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DEHYDROIRIDODIAL, THE PUNGENT PRINCIPLE OF *ACTINIDIA POLYGAMA* MIQ.

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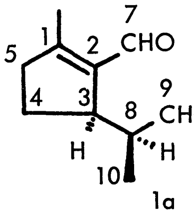
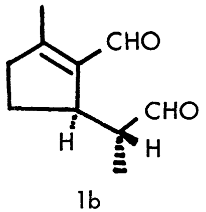
A new monoterpene dial, dehydroiridodial, was isolated from the volatile oils of the fresh fruits and the fruit galls of *Actinidia polygama* Miq. as the pungent principle. The stereostructure of this dial was confirmed by conversion of (-)-(4S,8S)-p-menth-1-en-9-ol to this compound.

Previously Sakan and coworkers$^{1)}$ reported a number of substances from *Actinidia polygama* Miq. which have activity of attraction for Felidae animals and the male adults of a sort of lacewing. It is well known that the fruits and the leaves of this plant have a characteristic pungent taste. However the components responsible for the pungent taste have not yet been studied. Recently, we have isolated a new monoterpene dial having the pungency of this plant. In this paper we report the isolation and characterization of this pungent principle, which we designated as dehydroiridodial.

Dehydroiridodial (1), $[\alpha]_D^{23}$ +80° (in $CHCl_3$), was isolated from the volatile oils of the fresh fruits and the unripe fruit galls by means of column chromatography on silica gel, and was also detected in the leaves and the flowers by GC-mass spectrometry. It has the molecular formula $C_{10}H_{14}O_2$ (M^+, m/e 166.0996, calcd., 166.0995) based on high resolution mass spectrometry. The UV (λ_{max}^{EtOH} 253 nm, ϵ=12,000), IR (ν_{max} 2740, 1725, and 1660 cm^{-1}), and NMR spectral data (δ ppm in $CDCl_3$, δ 9.96, 1H, d, J=1 Hz, and δ 10.02, 1H, s) suggested the presence of a simple aldehyde and an α,β-unsaturated aldehyde. Its NMR spectrum showed a doublet at δ 1.01 (3H, J=7 Hz, $-CH-CH_3$) and a singlet at δ 2.17 (3H, $-C=C-CH_3$). From these spectral data, the structure of 1 seems most likely to be (3R,8S)- or (3R,8R)-dehydroiridodial (1a or 1b). In order to confirm the structure of 1 including its absolute stereochemistry, we

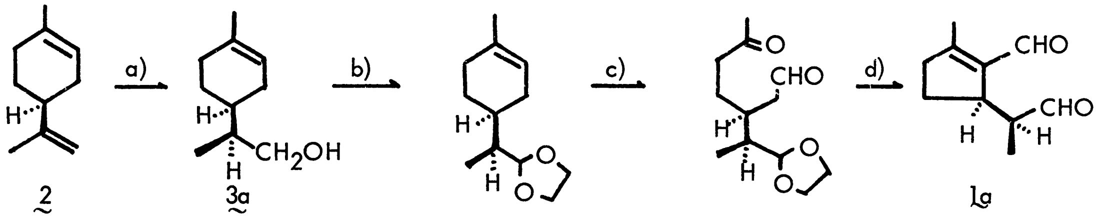


1a



1b

tried to derive one isomer (**1a**) of the dials from l-limonene (**2**, $[\alpha]^{20}_{D}$ −93.5°) via (4S,8S)-p-menth-1-en-9-ol (**3a**, $[\alpha]^{23}_{D}$ −102.9°),[2] of which the absolute configuration had been established by means of X-ray analysis.[3] The (3R,8S)-dehydroiridodial ($[\alpha]^{23}_{D}$ +71.8°) derived through the steps shown in Scheme 1 was identified with the natural dial (**1**) by comparison of spectral data. For providing that these isomeric dials (**1a** and **1b**) could be distinguished from each other in spectra, a mixture of **1a** and **1b** was afforded from the mixture of (4S,8S)- and (4S,8R)-p-menth-1-en-9-ols (**3a** and **3b**: 8β-H) obtained by hydroboration of **2** under the same procedure described above. The mixture of **1a** and **1b** could not be separated from each other by means of TLC and GLC. Its NMR spectrum showed besides the signals of **1a**, the additional ones at δ 0.90 (d, J=7 Hz, $-CH-CH_3$) and δ 9.70 (d, J=1 Hz, -CH-CHO) owing to the presence of **1b**. Thus, natural dial (**1**) should be represented by formula **1a**.



Scheme 1. a) i. Disiamyl borane, $NaOH-H_2O_2$. ii. 3,5-Dinitrobenzoyl chloride, Fractional recrystallization, Hydrolysis. b) i. Pyridinium chlorochromate. ii. Ethylene glycol-oxalic acid in CH_3CN. c) i. O_3. ii. Me_2S. d) i. AcOH-piperidine. ii. 1N-HCl/ether.

It is of interest that dehydroiridodial resembles to tadeonal (polygodial) isolated from Polygonum hydropiper as its pungent principle[4] in having the α,β-unsaturated dialdehyde structure. Furthermore, this dial might be considered as an intermediate in the biogenesis of iridoids of Actinidia plant.

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