

ROSE OXIDE AND IRIDODIAL FROM Aromia moschata L.

(COLEOPTERA : CERAMBYCIDAE)

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Odoriferous substances occur in many Coleoptera and secretions of numerous species have been examined. In most cases the components are thought to function in defence against predators.¹

To our knowledge, no member of the family Cerambycidae has been fully investigated and in this paper we report our studies on the constitution of the liquid secretion from adults of the wide-spread European Aromia moschata L. This Cerambycid lives preferentially on willow-trees during the summer and is well known for its delicate scent.

The secretion is manufactured in thoracic glands and is discharged through an opening on the metasternum, near the articulation of the coxa of the hind legs. It is discharged when the insect is menaced by reptiles, birds etc. and is therefore believed to act as defensive substance.

In earlier studies, the presence of salicylaldehyde² or of a salicylic ether³ in the secretion has been supposed, yet without any chemical evidence.

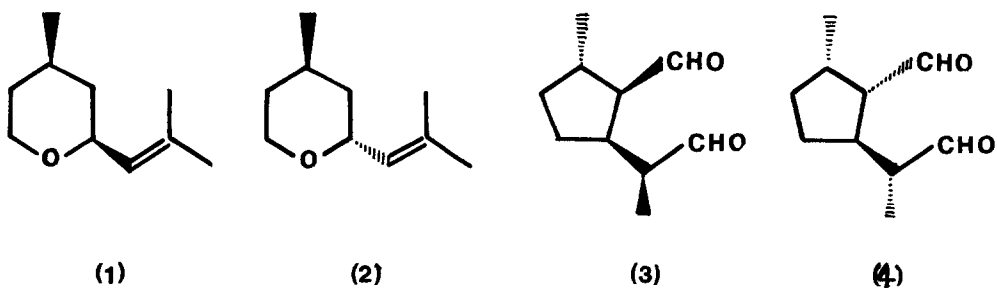
On the contrast, in this communication, we report evidence that the secretion of A. moschata L., consists largely of four monoterpenes: cis- and trans-rose oxide (1,2), δ - and γ -iridodial (3,4).

Glc examination (2,5% SF-96 ; temperature programmed from 50° to 170° at 5°/min.) of fresh secretion from one insect, immediately analysed after collection, revealed the presence of the above components in the relative concentrations of 22, 4, 63, 11, respectively.

Stored secretion showed no artefact in glc analysis, even after several weeks.⁴

Combined gc-ms analysis showed the same molecular ion at m/e 154 for (1) and (2), corresponding to a possible formula C₁₀H₁₈O, and a molecular ion at

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m/e 168, attributed to a likely formula $C_{10}H_{16}O_2$, for (3) and (4). Moreover mass spectra exhibit a similar fragmentation pattern for each of the two pairs of components, suggesting two pairs of stereoisomers. Preparative gas chromatography (2,5% SF-96) allowed to isolate a few milligrams of the main components (1) and (3), each impure of the minor compound.

Infrared spectrum of (1) showed no bands of alcohol or carbonyl functions but a strong band at 885 cm^{-1} attributed to an epoxydic structure. A trisubstituted double bond was demonstrated by absorption at 1680 cm^{-1} and at 845 cm^{-1} . Pmr spectra showed evident signals only for two methyls on a double bond ($3H, \delta(CDCl_3) 1.69, J 1\text{ Hz}$ and $3H, \delta 1.73, J 1\text{ Hz}$) and for a secondary methyl group ($3H, \delta 0.94, J 6\text{ Hz}$). Mass spectrum gave m/e 139 as base peak, corresponding to the loss of a methyl and indicating a fairly stable cyclic structure. Other significant signals are m/e 41 (43%), 55 (34), 69 (69), 83 (30), 84 (16), 85 (18).

These spectral features suggested for (1) (and likewise for (2)) the structure of the monoterpene rose oxide. Chromatographic and spectroscopical (ir, pmr and mass) comparison with authentic cis and trans isomers of rose oxide,⁵ confirmed that the more volatile compound is the cis isomer, the less volatile being the trans. Absolute configuration was established for (1) by the negative sign of the rotatory power. Comparison with literature data⁶ showed that (1) is (-)-(4R)-cis-rose oxide and that presumably (2) is the (-)-(4R)-trans-isomer.

Components (3) and (4) were identified as isomers of iridodial. Both infrared and pmr data established the presence of aldehyde functions. Losses of CH_3 , CHO , CH_3CHCHO , along with the presence of a methylcyclopentane ring, were evidenced in the mass spectrum by significant signals at m/e 153, 139, 111-110 and 81. Comparison of the spectral (ir, pmr, ms) data with those of an authentic iridodial⁷ and with previous literature⁸ proved the structure beyond any doubt.

As far as the stereochemistry is concerned, the glc retention times, compared with a mixture of the four stereoisomers⁹ of iridodial from natural sources,¹⁰ allowed to infer that compound (3) is δ -iridodial, whereas the γ -structure could be assigned to (4) only tentatively.

No sensible epimerization seems to occur during the isolation procedure. The other two possible isomers of iridodial were not present in appreciable amount to be detected by glc.

Iridodial has previously been identified in several species of ants,^{1,8} where it has always been found in association with 6-methylhept-5-en-2-one. To our knowledge, among Coleoptera it has been isolated only from the odoriferous glands of Staphylinus olens,¹¹ where it was suggested to have a different defensive rôle that in ants.

Rose oxide has never been found previously in secretions of Arthropods, whereas it has been isolated from plants (Rosa damascena Mill.,^{12a} Pelargonium graveolens Ait.,^{12a} Ribes nigrum L.,^{12b} Hamanasu oil^{12c}) and to our knowledge represents the first example of a monoterpene with a tetrahydropyrane ring found in the insect kingdom. It has been reported¹³ that cyclopentanoid derivatives are formed in insects from mevalonate, presumably by the usual pathways. Whether the compounds present in the secretion of Aromia moschata L. are really synthesized by the insect, or are taken up from plants, resorbed, stored and later used as a defensive scent, as proposed by the earliest authors,^{2,3} is an interesting problem under investigation.

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