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201. The Isolation, Structure, and Synthesis of Davana Ether, an Odoriferous Compound of the Oil of *Artemisia pallens* Wall.

by Alan F. Thomas and Gertrud Pitton

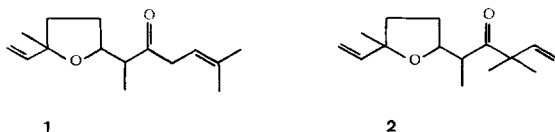
Firmenich & Co., Research Laboratory, Geneva

Dedicated to Dr. Roger Firmenich on the occasion of his 65th birthday

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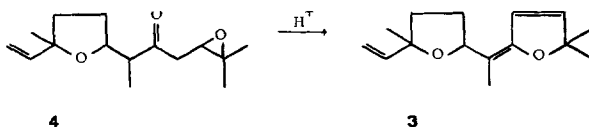
Summary. Several stereoisomers of 2,6,10-trimethyl-2:5,7:10-diepoxy-dodeca-3,5,11-triene (**3**) have been isolated from the oil of *Artemisia pallens*. The synthesis of the isomeric mixture is described.

The isolation [1] and synthesis [2] of davanone (**1**), one of the main components of the essential oil of *Artemisia pallens* Wall. (= 'davana'), and of its isomer artemone (**2**) [3] have recently been reported.



We have found these substances to be odourless when rigorously purified, and in this note report on the structure and synthesis of an odoriferous constituent of the natural oil. Separation was achieved by preliminary chromatography on silica gel, when the odour was associated with the fraction eluted immediately before davanone (**1**) and from which it could be distinguished by a spot on a silica gel thin-layer chromatographic plate that was visible in UV.-light, and gave an olive-grey colour at room temperature when sprayed with phosphomolybdic acid (davanone gives a green colour at 100°). Distillation of this fraction gave further enrichment, the substance responsible for the spot on the thin-layer plate having b.p. 71–75°/0.001 Torr, just lower than that of davanone. Finally, gas chromatography on a Carbowax column showed that the desired fraction has a retention time a little shorter than davanone. This fraction consisted of three closely related isomers having practically identical NMR. and mass spectra. The formula, C₁₅H₂₂O₂ (by microanalysis and mass spectra) is that of a dehydrodavanone, but the IR.-spectrum showed the absence of carbonyl and hydroxyl groups, so the two oxygens must be ether functions. The

NMR. spectrum shows the presence of three quarternary methyl groups with a fourth methyl group attached to a double bond. The methylvinylfuran part of the davanone NMR. spectrum¹⁾ is almost unchanged, so we formulated a working hypothesis of different isomers of structure **3** as representing the isomeric mixture.



This was confirmed by the following synthesis. Davanone was epoxidized with peroxyacetic acid in methylene chloride, and the epoxide **4** was treated for 38 h with *Dowex 50* ion-exchange resin (H^+ -form) in absolute ether, when ring opening of the epoxide occurred with participation of the carbonyl group and dehydration to yield a mixture of isomers having the same retention time on gas chromatography, the same thin-layer chromatographic characteristics, and the same spectra as the natural mixture.

Further details of these compounds and their synthesis will be published in due course.

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202. Recherches sur les arômes

17e communication [1]

Sur l'arôme de framboise, IV

par **M. Winter** et **P. Enggist**

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Dédié à *M. Roger Firmenich* à l'occasion de son 65e anniversaire

(4 IX 71)

Summary. The neutral fraction of medium volatility from raspberry oil has been analysed by gas chromatography and mass spectrometry. From the large number of constituents thirty-nine have been identified, 24 of them for the first time, including dihydro- β -ionone (I), epoxy- β -ionone (II), damascenone (III)¹⁾, theaspirane (IV) and 2-hexen-4-olide (V). According to these results raspberry oil consists mainly of alcohols, ketones, aldehydes and lactones.

Tous les travaux analytiques publiés à ce jour sur l'huile de framboise [2–9], à l'exception de l'analyse des acides [10], décrivent des résultats obtenus par des méthodes d'analyse classiques. Dans la présente communication, l'investigation s'est

¹⁾ *Doriconone* (trade mark of *Firmenich & Cie*, Geneva).