Novel β-Triketones from Lepidoptera

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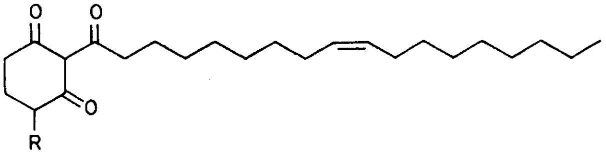
Summary Two novel natural products 4-hydroxy-2-oleoylcyclohexane-1,3-dione and 2-oleoylcyclohexane-1,3-dione were found in the larval mandibular glands of *Anagasta kuehniella* (Zeller).

In the course of investigations into the pheromones and kairomones of some Lepidopteran pests of stored products[1,2] two novel natural products, 4-hydroxy-2-oleoylcyclohexane-1,3-dione and 2-oleoylcyclohexane-1,3-dione were isolated from an ether extract of the larval mandibular glands of *Anagasta kuehniella* (Zeller). These compounds also appear to be present in the larval mandibular glands of *Ephestia cautella* (Wlk.), *Ephestia elutella* (Hübn.), and *Plodia interpunctella* (Hübn.).[2] This is believed to be the first time β-triketones have been found in insects.

Structures (**1**) and (**2**), which appear to be fully enolised in deuteriochloroform are proposed for these compounds on the basis of the following experimental evidence.

The alcohol (**1**) has a molecular ion (M^+ 393·2923) with composition $C_{24}H_{40}O_4$ (calc. 392·2925) indicating five double bond equivalents. Its i.r. spectrum showed the presence of hydroxy (ν 3420 cm^{-1}, broad), conjugated carbonyl (ν 1665 cm^{-1}), and conjugated, chelated carbonyl groups (ν 1565 cm^{-1}).[3]



(1) R = OH
(2) R = H

The ^{1}H n.m.r. spectrum of (**1**) showed the presence of an enolic proton, δ 18·26 (1H, s), a disubstituted isolated double bond, δ 5·38 (2H, m), and an alkyl chain, δ 1·28 (>20 H), with a terminal methyl group δ 0·88 (3H). In addition the spectrum showed two multiplets, δ 3·02 and 2·76 (each 2H) suggesting methylene groups adjacent to carbonyl groups and a double doublet (*J* 13 and 4 Hz) centred at δ 4·09 (1H), consistent with an RCH$_2$–CH(OH)– group adjacent to a carbon bearing no protons.

The ^{13}C n.m.r. spectrum of (**1**) contained three downfield peaks, δ 206·2, 198·5, and 195·2, two barely resolved peaks at δ 129·9 indicating an isolated *cis*-double bond, and signals at δ 110·4, 71·7, 40·2, 31·9, 31·3, 29·4, 27·7, 27·2, 24·6, 22·6, 18·2, and 14·0 p.p.m. The off-resonance ^{13}C n.m.r. spectrum showed no splitting of the peak at δ 110·4 p.p.m. whereas the peak at δ 71·7 p.p.m. became a doublet suggesting a secondary alcohol.

Ozonolysis of (**1**) produced nonanal indicating that the double bond is nine carbon atoms from the end of the alkyl chain.

An enol form of structure (**1**) is consistent with the spectroscopic and chemical data; alternative five-membered ring structures were considered unlikely because of the exceptionally large downfield shift, δ 18·26, of the enolic proton. The enolic proton in 2-acetylcyclohexane-1,3-dione occurs at δ 18·03 whereas in 2-acetylcyclopentane-1,3-dione it occurs at δ 14·75, the difference being ascribed to the length and hence strength of the hydrogen bonds formed.[4]

The proposed 6-membered ring structure was confirmed by spin decoupling experiments. Irradiation at δ 1·95 collapsed both the multiplet at δ 2·76 (2H) and the double doublet centred at δ 4·09 (1H) to singlets. No discrete signal, due to the two ring protons centred at δ 1·95 was discernible, this region forming part of the methylene envelope. Irradiation at δ 1·28 collapsed the multiplet at δ 3·02 (2H) to a singlet.

The presence of the β-triketone group in compound (**1**) was supported by its u.v. spectrum: λ_{max} 273 (ε 11,000) and 233 nm (11,700) in methanol. Adding base caused enhancement of the peak at 273 nm and disappearance of the peak at 233 nm; the original spectrum was regenerated on acidification.[3,5]

The structure of compound (**2**), M^+ 376·2977 ($C_{24}H_{40}O_3$, calc. 376·2977), λ_{max} 273 (ε 14,700), 233 (14,300), and 204 nm (shoulder) (ε 7,200) is supported by similar spectroscopic and chemical evidence.

C.d. measurements showed that the alcohol (**1**) was optically active, $\Delta\epsilon_{236}$ + 0·46, $\Delta\epsilon_{252}$ − 0·42, $\Delta\epsilon_{288}$ + 0·61, and $\Delta\epsilon_{308}$ + 0·25, whereas compound (**2**) was optically inactive.

The antibiotic activity of these compounds and their effect upon the behaviour of the Lepidoptera and their parasite *Venturia canescens* (Grav.) will be reported elsewhere.

I thank Dr. P. M. Scopes, Westfield College, London, for the c.d. measurements and Dr. N. F. Janes, Rothamsted Experimental Station, for the n.m.r. measurements.

(*Received, 3rd August* 1978; *Com.* 855.)

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