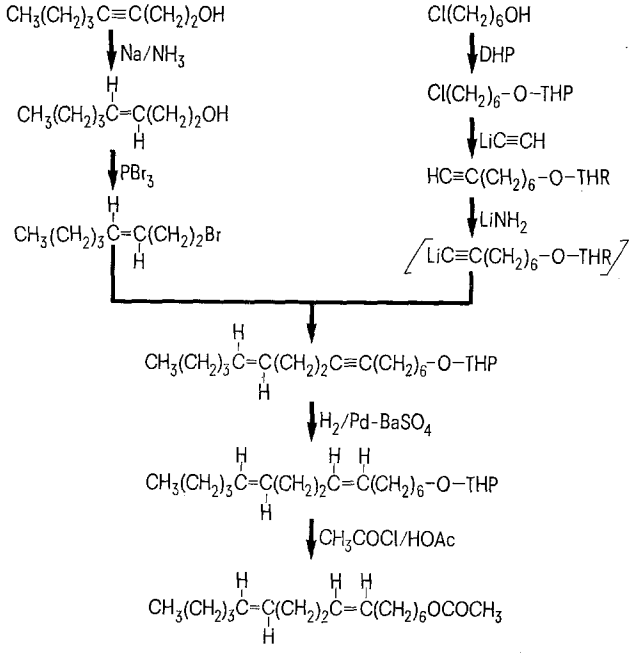

Fig. 1. Scheme used to synthesize (Z, E)-7,11-hexadecadien-1-ol acetate.

The methods used to rear the insects, extract the females and bioassay the samples were previously described in detail[3]. In brief, all fractions obtained during the purification of the natural material were bioassayed for male attraction by a technique based on the number of males attracted within 3 cm of a sample inserted into the upwind end of 1.9 cm ID × 44 cm acrylic plastic tubes. Removal of solvent from diethyl ether extracts of 7,000, 1 to 5-day-old females yielded 6.6 g of viscous oil. This oil was fractionated by liquid chromatography in 1.5-g batches on 2.5 × 24-cm silicic acid columns by using the petroleum ether (p.b. 30–60 °C)/diethyl ether gradient elution system previously described[3]. The fractions that elicited a response from the males were combined and further purified by sweep co-distillation at 180 °C and 0.5 l/min N_2 by using hexane as the flushing solvent. The active sweep co-distillation fraction was then sequentially purified by gas chromatography on columns 1, 2, and 3[4].

The purified sex pheromone eluted as a single symmetrical peak upon gas chromatography with columns 2 (retention time = 11.4 min), 4 (15.0 min), and 5 (14.5 min). This chemical had biological activity equal to crude female extracts containing equivalent amounts of the same material. None of the other fractions from the female extracts had sex pheromone activity.

Saponification of the sex pheromone with 0.5% methanolic NaOH caused complete loss of activity, but the activity was restored by acetylation of the saponified sex pheromone with acetyl chloride. Hydrogenation of 2 μg of the sex pheromone in hexane with 5% palladium

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[2] R. E. Keys and R. B. Mills, J. econ. Ent. *61*, 46 (1968).
[3] L. L. Sower, K. W. Vick and J. S. Long, Ann. ent. Soc. Am. *667*, 184 (1973).
[4] The following 2 mm I.D. gas chromatograph columns were used during the course of this study a with a carrier gas flow rate of 30 ml/min N_2 or He: Column 1–3.3 m, 20% FFAP on Chromosorb W, 100/120 mesh at 210 °C; Column 2–3.3 m, 5% Carbowax 20 *M* on Chromosorb W, 100/120 mesh at 180 °C; Column 3–6.6 m, 3% SE-30 on Gas Chrom Q, 100/120 mesh at 210 °C; Column 4–2.0 m, 15% DEGS on Chromosorb W, 100/120 mesh at 160 °C; Column 5–4.0 m, 10% OV-1 on Chromosorb W, 100/120 mesh at 200 °C; Column 6–2.0 m, Porapak Q at 140 °C.

on charcoal yielded a new product identical in gas chromatographic retention times to hexadecan-1-ol acetate on columns 4 and 5. These data suggested that the pheromone is the acetate of a 16-carbon, straight-chain alcohol.

The ratio of the gas chromatographic retention time of the sex pheromone to that of hexadecan-1-ol acetate was 0.87 on column 3 (SE-30), 1.21 on column 2 (Carbowax 20 *M*), and 1.43 on column 4 (DEGS). By comparison, the ratios of z-7-hexadecen-1-ol acetate to hexadecan-1-ol acetate were 0.91, 1.08, and 1.18 on the same 3 columns. The longer retention times on the polar columns of the pheromone compared with z-7-hexadecen-1-ol acetate suggested that the pheromone has more than one double bond.

A mass spectrum of the purified sex pheromone obtained from a mass spectrometer equipped for chemical ionization showed the following diagnostic peaks: A cluster of ions at *m/e* 281, 280, and 279 resulting from $(P + 1)^+$, P^+, and $(P - 1)^+$, respectively; *m/e* 221, $[(P + 1) - CH_3COOH]^+$; *m/e* 61, $(CH_3COOH_2)^+$; and *m/e* 123, base peak[5]. These data confirmed that the sex pheromone is a 16 carbon-alcohol acetate with 2 double bonds.

Microozonolysis[6] of 1-µg quantities of the sex pheromone in hexane (99% mole pure) yielded a compound with GC retention times on columns 2, 3 and 4 identical to those of 7-oxoheptyl acetate formed by the ozonolysis of Z-7-hexadecen-1-ol acetate. A second fragment formed during the ozonolysis of the sex pheromone had retention times identical to those of valeraldehyde on columns 2, 4, and 6. Therefore, the sex pheromone was identified as one of the 4 possible isomers of 7, 11-hexadecadien-1-ol acetate.

An active isomer, (Z, E)-7, 11-hexadecadien-1-ol acetate, was synthesized from 3-octyn-1-ol and 6-chloro-1-hexanol as starting materials with a 7.1% overall yield by the scheme outlined in Figure 1. The other 3 isomers were also synthesized by analogous procedures but elicited almost no biological activity from the males. The detailed synthesis will be reported elsewhere. The isomeric identity of the synthetic pheromone was confirmed by spectrometric means[7]. Diagnostic peaks of the mass spectrum and GC retention times on columns 2, 4, and 5 were identical for Z-7-, E-11-hexadecadien-1-ol acetate and for the isolated natural sex pheromone.

No significant differences between male responses to the natural sex pheromone and to (Z, E)-7, 11-hexadecadien-1-ol acetate could be detected by laboratory bioassay (Figure 2, paired $t = 0.03$). A preliminary field test was run as follows: Two sticky traps, one baited with 25 ng of natural and one baited with 25 ng of synthetic sex pheromone each impregnated on filterpaper strips, were suspended against the walls of a $6 \times 6 \times 2.4$-m room at a height of 1.5 m. The locations of the two baited traps were alternated nightly for 8 nights. Each night 100 males were released into the center of the room midway through the 10-h scotophase. Male catches were recorded 5 h later. Used traps, baits, and untrapped insects were discarded after each test. Traps baited with natural and synthetic pheromone caught 21 ± 8 ($\bar{X} \pm SD$) and 20 ± 12 males, respectively, each night. Untreated control traps tested simultaneously with the treated traps caught 3.5 ± 2 males per night. The difference between the treatment means was not significant ($t = 0.25$). We therefore conclude that (Z, E)-7, 11-hexadecadien-1-ol acetate is the sex pheromone produced by the female Angoumois grain moth.

Zusammenfassung. Der Sexuallockstoff der Angoumois Getreidemotte, *Sitotroga cerealella* (Olivier), wurde als (Z, E)-7, 11-Hexadecadien-1-ol Acetat identifiziert. Die synthetisierte Verbindung ist chromatographisch, spektroskopisch, und verhaltensmässig identisch mit dem von den Weibchen produzierten Sexuallockstoff.

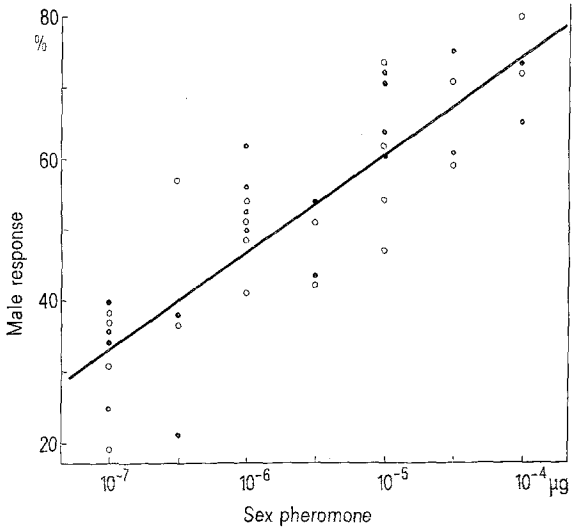

Fig. 2. Responses of male Angoumois grain moths to the synthetic pheromone (solid circles) and the natural pheromone (open circles). The 2 treatments were not significantly different ($t = 0.03$ at 19 df).

K. W. VICK[8], H. C. F. SU[9], L. L. SOWER[8], P. G. MAHANY[9] and P. C. DRUMMOND[8]

Insect Attractants, Behavior and Basic Biology Research Laboratory, USDA Agric. Res. Serv., P.O. Box 14565, Gainesville (Florida 32604, USA); and Stored-Product Insects Research and Development Laboratory, USDA, Agric, Res, Serv., Savannah (Georgia 31403, USA), 10 July 1973.

[5] We thank J. H. TUMLINSON, Insect Attractants Laboratory, Gainesville, Fla., and J. NELSON and F. MATSUMURA, Entomology Dept., University of Wisconsin, Madison, Wisconsin, for the mass spectra of the isolated female sex pheromone.

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[7] We thank J. H. TUMLINSON and R. R. HEATH for confirming the location and configuration of the double bonds in the synthetic sex pheromone. The double bonds were individually epoxidized and examined by IR, NMR, and chemical ionization mass spectrometry. This technique will be published shortly.

[8] Insect Attractants, Behavior and Basic Biology Research Laboratory, P.O. Box 14565, Gainesville, Fla. 32604, USA.

[9] Stored-Product Insects Research and Development Laboratory, Savannah, Georgia 31403, USA.

Oxidized Furanoterpenes from the Sponge *Spongia officinalis*

Previous work[1,2] on the sponge *Spongia officinalis* has resulted in the isolation of 6 closely related linear C_{21}-difuranoterpenes, all possessing the same carbon skeleton. An accurate analysis of the more polar fractions from the methanolic extracts of *S. officinalis* has now led to the isolation, in small amount, of 4 C_{21}-monofuranoterpenes, closely related to furospongin-1 (**1**)[1], the major C_{21}-terpene component of the same sponge, with 1 furan ring