Identification and Synthesis of the Major Sex Pheromone of the Olive Fly (*Dacus oleae*)

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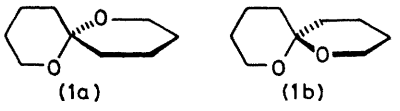
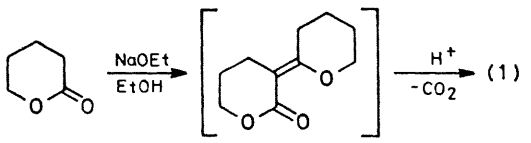
Summary The major component of the sex pheromone of the olive fly has been shown to be 1,7-dioxaspiro[5.5] undecane (**1**) and its structure has been confirmed by unambiguous synthesis; field studies have confirmed its biological activity.

THE olive fruit fly, *Dacus oleae* (Gmelin), is widely distributed throughout the Mediterranean basin and parts of North Africa. It is the major pest of olives, having its most serious effects in Italy, Spain, Greece, and Israel. The main means of control is by insecticide sprays, and monitoring traps are in use, in certain areas, which rely on visual

attraction (colour) and food baits to attract the flies. It is known in this species that the female produces a volatile pheromone that attracts males.[1] Previously a series of nonen-1-ols have been reported to have biological activity and (*Z*)-non-6-en-1-ol exhibited the highest attractiveness.[2] Some evidence that a non-6-en-1-ol is present in the anal glands of female flies has been presented[2] but, in our hands, this compound showed no marked activity in field studies. We report the identification and synthesis of the major component of the sex pheromone of the olive fly.

The rectal glands were dissected from sexually mature adult flies, about one week old, and sealed in batches of five (male or female) in glass capillaries. Solid-sample gas chromatography[3]† indicated the presence of a major female specific component, estimated to be at the level of *ca.* 0·3 μg per fly. G.c.–m.s. on a further five female glands gave the mass spectrum of this major compound: *m/e* 156 (18%; M^+), 111 (15%), 101 (100), 100 (50), 98 (80), 83 (26), 56 (23), 55 (48), 43 (31), and 41 (28). From the high resolution spectrum the molecular ion was found to have the atomic composition, $C_9H_{16}O_2$. From a consideration of this mass spectrum and those recently published for alkyl-1,6-dioxaspiro[4.4]nonanes[4] the structure of (**1**) was assigned as 1,7-dioxaspiro[5.5]undecane. This has also been confirmed by synthesis but no information on the chirality of (**1**) is currently available.





The spiroacetal (**1**) was synthesised by the general method of Erdmann,[5] which proved to be a convenient method for large scale preparation. δ-Valerolactone (**2**) (20 g) in absolute ethanol (50 ml) was added dropwise to a stirred solution of sodium (2·3 g) in absolute ethanol (50 ml) at 5—10 °C. After addition, the mixture was refluxed for 3 h and the alcohol was distilled to leave a residue which was dissolved in hot water and acidified with dilute hydrochloric acid. The product was then co-distilled with water. After work-up and distillation, (**1**) was obtained, 10·2 g (65%), b.p. 77—78 °C at 13 mmHg, ^{1}H n.m.r. (C_6D_6): δ 3·65 (2H) 3·52 (2H), 1·95 (2H), 1·63 (2H), and 1·20—1·45 (8H); ^{13}C n.m.r. (C_6D_6): 94·91 (s), 60·24 (t), 36·24 (t), 25·89 (t), and 19·01 (t) p.p.m.[6] This product was identical to that obtained by the method of Stetter and Rauhut which involved the cyclisation of 1,9-dihydroxynonan-5-one. The mass spectrum of the synthetic compound (**1**) and its gas chromatographic properties were found to be identical to those of the natural product.

Field trials with the racemic mixture of the spiroacetal (**1**) have been carried out in Southern Spain (Granada). Triangular, sticky 'delta' traps‡ baited with rubber sleeve stoppers impregnated with 1—50 mg of the spiroacetal (**1**) caught large numbers of olive flies, of which more than 99% were males and less than 1% were females. Similar unbaited traps caught no flies. These preliminary results suggest that the synthetic mixture is acting in a similar way to the pheromone produced by the female fly in having specific attraction for male flies.[1]

Several spiroacetals have been found in insects. 2-Ethyl-1,6-dioxaspiro[4.4]nonane (chalcogran) has been identified as the principal aggregation pheromone of a bark beetle, *Pityogenes chalcographus* (L),[7] and methyl-1,6-dioxaspiro-[4.5]decanes have been found in the odours of the common wasp, *Paravespula vulgaris*,[8] which appear to act as aggression inhibitors. However, 1,7-dioxaspiro[5.5]undecane is the parent compound of a class of spiroacetals previously unknown in insects, and is the first spiroacetal to be identified as a specific sex pheromone of an insect.

The identification of this spiroacetal as the major sex pheromone component of *Dacus oleae* has major implications for the use of trapping systems for the control of the olive fly. Studies to determine the chirality of (**1**) are in progress.

Thanks are due to Dr. P. Ramos of the Estacion Experimental del Zaidin for his assistance with the field trials, and to Dr. D. Campion of C.O.P.R. for the supply of pupae. A grant from the S.R.C. (R.H.) and the valuable assistance of P. Wagner and W. Speed is gratefully acknowledged.

(*Received*, 17*th October* 1979; *Com.* 1106.)

† G. C. analysis; solid sample injector/heater at 140 °C for 5 min; 3 m × Carbowax 20 M 5% (Diatomite C AAW) analytical column, temperature programme 80 °C—200 °C at 6 °C/min.

‡ OECOS Ltd., Kimpton, Herts.

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[6] The compound was first reported by H. Stetter and H. Rauhut, *Chem. Ber.*, 1958, **91**, 2543, but no spectral characteristics were given; a mention of the formation of (**1**) as a minor reaction product was reported by V. M. Micovic, S. Stojcic, M. Bralovic, S. Mladenovic, D. Jeramic, and S. Steganovic, *Tetrahedron*, 1969, **25**, 985, but only a partial n.m.r. spectrum was given.
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