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A VALENCANE SESQUITERPENOID FROM *TEUCRIUM CAROLIPAUI*

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Key Word Index—*Teucrium carolipaui*; Labiatae; sesquiterpene; neo-clerodane diterpene; 11-hydroxy-valenc-1(10)-en-2-one; 19-acetylgnaphalin.

Abstract—11-Hydroxy-valenc-1(10)-en-2-one was isolated from the aerial parts of *Teucrium carolipaui*; it was identical to a synthetic compound previously obtained from isonootkatone (α-vetivone). The already known neo-clerodane diterpenoid 19-acetylgnaphalin was also found in the same source.

INTRODUCTION

In our search for new natural diterpenoids in the genus *Teucrium* [1–4], we have examined the aerial parts of *T. carolipaui* C. Vicioso *ex* Pau. [synonym *T. pumilum* L. subsp. *carolipaui* (C. Vicioso *ex* Pau.) D. Wood.], a species which grows only in small areas of S.E. Spain. From this material we have isolated the neo-clerodane diterpenoid 19-acetylgnaphalin [5–7] as the sole diterpene constituent, together with the sesquiterpene 11-hydroxy-valenc-1(10)-en-2-one (**1**). This last substance has been previously obtained as a synthetic compound starting from β-pinene [8] and sabinene [9] via isonootkatone (α-vetivone) [10, 11] and valenca-1(10),6-dien-2-one, respectively.

RESULTS AND DISCUSSION

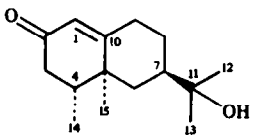
The $[\alpha]_D$ value and the IR, UV, ^{1}H NMR and mass spectra of the sesquiterpenoid found in *T. carolipaui* (see Table 1 and Experimental) were identical with those reported [8, 9] for the synthetic compound. Moreover, the ^{13}C NMR spectrum of **1** (Table 2) was in agreement with the proposed structure, since it showed C-1–C-5, C-9, C-10, C-14 and C-15 carbon atom resonances identical with those of nootkatone (**2**) [12], whereas the chemical shift differences in their C-6–C-8 and C-11–C-13 carbons were consistent with the presence in compound **1** of a tertiary hydroxyl group at the C-11 position instead of the C-11,C-12 double bond of nootkatone (**2**, see Table 2). In particular, the γ-effects on the C-6 and C-8 carbon atoms of **1** ($\Delta\delta$ −4.5 and −4.1, respectively) clearly confirmed this point.

To our knowledge this is the first report of compound **1** as a natural substance.

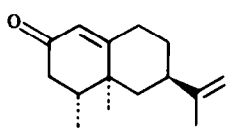
EXPERIMENTAL

For general details on methods, see refs [1–5, 7]. Plant material was collected in June 1985, at Sierra de Orihuela, Alicante (Spain), and voucher specimens are deposited in the Herbarium of the Dipartimento di Biologia, University of Milan, Italy.

Extraction and isolation of the constituents. Dried and finely powdered aerial parts (310 g) were extracted with Me_2CO (3 l. × 3) at room temp. for 3 days. The extracts were evaporated to dryness under red. pres. and low temp. (30°). The residue (18 g) was chromatographed on a silica gel (Merck, No. 7734, deactivated with 15% H_2O) column (350 g). Elution with *n*-hexane–EtOAc (2:1) gave the sesquiterpene **1** (800 mg) and elution with EtOAc–*n*-hexane (2:1) yielded 19-acetylgnaphalin (300 mg) [5–7].



1



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The previously known diterpenoid, 19-acetylgnaphalin, was identified by its physical (mp, $[\alpha]_D$) and spectroscopic IR, ^{1}H NMR, MS) data and by comparison (mmp, TLC) with an authentic sample.

Table 1. ^{1}H NMR data of compound **1** [300 MHz, $CDCl_3$–C_6D_6 (1:1), TMS as internal standard]*

H	δ	H	δ
1	5.76 *d*	8β	1.18 *m*
3α, 3β	2.18–2.36†	9α	2.47 *tdd*
4β	~2.0†	Me-12, Me-13	1.19 *s*, 1.20 *s*
6α	~2.0†	Me-14	0.97 *d*
6β	0.98 *t*	Me-15	1.08 *s*
7α	1.72 *tt*		

J (Hz): 1,9α = 1.7; 4β,14 = 7.0; 6α,6β = 6β,7α = 7α,8β = 12.5; 7α,6α = 7α,8α = 3.1; 8α,9α = 5.1; 8β,9α = 9α,9β = 13.3.

*All these assignments were confirmed by double resonance experiments.

†Overlapped signal.

Table 2. ^{13}C NMR chemical shifts of compounds 1 and 2* ($CDCl_3$ solution, TMS as internal standard)

C	1	2	C	1	2
1	124.2 *d*†	124.7 *d*	9	33.0 *t*	33.1 *t*
2	199.9 *s*	199.2 *s*	10	171.6 *s*	170.1 *s*
3	42.0 *t*	42.2 *t*	11	72.0 *s*	149.0 *s*
4	40.5 *d*	40.5 *d*	12	27.2 *q*‡	109.3 *t*
5	39.1 *s*	39.4 *s*	13	26.8 *q*‡	20.8 *q*
6	39.6 *t*	44.1 *t*	14	14.9 *q*	14.9 *q*
7	43.8 *d*	40.6 *d*	15	16.9 *q*	16.9 *q*
8	27.7 *t*	31.8 *t*			

*Taken from ref. [12].
†SFORD multiplicity.
‡These assignments are interchangeable.

11-*Hydroxy-valenc*-1(10)-*en*-2-*one* (1). A thick oil; $[\alpha]_D^{19}$ +131.2° (EtOH; *c* 0.188); IR ν_{max}^{NaCl} cm^{-1}: 3440 (hydroxyl group), 3020, 1660, 1620 (α,β-unsaturated ketone), 2965, 2880, 1465, 1380, 1300, 1200, 940, 850; UV λ_{max}^{MeOH} nm (log ε): 239 (4.12); ^1H NMR (300 MHz, $CDCl_3$–C_6D_6 1:1): see Table 1; ^{13}C NMR (75.4 MHz, $CDCl_3$): see Table 2; EIMS (direct inlet) 70 eV, *m/z* (rel. int.): 236 $[M]^+$ (2.3), 221 (3.4), 218 (29), 178 (22), 163 (11), 136 (16), 121 (43), 91 (12), 59 (100), 43 (21). (Found: C, 76.41; H, 10.37. Calc. for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24%.) Identical in all respects with the synthetic compound previously described [8, 9].

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