Table 1. Fatty acid composition of lipids (percentage in each class) from the secretion of glandular trichomes

Lipid classes	Total lipids (%)	Fatty acids 12:0	14:0	16:0	16:1	18:0	18:1	18:2
Total lipids	—	1.5	1.2	21.7	1.6	3.9	51.8	18.3
Free fatty acids	53.7	2.5	1.4	18.0	tr.	2.4	73.2	2.8
Pigments	23.8	tr.	1.1	43.2	3.7	5.2	34.5	12.3
MG	0.8	10.1	tr.	13.2	tr.	—	67.2	9.5
TG	1.6	—	7.9	19.5	4.3	—	54.3	1.4
MGDG	16.2	—	—	1.8	tr.	6.4	17.5	74.3
DGDG	3.3	—	—	29.5	1.5	14.2	tr.	54.8

tr., Trace.

The fatty acid components of the total lipids extract and that of each of the lipid classes were determined by converting an aliquot of each fraction into methyl esters [5]. Qualitative and quantitative analysis of the fatty acid methyl esters were performed isothermally at 165° on a Varian aerograph 1400 (connected with a calculator CDS 111) using 3 m × 3 mm columns of 4% DEGS on Chromosorb with a N_2 flow rate of 20 ml/min. The int standard was heptadecanoic acid, which is not present in lipids of *Ailanthus altissima.*

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p-HYDROXYACETOPHENONE DERIVATIVES FROM *SENECIO GRAVEOLENS*

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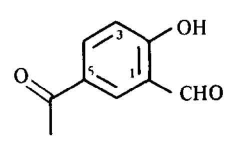
Key Word Index—*Senecio graveolens*; Compositae; *p*-hydroxyacetophenone derivatives; dihydroeuparin.

Abstract—5-Acetylsalicylaldehyde and 4-hydroxy-3(3′-hydroxyisopentyl) acetophenone were isolated from *Senecio graveolens* in addition to the already known compounds dihydroeuparin, 4-hydroxy-3-(isopenten-2-yl)acetophenone and 3-hydroxy-2,2-dimethyl-6-acetylchromane.

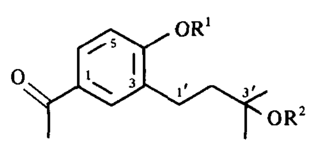
INTRODUCTION

Senecio (tribe Senecioneae) comprises *ca* 1300 species, of which 208 are represented in Chile [1]. *Senecio graveolens*, 'chachacoma' an endemic species found in northern Chile at altitudes above 3000 m, is a shrub widely employed as a remedy for altitude sickness ('puna' or 'soroche'). In this paper we report the isolation and structural elucidation of five aromatic compounds present in *S. graveolens*, namely, dihydroeuparin [2], 4-hydroxy-3-(isopenten-2-yl)acetophenone [3], 3-hydroxy-2,2-dimethyl-6-acetylchromane [4] and two new *p*-hydroxyacetophenone derivatives, 5-acetylsalicylaldehyde (**1**) and 4-hydroxy-3-(3′-hydroxyisopentyl)acetophenone (**2**).

In connection with the popular medicinal use of this plant it is of interest to note that dihydroeuparin was recently shown [5] to exhibit a strong hypotensive activity



1



2 $R^1 = R^2 = H$
3 $R^1 = OAc, R^2 = H$
4 $R^1 = R^2 = OAc$

in rats at physiological concentrations. This biological activity, which may also be extended to the other acetophenone derivatives reported in this communication, could be directly associated to its popular use.

RESULTS AND DISCUSSION

Redissolution of the ethanolic extract in ethanol–water (2:1) gave a soluble fraction (A) and a semicrystalline precipitate (B). Silica gel CC of A, after treatment with lead acetate [6] afforded **1** and **2**. The known compounds were isolated after silica gel CC of fraction B and identified by comparison with authentic samples (TLC, IR, ^{1}H NMR and mass spectra).

Compound **1**, $C_9H_8O_3$ ($[M]^+$ *m/z* 164), contained an aldehyde, a ketone and a phenolic group (IR ν_{max} cm^{-1}: 1680, 1660 and 3200, respectively). The ^{1}H NMR spectrum showed a $C\underline{H}_3CO$ singlet (δ2.59), an aldehyde proton at δ9.99 and a broad singlet at δ11.40 indicative of a phenolic proton *ortho* to a carbonyl group. The remaining signals indicated a 3,4-disubstituted acetophenone derivative [7]: one proton doublet at δ7.08 (J = 8.5 Hz, H-3), a double doublet at δ8.15 (J = 8.5, 2.5 Hz, H-4) and doublet at δ8.25 (J = 2.5 Hz, H-6). Compound **1** was thus established as 5-acetylsalicylaldehyde. The alternative structure, 4-acetylsalicylaldehyde, was discarded on the basis of biogenetic considerations and comparison of the chemical shifts of the aromatic protons with those of related compounds [3, 7].

Compound **2**, $C_{13}H_{18}O_3$ ($[M^+$ *m/z* 222) showed absorptions corresponding to an aromatic ketone and two hydroxyl groups (IR ν_{max} cm^{-1}: 1650, 3360 and 3140, respectively). Acetylation at room temperature gave an aromatic monoacetate, **3** and a diacetate, **4**, when the acetylation was carried out in refluxing pyridine. The ^{1}H NMR spectrum of **2** (Table 1) was consistent with a 3,4-disubstituted acetophenone derivative, bearing an isopentyl residue and a phenolic hydroxyl: the monoacetylated derivative, **3**, indicated a *p*-hydroxyacetophenone ($\Delta\delta$0.3 downfield shift of H-5) and a tertiary aliphatic hydroxyl on the isopentyl substituent (a 6H singlet at δ1.3 shifted to δ1.5 in the diacetate, **4**). Structures **3** and **4** are consistent with these data. The assignment of the ^{13}C NMR spectrum of **2**, 4-hydroxy-3-(3'-hydroxyisopentyl)acetophenone, was made on basis of the observed multiplicities (SFORD) and aromatic additivities rules.

EXPERIMENTAL

Plant material. Senecio graveolens Wedd. was collected in Toconce (Calama) in April 1979 Voucher specimens are deposited in the Herbarium of the University of Concepción.

Extraction and separation. Dried and ground aerial parts (800 g) were Sohxlet extracted with EtOH and the extract separated into soluble (A) and insoluble (B, 187 g) fractions after treatment with EtOH–H_2O (2:1).

Silica gel CC of fraction B (20 g) gave, after elution with petrol containing increasing amounts of EtOAc, dihydroeuparin (940 mg), 4-hydroxy-3-(isopenten-2-yl)acetophenone (200 mg) and 4-hydroxy-2,2-dimethyl-6-acetylchromane (25 mg). Their identity was confirmed by direct comparison with authentic samples.

Fraction A, after treatment with $Pb(OAc)_2$ [6], was separated into C_6H_6 (6.8 g) and $CHCl_3$ (14 g) soluble fractions. The C_6H_6 fraction was chromatographed over silica gel and elution with 2% MeOH–$CHCl_3$ afforded **1** (20 mg) and **2** (983 mg).

5-Acetylsalicylaldehyde (**1**). Amorphous solid. IR ν_{max}^{KBr} cm^{-1}:

Table 1. ^{1}H NMR data of **2***, **3**† and **4**† (deuterochloroform, TMS as internal standard)

	2	3	4
H-2	7.75 (*d*, J = 2.0 Hz)	7.8 (*m*)	7.8 (*m*)
H-5	6.80 (*d*, J = 8.0 Hz)	7.1 (*d*, J = 9.0 Hz)	7.1 (*d*, J = 9.0 Hz)
H-6	7.73 (*dd*, J = 8.0, 2.0 Hz)	7.8 (*m*)	7.8 (*m*)
H-1'	2.76 (*t*, J = 7.0 Hz)	2.7 (*m*)	2.6 (*m*)
H-2'	1.79 (*t*, J = 7.0 Hz)	1 8 (*m*)	2.0 (*m*)
H-4'	1.30 (*s*)	1.3 (*s*)	1.5 (*s*)
H 5'	1.30 (*s*)	1.3 (*s*)	1.5 (*s*)
CH_3–CO	2.54 (*s*)	2.6 (*s*)	2.6 (*s*)
CH_3–COOR	—	—	2.0 (*s*)
CH_3–COOAr	—	2.3 (*s*)	2.4 (*s*)

*Measured at 400 MHz.
†Measured at 60 MHz.

3200, 2860, 1680, 1580, 1480; MS m/z (%). 164 $[M]^+$ ($C_9H_8O_3$), 149 (100), 147 (8), 135 (18), 121 (15), 93 (33); ^1H NMR (400 MHz, $CDCl_3$). see text.

4-*Hydroxy*-3-(3′-*hydroxyisopentyl*)*acetophenone* (**2**). Colourless needles, mp 100–102° (C_6H_6). IR ν_{max}^{KBr} cm^{-1}: 3360, 3140, 1650, 1600, 1650, 1600, 1580, 1430; MS m/z (%): 222 $[M]^+$ ($C_{13}H_{18}O_3$), 207 (9), 205 (6), 189 (54), 161 (17), 149 (76), 133 (28), 43 (100); ^1H NMR (400 MHz, $CDCl_3$): see Table 1; ^{13}C NMR (20 MHz, $CDCl_3$): δ24.82 (*t*, C-2′), 26.19 (*q*, C-4′, C-5′) 29.40 (*q*, $\underline{Me}$–CO), 42.85 (*t*, C-1′), 71.98 (*s*, C-3′), 116.02 (*d*, C-5), 129.01 (*d*, C-6), 129.78 (*s*, C-1, C-3), 130.95 (*d*, C-2), 159.48 (*s*, C-4) 184.57 (*s*, Me–$\underline{C}$O).

4-*Acetoxy*-3-(3′-*hydroxyisopentyl*)*acetophenone* (**3**). Colourless oil IR ν_{max}^{film} cm^{-1}: 3450, 1760, 1680, 1370, 1210; ^1H NMR (60 MHz, $CDCl_3$): see Table 1.

4-*Acetoxy*-3-(3′-*acetoxyisopentyl*)*acetophenone* (**4**). Colourless oil. IR ν_{max}^{film} cm^{-1} 1760, 1680, 1580, 1370; ^1H NMR (60 MHz, $CDCl_3$): see Table 1.

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TERPENOIDS FROM THE SEED OF *PLATYCLADUS ORIENTALIS*

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Key Word Index—*Platycladus orientalis*; Cupressaceae; diterpenoids; pinusolide; 15,16-bisnor-13-oxo-8(17)-labden-19-oic acid; 15,16-bisnor-13-oxo-8(17),11*E*-labdadien-19-oic acid; 14,15,16-trisnor-8(17)-labdene-13,19-dioic acid; 12*R*,13*RS*-dihydroxycommunic acid.

Abstract—Four labdane-type diterpenoids have been isolated from the seed of *Platycladus orientalis*. Their structures have been elucidated by spectroscopic and chemical methods.

INTRODUCTION

Platycladus is a monotypic genus. The heartwood constituents of *Platycladus orientalis* (L.) Franco (= *Biota orientalis* Endl.) have been extensively investigated [1–5]. We have now investigated the terpenoid components of the seed of this species, from which we have isolated and identified several diterpenoids. This paper deals with the isolation and structural elucidation of these compounds.

RESULTS AND DISCUSSION

The ethyl acetate extract was fractionated into an acidic and a neutral fraction. The neutral fraction from which acylglycerols had been removed was analysed by GC/MS. The mass spectra revealed the presence of cedrol, sitosterol and pinusolide (**1**), the latter of which was also isolated from the fraction by CC.

The acidic fraction gave two bisnor diterpenoids (A and B), one trisnorditerpenoid (C) and a communic acid derivative (D), as well as *trans*-communic, sandaracopimaric and isopimaric acids.

Compound A (**2**) was purified as its methyl ester, after methylation with diazomethane. The methyl ester (**2a**), $C_{19}H_{30}O_3$, $[\alpha]_D^{30}$ +60.6°, MS m/z: 306 $[M]^+$ showed IR absorptions at 3080, 1640, 890 ($>C=CH_2$), 1710 and 1155 cm^{-1} (–COOMe). The ^1H NMR spectrum (Table 1) indicated the presence of two tertiary methyl groups, a methyl ketone group, a methoxycarbonyl group and an exomethylene group. These spectral data suggested that **2** was a bisnor diterpenoid identical with a labdane isolated