well be the cause of the respiratory ailments associated with the crushed fruits. These volatiles may also be excreted from the flowers as widespread respiratory distress occurs when the tree is in bloom [1].

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TWO FURTHER EREMOPHILANE DERIVATIVES FROM *TESSARIA ABSYNTHIOIDES*

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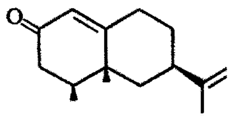
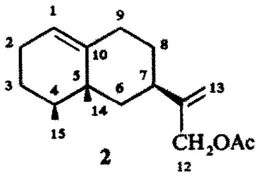
Key Word Index—*Tessaria absinthioides*; *T. integrifolia*; Inuleae; Compositae; new eremophilene derivatives.

From *Tessaria dodoneifolia* (H. et A.) Cabr. a flavanone [1] and from *T. absinthioides* (H. et A.) DC the eremophilene tessaric acid (**1**) [2] has been isolated. A re-investigation of the latter species affords two further eremophilenes, their structures being elucidated by spectroscopic methods. All data are in agreement with the given structures. The retro-Diels–Alder-fragmentation observed in the mass spectra of **2** and **3** establishes the position of the ring double bond and with that also the position of the methyl groups. Though the absolute configuration was not established, the one given in the Scheme is that of all known compounds of this type.

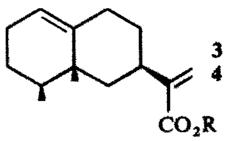
In addition the thiopheneacetylene **5** [3] and the known eudesmane derivative carrissone (**6**) [4] were isolated. The structure of **6** was confirmed by dehydration to **7**. Tessaric acid however was not found.



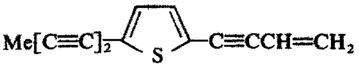
1



2



3: R = H
4: R = Me



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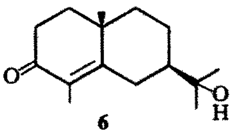

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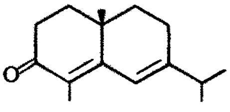

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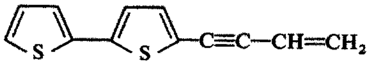

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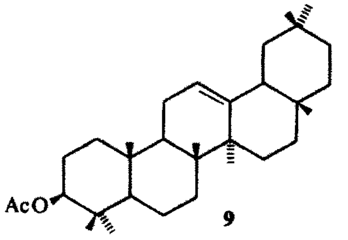

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* Part 103 in the series 'Naturally Occurring Terpene-Derivatives', part 102: Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 780.

Table 1. ^{1}H-NMR signals of **2** and **4** (δ-values, TMS as internal standard, $CDCl_3$)

	2	**4**	*J* (Hz)	Δ*
1-H	*s*(*br*) 5.38	*s*(*br*) 5.39	6β, 7α = 10	0.10
2-H	*m* 2.00	*m* 2.01	6α, 7α = 4	0.16
7-H	*m* 2.40	*dddd*(*br*) 2.58	8β, 7α = 10	0.72
12-H	AB*q* 4.59		8α, 7α = 4	
13-H	*s*(*br*) 5.07	*s*(*br*) 6.12		1.09
13′-H	*s*(*br*) 5.02	*s*(*br*) 5.54		0.39
14-H	*s* 0.93	*s* 0.91		0.18
15-H	*d* 0.88	*d* 0.86	4, 15 = 17	0.14
OAc	*s* 2.11	—		—
OMe	—	*s* 3.76		0.82

*δ-values after addition of about 0.2 equivalents of $Eu(fod)_3$.

The roots of *T. integrifolia* R. et P. contain the dithiophene **8** [3], while the aerial parts afford β-amyrin acetate (**9**) only together with an unidentified isomer. The isolation of two more eremophilenes surely is of chemotaxonomic importance. The only other instances of the occurrence of these compounds outside the Senecioneae are the lactones in *Dugesia mexicana* [5] and *Xanthium canadense* Mill. [6] both Heliantheae. The stereochemistry of the Dugesialactone at C-7 and -8 has to be corrected; the lactone is identical with xanthanodien as shown by comparison of the NMR spectra [6].

EXPERIMENTAL

IR: Beckman IR 9, CCl_4. ^{1}H-NMR: Bruker WH 270, δ-values TMS as internal standard. MS: Varian MAT 711, 70 eV. The air dried plant material was extracted by Et_2O–petrol (1:2) and the extract separated by chromatography (Si gel, act. grade II) and further by TLC (Si gel, GF 254) using Et_2O–petrol (E–P)-mixtures as solvents.

Tessaria absynthioides (*H. et A.*) *DC.* Collected in Aconcaqua, Chile, identified by Prof. C. Marticovena, Conception. 100 g of areal parts yield 2 mg **5** 8 mg **2** (E–P 1:10) 50 mg **3** (E–P 1:2) and 60 mg **6**. **3** is converted to **4** by treatment with etheral diazomethane.

Tessaria integrifolia *R. et P.* Dr. R. King, collected in Ecuador, voucher specimen 6958. 20 g of roots afford 1 mg **8** and 70 g of areal parts, 30 mg **9** and 30 mg of an isomer of **9**.

12-Acetoxyeremophilene (**2**). Colourless oil, IR: OAc 1750, 1240 cm^{-1}. MS: M$^+$ *m/e* 262.193 (6%) (calc. for $C_{17}H_{26}O_2$ 262.193); $-{}^{\bullet}CH_3$ 247(4); $-H_2C{=}CH{-}Me$ (RDA) 220(18); $-AcOH$ 202(72); 202 $-{}^{\bullet}CH_3$ 187(64); 220 $-AcOH$ 160(35); $MeCO^+$ 43(100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546\text{nm}}{-67 \quad -70 \quad -80^\circ} (c = 0.7)$$

Methyleremophilen-12-oic acid (**4**). Colourless oil, IR: $C{=}CCO_2R$ 1720, 1628 cm^{-1}. MS: M$^+$ *m/e* 248.178 (100%) (calc. for $C_{16}H_{24}O_2$ 248.178): $-{}^{\bullet}CH_3$ 233(61): $-{}^{\bullet}OMe$ 217(25): $-MeOH$ 216(31); $-H_2C{=}CHMe$ (RDA) 206(32); 216 $-{}^{\bullet}CH_3$ 201(47); $-{}^{\bullet}CO_2Me$ 189(95).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546\text{nm}}{-91 \quad -96 \quad -109^\circ} (c = 2.6)$$

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