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2-OXO-LABDA-8(17),13-DIEN-15-OL FROM *OPHRYOSPORUS CHILCA*

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Key Word Index—*Ophryosporus chilca, O peruvianus*, Compositae, labdane derivatives, prenylated *p*-hydroxyacetophenones, cinnamyl derivative

Abstract—The aerial parts of *Ophryosporus chilca* afforded several prenylated *p*-hydroxyacetophenones, two labdane derivatives and a cinnamyl ester *Ophryosporus peruvianus* also contains prenylated *p*-hydroxyacetophenones Three compounds were isolated for the first time, their structures were established by ^{1}H NMR spectroscopy

The South American genus *Ophryosporus* (Compositae, tribe Eupatorieae) has been placed in the subtribe Critoniinae [1] So far only one species has been studied chemically [2] We have now investigated two more species from Peru The aerial parts of *O chilca* (HBK) Hieron afforded, in addition to known compounds, the cinnamyl ester **2** and 2-oxo-labda-8(17),13-dien-15-ol (**3**) together with the corresponding 2-hydroxy derivative **4**, which had been isolated previously [3] The ^{1}H NMR spectrum (Table 1) of **3** was close to that of **4** The presence of a keto group at C-2 followed from the pairs of doublets at δ2 19, 2 42 and 2 16, 2 33 The stereochemistry of the Δ^{13}-double bond was established from the ^{1}H NMR spectrum of the corresponding aldehyde **5**, obtained by oxidation of **3**, as the H-16 signal was shifted downfield (δ2 17) while the other signals were nearly identical to those of **3** except for the H-15 signal which was a low-field doublet at δ10 00, in the spectrum of **5** The absolute configuration of **3** and **4** was not determined

The ^{1}H NMR spectrum of **2** indicated the presence of a cinnamyl derivative (see Experimental) With regard to the molecular formula, pairs of doublets which were coupled with a low-field broadened double-doublet at δ5 17 showed a β-hydroxyprenyl propionic ester

The aerial parts of *O peruvianus* (Gmel) K et R gave several widespread compounds and the new *p*-hydroxyacetophenone derivative **1** The structure could be easily deduced from the molecular formula and the ^{1}H NMR spectrum (see Experimental), which indicated the presence of a symmetrical tetrasubstituted aromatic compound As all the signals could be assigned, the structure directly followed from the chemical shifts of the protons

The investigations of *Ophryosporus* species have shown that anol and prenylated *p*-hydroxyacetophenone derivatives may be of chemotaxonomic relevance

EXPERIMENTAL

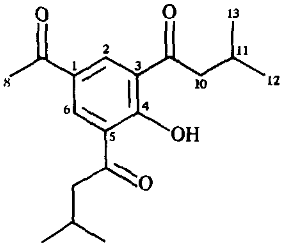
The air-dried plant material, collected in January 1982 in Peru, was extracted with Et_2O–petrol, 1 2 (12 hr room temp), and worked up in the usual fashion Known compounds were identified by comparing 400 MHz ^{1}H NMR spectra with those of authentic samples The extract of the aerial parts of *O chilca* (480 g, voucher RMK 9042) gave CC fractions (100 ml) as follows 1 (petrol), 2 (Et_2O–petrol, 1 10), 3 (Et_2O–petrol, 1 3), 4 (Et_2O–petrol, 1 1) and 5 (Et_2O and Et_2O–MeOH, 10 1) TLC (always SiO_2, PF 254), (Et_2O–petrol, 1 3, detection by UV light, 255 nm) of combined fractions 2 and 3 afforded 120 mg anol isovalerate [4] and 30 mg of the corresponding epoxide [4] TLC (Et_2O–petrol, 1 1) of fraction 4 gave 180 mg 3-[3,3-dimethylallyl]-*p*-hydroxyacetophenone (R_f 0 55), 300 mg 3-[3,3-dimethylallyl]-5-senecioyl-*p*-hydroxyacetophenone [5] (R_f 0 50) and 120 mg 6-acetyl-8-isovaleryl-2,2-dimethylchromene [5]

Table 1 ^{1}H NMR spectral data of compounds **3** and **5** (400 MHz, $CDCl_3$ TMS as internal standard)

	3*	5
H-1	2 19 *dd*	2 19 *dd*
H-1′	2 42 *d*	2 42 *d*
H-3	2 16 *d*	2 17 *dd*
H-3′	2 33 *dd*	2 35 *d*
H-5	1 66 *dd*	1 68 *dd*
H-6	1 49 *m*	1 43 *m*
H-6′	1 84 *m*	1 86 *m*
H-7	2 05 *m*	2 07 *m*
H-7′	2 46 *ddd*	2 48 *ddd*
H-14	5 38 *tq*	5 86 *dtq*
H-15	4 16 *br d*	10 00 *d*
H-16	1 66 *br s*	2 17 *d*
H-17	4 59 *br s*	4 58 *br s*
H-17′	4 91 *br s*	4 96 *br s*
H-18	0 70 *s*	0 75 *s*
H-19	0 85 *s*	0 80 *s*
H-20	1 06 *s*	1 09 *s*

*Signals of H-1 and H-3 may be interchangeable

J (Hz) 1, 1′ = 3, 3′ = 13, 1′, 3 = 2, 5, 6 = 3, 5, 6′ = 12, 6, 7′ = 2 5, 6′, 7′ = 4, 7, 7′ = 13, 12, 14 = 14, 16 = 1, compound **3** 14, 15 = 7, compound **5** 14, 15 = 7 5



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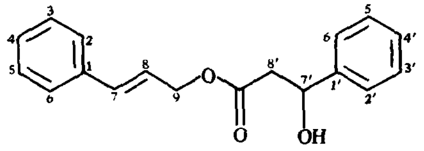

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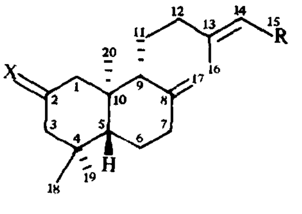

	3	**4**	**5**
X	=O	α OH, H	=O
R	CH_2OH	CH_2OH	CHO

(R_f 0 47) TLC (Et_2O) of fraction 5 afforded 20 mg **2** (R_f 0 73), 80 mg **3** (R_f 0 62) and 100 mg **4** (R_f 0 42)

The extract of the aerial parts of *O peruvianus* (410 g, voucher RMK 9001) gave CC fractions (100 ml) as follows 1 (petrol), 2 (Et_2O–petrol, 1 10 and 1 3), 3 (Et_2O–petrol, 1 1) and 4 (Et_2O and Et_2O–MeOH, 10 1) TLC of fraction 4 (Et_2O–petrol, 1 1) afforded 10 mg 3-[3,3-dimethylallyl]-5-senecioyl-*p*-hydroxy-acetophenone (R_f 0 52), 20 mg 6-acetyl-8-isovaleryl-2,2-dimethyl-chromene (R_f 0 50), 15 mg **1** (R_f 0 47) and 10 mg 3-isovaleryl-5-[1-hydroxy-3,3-dimethylallyl]-*p*-hydroxyacetophenone [6] (R_f 0 40) Compounds **1–3** were homogeneous by TLC in different solvent mixtures (Et_2O–petrol and $CHCl_3$ mixtures), but could not be induced to crystallize Quantities were determined by weight

3,5-Bis-isovaleryl-p-hydroxyacetophenone (**1**) IR $\nu_{max}^{CCl_4}$ cm^{-1} 3520 (OH), 1680, 1640, 1592 (PhCO), MS *m/z* (rel int) 304 168 $[M]^+$ (17) ($C_{18}H_{24}O_4$), 289 $[M - Me]^+$ (14), 271 $[289 - H_2O]^+$ (42), 247 $[M - C_4H_9]^+$ (100), 229 $[247 - H_2O]^+$ (20), ^{1}H NMR ($CDCl_3$, 400 MHz) 8 57 *s* (H-2, H-6), 2 63 *s* (H-8), 2 99 *d* (H-10), 2 32 *tqq* (H-11), 1 05 *d* (H-12, H-13) [*J* (Hz) 10, 11 = 11, 12 = 11, 13' = 6 5]

Cinnamyl-3-hydroxy-3-phenyl propionate (**2**) IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1730 (CO_2R), MS *m/z* (rel int) 264 115 $[M - H_2O]^+$ (8) ($C_{18}H_{16}O_2$), 131 $[PhCH{=}CHCO]^+$ (18), 117 $[PhCH{=}CHCH_2]^+$ (41), 104 $[PhCH{=}CH_2]^+$ (100), CIMS (isobutane) 283 $[M + 1]^+$ (0 5), 117 $[PhCH{=}CHCH_2]^+$ (100), ^{1}H NMR ($CDCl_3$) 7 4–7 25 *m* (10 H), 6 66 *br d* (H-7), 6 27 *dt* (H-8), 4 81 *dd* (H-9), 2 83 *dd* (H-$8'_1$), 2 77 *dd* (H-$8'_2$), 5 17 *br dd* (H-7') [*J* (Hz) 7, 8 = 1 5, 7, 9 = 1, 8, 9 = 6 5, 7', $8'_1$ = 8 5, 7', $8'_2$ = 4 , $8'_1$, $8'_2$ = 16]

2-Oxo labda-8(17),13-*dien*-15 *ol* (**3**) IR $\nu_{max}^{CCl_4}$ cm^{-1} 3360 (OH), 1710 (C=O), MS *m/z* (rel int) 304 240 $[M]^+$ (5) ($C_{20}H_{32}O_2$), 289 $[M - Me]^+$ (14), 205 $[M - CH_2CH_2C(Me){=}CHCH_2OH]^+$ (18), 55 $[C_4H_7]^+$ (100) 3 mg **3** in 1 ml CH_2Cl_2 were stirred for 6 hr with 10 mg pyridine dichromate TLC (Et_2O–petrol, 1 1) afforded 1 mg **5**, ^{1}H NMR see Table 1

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