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SHORT REPORTS

9-ACETOXYNEROLIDOL FROM *PHRODUS BRIDGESII*

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Key Word Index—*Phrodus bridgesii*; Solanaceae; sesquiterpene; nerolidol derivative.

Abstract—A new sesquiterpene, 9-acetoxynerolidol, and the known compounds naringenin-4',7-dimethyl ether, naringenin-4'-methyl ether, and kaempferol-3,7,4'-trimethyl ether were isolated from the aerial parts of *Phrodus bridgesii*. The structure of the new compound was established by spectroscopic methods.

INTRODUCTION

Phrodus is an endemic genus, with *ca* four species, distributed in the northern part of central Chile [1]. Up to now nothing has been reported about the chemistry of these species. This paper describes the isolation and structure elucidation of the major compound, a new nerolidol derivative, 9-acetoxynerolidol (**1**), from the aerial parts of *P. bridgesii*.

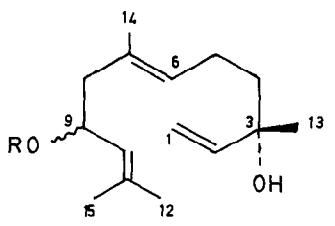
RESULTS AND DISCUSSION

The petrol extract from the aerial parts of *P. bridgesii* afforded naringenin-4',7-dimethyl ether, kaempferol-3,7,4'-trimethyl ether, naringenin-4'-methyl ether and 9-acetoxynerolidol (**1**).

The new sesquiterpenoid **1**, $[\alpha]_D^{25}$ + 13.1 (*c*1.99; EtOH), had a molecular formula $C_{17}H_{28}O_3$ (MS and ^{13}C NMR) which required four sites of unsaturation. As the ^{13}C NMR spectrum (Table 1) revealed three double bonds and one acetoxyl group, **1** had to be acyclic with a farnesane skeleton. The IR spectrum of **1** exhibited bands for an acetoxyl group (1740, 1250 cm^{-1}), double bonds (1650, 926 cm^{-1}), and a hydroxyl group (3450 cm^{-1}), which was considered to be tertiary because the compound could not be acetylated with acetic anhydride in pyridine under standard conditions. Its ^1H NMR spectrum (Table 1) confirmed the presence of an acetoxyl group (δ1.99, *s*, 3H) and had signals at δ5.05 (*dd*, J = 1.2, 10.8 Hz, H-1c), 5.20 (*dd*, J = 1.2, 17.5 Hz, H-1t), and 5.90 (*dd*, J = 10.8, 17.5 Hz, H-2), consistent with those of a vinyl group. This was confirmed by spin-decoupling experiments which showed that the two doublets of doublets centred at δ2.11 (H-8a) and 2.30 (H-8b) are the AB part of an ABX pattern, because irradiation of the signal at δ5.62 (*q*, J = 7.2 Hz, H-9) collapsed these signals to doublets, and the broad doublets at δ5.09 (J = 9.2 Hz, H-10) to a singlet. Irradiation of either of the H-8 protons only collapsed the H-9 proton (δ5.62). The above data, together with the remaining ^1H NMR signals of **1** and ^{13}C NMR absorptions were consistent with the structural features of a nerolidol skeleton, because with the exception of the signals near C-9, the ^1H and ^{13}C NMR data for **1** were very similar to those reported for nerolidol (**2**) [2, 3] and other related compounds [4]. Therefore, placing the acetoxyl group at C-9, **1** is shown to be 9-acetoxynerolidol.

EXPERIMENTAL

Mps uncorr. *Phrodus bridgesii* Miers, was collected in Vicuña, IV Región, Chile, in Sept 1984. A voucher specimen is deposited at Universidad Federico Santa María. The air dried aerial parts (1.0 kg) of *P. bridgesii* were extracted at room temp. with petrol for 24 hr, affording 14.3 g of a syrup. A portion of this syrup (5 g) was chromatographed on a silica gel column (200 g) eluting with 50 ml fractions of petrol–EtOAc (22: 3). The fractions were combined based upon TLC monitoring. Fractions 12–14, after crystallization from petrol, gave naringenin-4',7-dimethyl ether (680 mg). Fractions 16–20, contained a single compound (oil, 2.1 g) 9-acetoxynerolidol (**1**). Fractions 22 and 42–44 gave kaempferon-3,7,4'-trimethyl ether (30 mg) and naringenin-4'-methyl ether (210 mg) respectively. The flavonoids were identified



1 R = Ac
2 R = H

Table 1. NMR spectral data of compounds **1** and **2** [3]

	^{1}H NMR (1)*			^{13}C NMR	
C	δ	*m*	*J* (Hz)	**1**†‡	**2** [3]§
1	5.20 (H-1t)	*dd*	1.2, 17.5	111.7 *t*	111.8
	5.05 (H-1c)	*dd*	1.2, 10.8		
2	5.90	*dd*	10.8, 17.5	145.2 *d*	144.9
3	—	—	—	73.3 *s*	73.5
4	1.53	*m*	—	42.0 *t*	41.8
5	2.00	*m*	—	22.9 *t*	23.0
6	5.17	*t* (*br*)	7.1	128.0 *d*	127.7
7	—	—	—	136.9 *s*	134.8
8	2.30	*dd*	7.6, 13.5	45.4 *t*	48.1
	2.11	*dd*	6.1, 13.5		
9	5.62	*q*	7.2	70.1 *d*	66.0
10	5.09	*d* (*br*)	9.2	123.9 *d*	128.5
11	—	—	—	131.1 *s*	131.8
12	1.71	*s*	—	25.6 *q*	25.7
13	1.30	*s*	—	27.8 *q*	28.0
14	1.62	*s*	—	16.4 *q*	16.2
15	1.70	*s*	—	18.4 *q*	18.2
MeCO	—	—	—	170.3 *s*	
MeCO	1.99	*s*	—	21.2 *q*	

*360 MHz ($CDCl_3$, TMS).
†90.5 MHz ($CDCl_3$, TMS).
‡Multiplicities determined by SFORD.
§25.15 MHz ($CDCl_3$, TMS).

by comparison of their physical (mp, $[\alpha]_D^{25}$) and spectral (^{1}H NMR, MS) properties with those reported in the literature.

9-Acetoxynerolidol (**1**). Transparent oil, 2.1 g; $[\alpha]_D^{25}$ + 13.1 (*c* 1.99; EtOH). IR ν_{max}^{film} cm^{-1}: 3450, 3080, 2980–2860, 1740, 1650, 1450, 1380, 1250, 1030, 926, 840, 760; ^{1}H and ^{13}C NMR: see Table 1; MS *m/z* (rel. int.): 280 $[M]^+$ (3), 238 (15), 220 (5), 138 (12), 127 (23), 93 (10), 85 (100), 71 (12), 68 (11), 55 (16), 43 (63), 41 (23).

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