protons, 3 H, 5.6 to 6.4. – UV. (λ_{max}^{EtOH}): 272 nm/ε_{max} 5710. – MS.: 43 (100), 109 (97), 124 (64), 41 and 166 (48), 55, 151, and 163 (39), 149 and 234 (M^{+}) (35). – No OH band in IR.-spectrum.

$C_{15}H_{22}O_2$ (234.3) Calc. C 76.88 H 9.46% Found C 77.09 H 9.41%

The peak with the longer retention time was identified as *2,6,10-trimethyl-cis-7,10-oxido-dodeca-3*E*,11-dien-2-ol-5-one* (**9**). NMR.: 1.00 (3 H, *d*, $J = 7$ Hz, CH_3—CH); 1.23 (3 H) and 1.34 (6 H) (*s*, CH_3—C); 1.6 to 2.0 (4 H, *m*, CH_2CH_2); 2.45 (1 H, *m*, $CH-\underset{\substack{|\\ CO}}{CH}-CH_3$); 4.15 (1 H, *m*, $CH_2-\underset{\substack{|\\ O}}{CH}-CH$), the CH=$CH_2$ signals were at 4.90 ($d \times d$); 5.14 ($d \times d$) and 5.90 ($d \times d$, $J = 10$ and 17 Hz); 6.32 and 6.87 (each 1 H, *d*, $J = 15$ Hz, *CH*=*CH*—CO). – MS.: 43 (100), 111 and 113 (60), 55 and 93 (57), 41 (45), 85 (39), 67 and 69 (37), 95 (23)... 234 (M-18^{+}) and 237 (M-15^{+}) (3). – IR. (CCl_4): 1630, 1668, 1692 cm^{-1}. A satisfactory elemental analysis was not obtained, apparently because of the presence of water in the sample.

We thank Dr. *K. H. Schulte-Elte* for discussions, and information prior to publication.

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224. Terpenoids Derived from Linalyl Oxide. Part 5. 2-(2-Methyl-2-vinyltetrahydrofur-5-yl)-2,6,6-trimethyl-2,6-dihydropyr-3-one, a New Sesquiterpenoid Isolated from *Artemisia Pallens*

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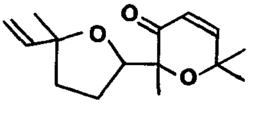
(26. VIII. 74)

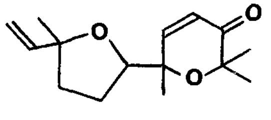
Summary. Based on spectra, the structure of the title compound has been attributed to a new sesquiterpenoid isolated from *Artemisia Pallens*. From the same fraction of the oil, the conjugated unsaturated ketone, isodavanone (**2**), was identified.

Previous papers [1] have described a number of novel compounds related to linalyl oxide that have been isolated from the essential oil of *Artemisia pallens* (= davana oil). In this note, we describe an oxidized, cyclized derivative (**1a**) of davanone (**2**) [1a], and the isolation of isodavanone (**3**), previously prepared as an intermediate in the synthesis of davanone [2].

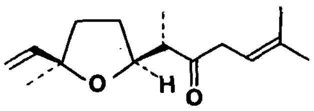
The fraction of davana oil boiling immediately after the main bulk of the davanone still contained much of the latter, but chromatography on silica gel enabled a fraction of higher polarity to be isolated. Gas chromatography of this fraction yielded two principal substances. The first of these, $C_{15}H_{22}O_3$, contained a 2-methyl-2-vinyltetrahydrofuran unit, as shown by the characteristic patters of NMR. signals, linked to a unit having three saturated methyl groups and an α,β-unsaturated ketone. The latter was confirmed by the UV. and IR. spectra, so the most likely structures for this compound were **1a** or **1b**. A decision in favor of **1a** was made on the grounds of the mass spectrum, which showed a strong fragment at *m/e* 140, implying that the pyran part of the molecule was fragmenting with transfer of a hydrogen atom from the tetrahydrofuran part. The easiest way this could occur is *via* a *McLafferty* rearrangement [3] to the ketone group, subsequent loss of a methyl radical accounting for another prominent fragment at *m/e* 125 (*scheme*). There is no certainty about the stereochemistry of this sesquiterpene, but precedent [1] would suggest a *cis*-substitution about the tetrahydrofuran ring.



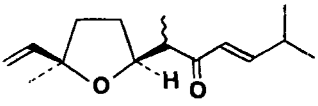
1a



1b

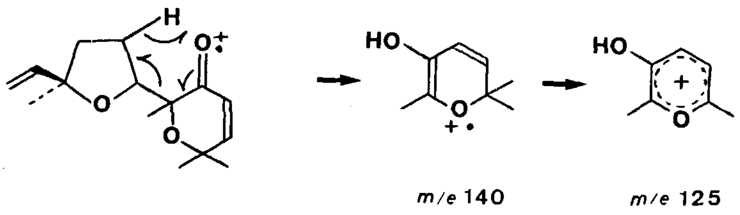


2



3

Scheme



The mass spectrum of the second substance in this fraction was identical with that of the synthetic «isodavanone» of *Ohloff* & *Giersch* [2], but the NMR.-spectrum showed small differences, the most noticeable being that in the synthetic product there were two singlets placed very close together near the position attributed to the 2-methyl group of the tetrahydrofuran ring. Since *Ohloff* & *Giersch* worked with a mixture of stereoisomers and separated the davanones at the last stage, we can now presume that their isodavanone was approximately a 1:1 mixture of two of the four possible stereoisomers. The natural product appeared to be a single isomer, and while it is clear that caution must be exercised in attributing stereochemistry in the absence of another isomer, we would suggest that the most likely stereochemistry is *cis*, as in the case of (+)-davanone [1], on account of the chemical shift of the position of the double doublet of the vinyl proton at 5.88 ppm (*trans*-isomers have this signal at higher field).

Experimental Part

^{1}H-NMR. spectra were measured in CCl_4 with a *Varian* A-60 instrument, and chemical shifts are given in ppm with tetramethylsilane as 0.00 ppm. Other spectral determinations were made as described in previous papers [1].

Isolation of natural materials from Davana Oil. From the fraction of the crude oil having b.p. 95–115°/0.2 Torr (*ca.* 40% of the total), 48 g was chromatographed on 1200 g of silica gel in toluene/ethyl acetate 95:5. After 34 g of almost pure davanone, 7 g of a more polar fraction were eluted. From this fraction, the two main products (about 60% of the total) were purified by gas chromatography on Carbowax, purity being checked by rechromatography on silicone oil. The products were identified (in order of elution) as follows. *2-(2-Methyl-2-vinyltetrahydrofur-5-yl)-2,6,6-trimethyl-2,6-dihydropyr-3-one* (**1a**). – NMR.: 1.22 (3H), 1.36 (3H), 1.42 (6H) (all *s*, CH_3—C$\leqslant$); 1.7–1.9 (4H, *m*, CH_2—CH_2); 4.16 (1H, *t*, *J ca.* 6 Hz, CH_2—$\overset{|}{C}$*H*—O); 4.85 and 5.10 (each 1H, *d* × *d*, *J* = 10 and 17 Hz + further coupling, CH=C*H*$_2$); 5.89 (*d* × *d*, *J* = 10 and 17 Hz, C*H*=CH_2), 5.80 and 6.78 (each 1H, *d*, *J* = 10 Hz, C*H*=C*H*—CO, *Z*-geometry). – MS.: 43 (100), 140 (79), 125 (68), 55 (32), 93 (30), 111 (26), 41 (23), 81 (17), 67 (15), 53 and 96 (11) ... 235 (*M* – 15$^+$, 1). – UV.: λ_{max}^{EtOH} 222 nm, ε_{max} 9850. – IR.: ν_{CCl_4} 1685, 922 cm^{-1}. $[\alpha]_D^{20}$ = – 8.6° (*c* = 10, $CHCl_3$).

$C_{15}H_{22}O_3$ (250.3) Calc. C 71.97 H 8.86% Found C 72.36 H 8.92%

*2,6,10-Trimethyl-7,10-oxidododeca-2*E*,11-dien-5-one* (isodavanone, **2**). – NMR.: 0.98 (6H, *d*, *J* = 7 Hz, C*H*$_3$—CH) superimposed on 1.10 (3H, *d*, *J* = 7 Hz, C*H*$_3$—CH$\leqslant$); 1.23 (3H, *s*, C*H*$_3$—C$\leqslant$); 1.5–2.0 (6H, *m*); *ca.* 4.05 (1H, *m*, CH_2—C*H*(O)—CH); 4.89 and 5.12 (each 1H, *d* × *d*, *J* = 10 and 17 Hz + further coupling, CH=C*H*$_2$); 5.88 (1H, *d* × *d*, *J* = 10 and 17 Hz, C*H*=CH_2); 6.09 (1H, *d*, *J* = 16 Hz, CH=C*H*—CO, *E*-geometry); 6.77 (1H, *d* × *d*, *J* = 6 and 16 Hz, CH—C*H*=CH—CO). – MS.: 97 (100), 41 (51), 93 and 111 (37), 55 (33), 43 (25), 69 (23), 126 (22), 27, 67, 68, 81 (12) ... 193 (8), 221 (3), 236 ($M^{+\cdot}$, 1.4). – UV.: λ_{max}^{EtOH} 227 nm, ε_{max} 8000. – IR.: ν_{CCl_4} 1695, 1672, 1625, 922 cm^{-1}. – $[\alpha]_D^{20}$ = + 29.7° (*c* = 10, $CHCl_3$).

$C_{15}H_{24}O_2$ (236.3) Calc. C 76.22 H 10.24% Found C 76.32 H 10.22%

We thank Dr. *G. Ohloff* & *W. Giersch* for discussions and spectra.

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