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IRIDODIAL FROM THE ODORIFEROUS GLANDS OF *Staphylinus olens*
(COLEOPTERA : STAPHYLINIDAE)

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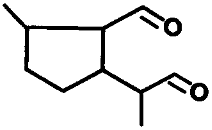
Odoriferous glands occur in many Staphylinid beetles, and in most species they are thought to function in defence. Schildknecht has recently examined the secretion from the odoriferous glands of the Staphylinid, *Stenus bipunctatus*, which was shown to be largely 1,8-cineole accompanied by small amounts of *iso*-piperitenol and 6-methylhept-5-en-2-one.[1] To our knowledge, this is the only member of this large family of beetles whose secretion has been fully investigated. We have now examined the constitution of the liquid secretion from the odoriferous glands of the largest British Staphylinid, *Staphylinus olens*, (popularly known as the Devil's Coach-horse), and we report evidence to show that this consists largely of the monoterpene di-aldehyde, iridodial (1).

G.l.c. examination (5% SE-30; 70°) of fresh samples of secretion from *S.olens* showed that it was composed of one major component (~90%) and two more volatile minor components. Stored chloroform or ethanol solutions of the secretion, however, showed two major components in g.l.c. analysis, but one of these (see later discussion) was found to be an artefact. High resolution mass spectrometry on the fresh secretion showed a molecular ion at $^{m}/e$ 168.1148, corresponding to a molecular formula $C_{10}H_{16}O_2$. The secretion produced an orange colouration with Brady's reagent, and both infrared and n.m.r. data established the presence of two aldehyde functions. These, and other spectral features suggested a saturated monoterpene



(1)

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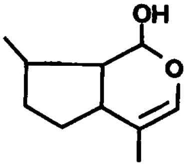
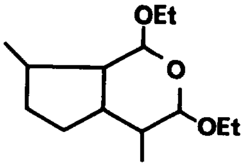


(2)



(3)

di-aldehyde structure, and chromatographic and spectral (i.r., n.m.r., and mass) comparison with authentic iridodial (1) (synthesised from citronellal[2]) confirmed that the major component of the secretion was (1). Infrared data showed that the open chain 1,5-di-aldehyde formulation (1) was in equilibrium with the cyclic tautomer (2), but spectral data provided no clues regarding the stereochemistry of the substituents about the cyclopentane ring in natural (1).

Synthetic iridodial dissolves in acid-ethanol solution to produce a mixture of isomers of a mono-diethylacetal, $^{m}/e$ 242, $\nu_{\text{max.}}$ 2840, 1115 cm.$^{-1}$; τ 5.05 - 5.7 (2X-O-C$\underline{\text{H}}$-O-), 6.1 and 6.5 (2X-OC$\underline{\text{H}}_2$CH$_3$), 8.4 - 8.7 (~9H), 8.8 (2XCH$\underline{\text{Me}}$), 9.05 (2XCH$_2$C$\underline{\text{H}}_3$) which does not contain a free aldehyde group (i.r. and n.m.r. evidence). This acetal, to which we have assigned the tetrahydropyran structure (3), *cf* ref. 3, has the same retention time in g.l.c. as that of the second major component, which is obviously an artefact, observed in stored chloroform or ethanol solutions of the secretion.

Iridodial has previously been identified in several species of ants, where it has always been found in association with 6-methylhept-5-en-2-one.[4] In these instances it has been suggested that the iridodial acts as a fixative for the volatile and insecticidal methylheptenone Although we have not been able to unambiguously identify the two more volatile components in the secretion of *S. olens*, mixed-g.l.c. data with authentic material have clearly demonstrated that neither corresponds to 6-methylhept-5-en-2-one. Whether the absence of 6-methylhept-5-en-2-one in the secretion from *S. olens* indicates a different defensive rôle for the iridodial is not known, but this interesting possibility is under investigation.

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