Tabelle 1. ^{1}H-NMR-Daten von **6**–**9** ($CDCl_3$, δ-Werte, TMS als innerer Standard 270 MH_z).

	6	**7**	**8**	**9**
1-H	*d(br)* 4.59	*d(br)* 4.17	*d(br)* 4.63	*d(br)* 4.82
2-H	*t(br)* 5.45	*t(br)* 5.41	*t(br)* 5.61	*t(br)* 6.21
4-H	*m* 2.0	*t* 2.14	*t* 4.02	—
5-H	*m* 2.0	*t* 2.06	*t* 2.28	*d* 3.44
6-H	*t* 5.11	*t* 5.12	*t* 5.10	*t(br)* 5.24
8-H	*m* 2.0	*t* 2.14	*m* 2.0	*m* 2.10
9-H	*m* 2.0	*t* 2.06	*m* 2.0	*m* 2.10
10-H	*t* 5.35	*t* 5.41	*t* 5.07	*t* 5.08
12-H	*s* 4.44	*s* 4.00	*s(br)* 1.71	*s(br)* 1.70
13-H	*s(br)* 1.57	*s(br)* 1.61	*s(br)* 1.59	*s(br)* 1.62
14-H	*s(br)* 1.68	*s(br)* 1.69	*s(br)* 1.68	*s(br)* 1.85
15-H	*s(br)* 1.62	*s(br)* 1.67	*s(br)* 1.62	*s(br)* 1 90
OAc	*s* 2.03		*s* 2.05	*s* 2.14
	s 2.05			

J (Hz): 1,2 = 5,6 = 9,10 = 4,5 = 7.

EXPERIMENTELLES

IR: Beckmann IR 9, CCl_4; ^{1}H-NMR Bruker WH 270; MS: Varian MAT 711, 70 eV, Direkteinlaß; optische Rotation. Perkin–Elmer-Polarimeter, $CHCl_3$. Die frisch zerkleinerten Pflanzenteile (aus Samen vom Botanischen Garten Leninogorsc) extrahierte man mit Et_2O–Petrol (1:2) und trennte die erhaltenen Extrakte zunächst grob durch SC (Si gel, Akt.-St. II), wobei der Blattextrakt zunächst durch Digerieren mit MeOH von gesättigten Kohlenwasserstoffen befreit wurde. Die einzelnen Fraktionen trennte man weiter durch DC (Si gel, GF 254). Als Laufmittel dienten Et_2O–Petrol -Gemische. 1.4 kg Wurzeln ergaben 80 mg **1**, 160 mg **2**, 40 mg **3**, 15 mg **4**, während 7 kg oberirdische Teile 3 mg **5**, 100 mg **6** Et_2O–Petrol, 1:10), 70 mg **8** (Et_2O–Petrol, 1.3), 10 mg **10** und 23 mg **11** lieferten.

12-Acetoxyfarnesolacetat (**6**). Farbloses Öl. IR OAc 1740, 1230 cm^{-1}. MS: M^+ *m/e*; $-H_2C{=}C{=}O$ 262.193 (3%) (ber für $C_{17}H_{26}O_2$ 262.193); 262—AcOH 202 (6); 202—CH_3 187 (6); $MeCO^+$ 43 (100). 20 mg **6** im 2 ml absol. Et_2O versetzte man mit 20 mg $LiAlH_4$. Nach Zusatz von verd. H_2SO_4 nahm man in Et_2O auf und reinigte durch DC (Et_2O–Petrol, 1:1). Man erhielt 12 mg **7**, farbloses Öl. IR: OH 3620 cm^{-1}.

4-Hydroxy-farnesolacetat (**8**). Farbloses Öl. IR: OH 3620; OAc 1740, 1230 cm^{-1}. MS. M^+ *m/e*; $-H_2O$ 262.193 (0.2%) (ber. für $C_{17}H_{26}O_2$ 262.193); —AcOH 220 (0.5); 262 —AcOH 202 (0.6); 138.141 (12) (ber. für $C_{10}H_{18}$ 138.141); $C_6H_{11}{}^+$ 83 (100); $MeCO^+$ 43 (42);.

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546\ \text{nm}}{+12.6 \quad +13.8 \quad +16.7^\circ} \quad (c = 1.0)$$

20 mg **8** in 3 ml CH_2Cl_2 rührte man 12 hr mit 100 mg Chromsäure–Pyridin-Komplex. Nach DC (Et_2O–Petrol, 1 3) erhielt man 10 mg **9**, farbloses Öl. IR OAc 1740, 1230; C=C CO 1690 cm^{-1}. MS. M^+ *m/e* 278 (4%); $-H_2C{=}C{=}O$ 236 (2); —AcOH 218 (5); 218 $-C_5H_9$ 149 (6); $C_6H_{11}{}^+$ 83 (100); $MeCO^+$ 43 (49).

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8β-HYDROXYFRUTICOLONE, A DITERPENOID FROM *TEUCRIUM FRUTICANS*

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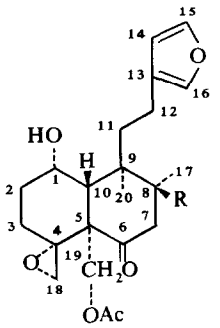
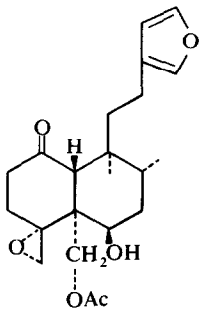
Key Word Index—*Teucrium fruticans*; Labiatae; diterpenoid; clerodane; fruticolone

Examination [1–3] of *Teucrium* species has led to the isolation of a number of clerodane diterpenoids. Recently we have described [4] the isolation and structures of fruticolone and isofruticolone (**1** and **2**) from *T. fruticans*. In continuation of this work, we have isolated a new diterpenoid, 8β-hydroxyfruticolone, $C_{22}H_{30}O_7$, from the more polar fractions. The 8β-hydroxyfruticolone slowly decomposed to form an $\alpha\beta$-unsaturated ketone (**4**). However it could be oxidized to a more stable crystalline diketone (**5**), $C_{22}H_{28}O_7$. The IR absorption and ^{1}H NMR spectra of 8β-hydroxyfruticolone (**3**) together with the ^{13}C NMR spectra of the unsaturated ketone (**4**) and the diketone (**5**), revealed the nature of the oxygen functions. Thus 8β-hydroxyfruticolone (ν_{max} 3450, 1735 (*br*), 875 cm^{-1}) contained a secondary (δ_H 4.42) and a tertiary (δ $^{13}C_{diketone}$ 80.2 (*s*)) hydroxyl group together with an acetoxyl (δ_H 2.00; δ $^{13}C_{diketone}$ 20.6 and 170.2) group. Since the oxidation product (8β-hydroxyfruticolone-2H) showed two cyclohexanone ^{13}C NMR resonances (δ ^{13}C 203.8 and 208.0), the parent compound must possess a cyclohexanone. The remaining oxygen atoms were contained in a terminal epoxide (δ_H 2.26, 3.37, J 5 Hz; δ $^{13}C_{diketone}$ 59.3 (*s*), 52.1 (*t*)) and a β-substituted furan ring (δ_H 6.20, 7.71 and 7.34; δ $^{13}C_{diketone}$ 110.8 (*d*), 125.3 (*s*), 138.4 (*d*), 142.6 (*d*)). In addition the ^{1}H NMR spectrum contained signals

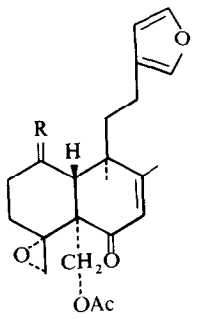
attributable to two tertiary methyl groups (δ_H 1.29(*s*) and 1.47(*s*)), the latter deshielded by an adjacent oxygen function, a pair of doublets (δ_H 2.55 and 3.22, J = 15 Hz) ascribed to a methylene ketone and an AB quartet (δ_H 3.92 and 4.19, J = 11 Hz) corresponding to a —C(—)—CH_2OAc group. The ^{13}C NMR spectrum of the diketone showed that the remaining carbon atoms were five methylenes, one methine and two quarternary carbon atoms. In the mass spectrum there were strong ions at *m/e* 81 and 95 typical of an alkyl furan. The dehydration product of 8β-hydroxyfruticolone had ^1H NMR signals at δ 1.92 (3H) and 5.93 (1H,*s*) and ^{13}C NMR signals at δ 195 (*s*), 163.8 (*s*), 128.6 (*d*) and 24.1 (*q*) typical of a O=C.CH=C(Me) group. A dehydration product (**6**) was also isolated as a minor product during the preparation of the diketone. Hence the tertiary alcohol was β to the cyclohexanone. Brief treatment of the diketone with HCl led to the opening of the epoxide ring and the formation of a compound containing a $-CH_2Cl$ grouping (δ_H 4.51). In view of the isolation of fruticolone (**1**) from *T. fruticans*, the new diterpenoid has been assigned the structure (**3**). The replacement of the C-17 methyl doublet by a singlet and the appearance of a clear methylene ketone signal in the ^1H NMR spectrum is in accord with this. Furthermore the ^{13}C NMR signals (see Table 1) attributable to C-7, C-8 and C-9 show the anticipated downfield shift whilst C-6 and C-10 show a γ-carbon upfield shift consonant with the presence of an additional hydroxyl group at C-8. Since the 1-H signal (δ_H 4.42, *w*/2 7 Hz) was identical to that of fruticolone, the new diterpenoid was assigned the same stereochemistry at that centre. We suggest that the C-8 hydroxyl group has the β-(axial) configuration in view of its ready dehydration and the fact that the adjacent (trans) 20-H_3 NMR signals were little different (δ 1.29 *v* 1.33) from the corresponding signals in fruticolone.



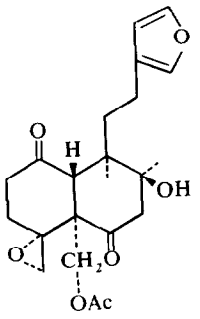
1 R = H
3 R = OH



2



4 R = H, OH
6 R = O



5

EXPERIMENTAL

Teucrium fruticans (2 kg) (collected and identified in the Botanic Gardens, University of Palermo), was extracted and the extract chromatographed as in ref. [4]. Examination of the

Table 1. ^{13}C NMR Signals of **4** and **5** in $CDCl_3$; ppm from Me_4Si

Carbon	Compound **4**, multiplicity		Compound **5**, multiplicity	
1	65.9	*d*	208.0	*s*
2	38.6	*t*	39.4*	*t*
3	34.2	*t*	36.9*	*t*
4	60.6	*s*	59.3	*s*
5	50.8	*s*	55.9	*s*
6	195.4	*s*	203.8	*s*
7	128.6	*d*	51.6	*t*
8	163.8	*s*	80.2	*s*
9	43.0	*s*	42.1	*s*
10	47.2	*d*	53.6	*d*
11	27.8	*t*	30.9	*t*
12	19.9	*t*	22.0	*t*
13	124.2	*s*	125.3	*s*
14	110.5	*d*	110.8	*d*
15	138.5	*d*	138.4	*d*
16	143.2	*d*	142.6	*d*
17	24.1	*q*	24.5	*q*
18	50.8	*t*	52.1	*t*
19	65.2	*t*	62.7	*t*
20	19.2	*q*	29.4†	*q*
O$\underline{C}$O.Me	170.5	*s*	170.2	*s*
OCO.$\underline{C}H_3$	21.1	*q*	20.6†	*q*

*†These assignments may be interchanged.

fraction eluted with 50% EtOAc–petrol gave an oil which was further purified by PLC to afford 8β-hydroxyfruticolone (0.5 g) as an oil which was homogeneous by TLC. It showed ν_{max} 3450, 1735 (*br*), 875 cm^{-1}; δ 1.28 (3H, *s*, 20-H_3), 1.46 (3H, *s*, 17-H_3), 2.01 (3H, *s*, OAc), 2.55 and 3.22 (each 1H, *d*, *J*-15 Hz, 7-H_2), 2.25 and 3.37 (each 1H, *d*, *J* = 5 Hz, 18-H_2), 2.62 (1H, *m*, 10-H), 4.41 (1H, 27 Hz, 1-H), 4.94 and 5.47 (each 1H, *d*, *J* = 13 Hz, 19-H_2), 6.25, 7.18 and 7.30 (each 1H, *m*, 14, 15, and 16-H), MS 406 (M^+, $C_{22}H_{30}O_7$), 388, 373, 328, 315, 297, 234, 215, 203, 175, 159, 135, 121, 109, 95, 81.

Oxidation with chromium trioxide. 8β-Hydroxyfruticolone (200 mg) in dry Py (3 ml) was treated with CrO_3 (200 mg) at room temp. 18 hr. The soln was diluted with EtOAc and washed with dil. HCl, H_2O and dried. The solvent was evapd and the residue chromatographed on SiO_2. Elution with 30% EtOAc–petrol gave (**6**) as an oil, δ 1.48 (3H, *s*, 20-H_3), 1.97 (3H, *s*, 17-H_3), 1.99 (3H, *s*, OAc), 2.85 and 3.25 (each 1H, *d*, *J* = 4 Hz, 18-H_2), 3.28 (1H, *s*, H-10), 3.92 and 4.19 (each 1H, *d*, *J* = 11 Hz, 19-H_2), 5.92 (1H, *s*, 7-H), 6.20, 7.17 and 7.24 (each 1H, *m*, 14, 15, 16-H), MS 386 (M^+), 371, 313, 292, 261, 231, 219, 201, 159, 109, 95, 81. Elution with 50% EtOAc–petrol gave the diketone (**5**) which crystallized from EtOAc–petrol as needles, mp 155° (Found: C, 65.5; H, 6.9 $C_{22}H_{28}O_7$ requires C, 65.3, H, 6.9%), ν_{max} 3400, 1760, 1700, 1250, 875 cm^{-1}, δ 1.38 (3H, *s*, 20-H_3), 1.49 (3H, *s*, 17-H_3), 2.10 (3H, *s*, OAc), 2.79 and 3.21 (each 1H, *d*, 4 Hz, 18-H_2), 2.30 and 3.16 (each 1H, *d*, *J* = 15 Hz, 7-H_2), 3.81 (1H, *s*, H-10), 4.42 (2H, *dd*, *J* = 11.5 Hz), 19-H_2), 6.26, 7.20 and 7.33 (each 1H, *m*, 14, 15 and 16-H), MS 404 (M^+), 386, 313, 292, 159, 109, 95, and 81. The diketone (5) (50 mg) in EtOAc (5 ml) was shaken with 6N HCl (5 ml) for 10 min. The organic phase was dried and the solvent evapd to afford a gum, δ 1.31 and 1.34 (each 3H, *s*, 17 and 20-H_3), 1.98 (3H, *s*, OAc), 2.25 and 3.05 (each 1H, *d*, *J* = 15 Hz, 7-H_2), 3.50 (1H, *s*, 10-H), 3.90 and 4.15 (each 1H, *d*, *J* = 13 Hz, 19-H_2), 4.51 (2H, *s*, 18-H_2), 6.22, 7.15 and 7.30 (each 1H, *s*, 14, 15 and 16-H).

Dehydration of 8β-hydroxyfruticolone. The diterpenoid (100 mg) was allowed to stand in $CHCl_3$ (2 ml) for 3 days. The solvent was evapd and the product purified by PLC to afford the unsaturated ketone (4), ν_{max} 1735, 1680, 875 cm^{-1}, δ 1.46 (3H, *s*, 20-H_3), 1.93 (3H, *d*, *J* = 1 Hz, 17-H_3) 1.98 (3H, *s*, OAc), 2.82 and 3.30 (each 1H, *d*, *J* = 4 Hz, 18-H_2) 3.30 (1H, *m*, 10-H), 3.92 and 4.20 (each 1H, *d*, *J* = 11 Hz, 19-H_2), 5.93 (1H, *s*, 7-H), 6.23, 7.20 and 7.37 (each 1H, *s*, 14, 15 and 16-H), MS 388 (M^+), 373, 313, 292, 232, 219, 201, 189, 173, 159, 95, 81.

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ABSCISIC ACID FROM *PINUS DENSIFLORA* POLLEN*

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Key Word Index—*Pinus densiflora*; Pinaceae; pollen; abscisic acid; germination inhibitor.

Abstract—(+)-Abscisic acid was isolated as the methyl ester from *Pinus densiflora* pollen and identified spectroscopically.

INTRODUCTION

The pollen of *Pinus attenuata* contains growth-inhibitors and growth-stimulators [1, 2]; that of *P. densiflora* contains two ether soluble acidic substances which inhibit the growth of the pollen tubes of this plant, *Tradescantia* spp. and *Impatiens balsamina* [3], and the germination of *Brassica* seeds [4]. Since one of these growth-inhibitors occurs in the so-called β-inhibitor zone, it was suggested that ABA or a closely related compound was present [5]. In this paper the first identification of an inhibitor from the pollen of *P. densiflora* is reported.

RESULTS AND DISCUSSION

The plant material was extracted with CH_2Cl_2 and the extract was fractionated as described in the Experimental. Attempts to isolate the inhibitor by gel filtration through Sephadex LH-20, employing MeOH as eluent, were unsuccessful because of poor resolution from the

*Part 1 in the series 'Constituents of Pine Pollen'.

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