146 (69), 131 (47), 119 (30), 103 (37), 91 [$PhCH_2$]$^+$ (44), 77 [Ph]$^+$ (40), 69 (45).

Synthesis of **1**. *Trans*-3, 4-methylenedioxycinnamic acid (2.5 g) was treated with CH_2N_2 to give *trans*-3, 4-methylenedioxymethyl cinnamate (2 g) as qhite crystals from MeOH, mp 132–133° (lit.[1], mp 133–134°). The Me ester (2 g) on refluxing with $LiAlH_4$–Et_2O afforded *trans*-3, 4-methylenedioxycinnamyl alcohol (1.5 g) as white needles from petrol, mp 120–121° (lit.[2], mp 123°). The alcohol (100 mg) dissolved in 2 ml DMSO was stirred for 15 min under N_2 with a soln of 0.3 ml $DMSO^-$ (prepared from DMSO and NaH). An excess of MeI (0.3 ml) was then added and the soln stirred for a further 30 min. The mixture was added to H_2O and the soln extracted twice with CH_2Cl_2. The CH_2Cl_2 soln, dried ($MgSO_4$) was evapd *in vacuo* to give **1**, an oil (50 mg), bp 247–249°. IR, ^{1}H NMR and MS were identical to those of the natural product.

Synthesis of **2**. The same steps were used. *Trans*-3, 4-dimethoxy cinnamic acid (2.5 g) treated with CH_2N_2 gave *trans*-3, 4-dimethoxy methyl cinnamate (2.2 g) as colourless crystals from MeOH, mp 61–62° (lit.[3], mp 63–64°). $LiAlH_4$ reduction of the ester in turn afforded *trans*-3,4-dimethoxycinnamyl alcohol (1.6 g) as colourless needles from aq. MeOH, mp 76–77° (lit.[4], mp 78°). Methylation of the alcohol (100 mg) was achieved with $DMSO^-$–MeI as described above, to give **2** as an oil (55 mg), bp 253–255°. The IR, ^{1}H NMR and MS were identical to those of the natural material.

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REFERENCES

1. Robinson, R. and Young, P. C. (1935) *J. Chem. Soc.* 1412
2. Pauly, H., Schmidt, H. and Böhme, E. (1924) *Chem. Ber.* **57B**, 1327.
3. Klosterman, H. J. and Muggli, R. Z. J. (1959) *J. Am. Chem. Soc.* **81**, 2188.
4. Freudenberg, K. and Schumacher, G. (1954) *Chem. Ber.* **87**, 1882.

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A COMPOUND WITH ANTIMICROBIAL ACTIVITY ISOLATED FROM THE RED SEAWEED *LAURENCIA CHILENSIS*

HUGO VALDEBENITO, MAGALIS BITTNER, PETER G. SAMMES,* MARIO SILVA† and WILLIAM H. WATSON‡

Chemistry of Natural Products Laboratory, Department of Botany, Facultad de Ciencias Biológicas y de Recuros Naturales, Universidad de Concepción, Chile; *Department of Organic Chemistry, University of Leeds, Leeds, U.K.; ‡Department of Chemistry, Texas Christian University, Texas, U.S.A.

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Key Word Index—*Laurencia chilensis*; Rhodomelaceae; Ceramiales; alga; 3-hydroxy-4-methylacetophenone.

Abstract—3-Hydroxy-4-methylacetophenone has been investigated in the red seaweed *Laurencia chilensis*.

The constituents of *Laurencia chilensis* De Toni, Forti et Howe, have not been previously investigated and a mixed collection of ⊕, ♂ and ♀ stages was collected in February 1980 at Cocholgüe (36°36'S: 72°59'W), Bahía Concepción, Chile.

The fresh ground alga (11.5 g) was extracted with $CHCl_3$ and after removal of solvent, *in vacuo* at 40°, it gave a non-volatile extract *A* (29 g). The yellowish $CHCl_3$ soln was distilled at 30° *in vacuo* to give a volatile extract *B* (6.5 g).

†To whom enquiries should be addressed.

The $CHCl_3$ extract *B* was chromatographed over Si gel (Merck 0.05–0.2 nm) and elution with $CHCl_3$ gave a mixture of compounds which was purified by further chromatography over Si gel. Elution with $CHCl_3$ gave 3-hydroxy-4-methylacetophenone (13 mg), mp 105–107° ($CHCl_3$). λ_{max}^{MeOH} nm (ϵ): 214 (7500), 222 (8470.5), 260 (5117.6), 310 (1588.2). $\lambda_{max}^{MeOH+NaOH}$ nm: 240, 270, 352. ν_{max}^{Nujol} cm^{-1}: 3400, 1660, 1610, 1580, 1130, 1070, 1020, 980, 900, 890 and 810. ^{1}H NMR ($CDCl_3$, 100 MHz) (δ): 7.48 (2H, *s*, H-5, H-6), 7.38–7.40 (1H, *d*, H-2, J = 1.82 Hz), 5.68 (1H, *s*, OH), 2.57 (3H, *s*, $CO-CH_3$), 2.31 (3H, *s*, CH_3). MS *m/z* (%) 150 M$^+$ (36), 136

(8.9), 135 (100), 133 (5.5), 121 (2.4), 108 (4.6), 107 (23.5), 106 (2.7), 105 (1.6), 79 (17.7), 78 (6.3), 77 (21), 53 (5.4). The structure of this compound was further confirmed by X-ray diffraction. 3-Hydroxy-4-methylacetophenone is one of the active components of the extract, which shows moderate antimicrobial activity against *Staphylococcus aureus* ATCC 6538P, *Escherichia coli* UCCS1, *Flavobacterium* sp., *Alcaligenes* sp. and *Candida albicans*.

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SIMPLE COUMARINS FROM TWO POPULATIONS OF *DIOSMA ACMAEOPHYLLA**

WILLIAM E. CAMPBELL, GORDON J. PROVAN† and PETER G. WATERMAN†,‡

Department of Organic Chemistry, University of Cape Town, Rondebosch, 7700, South Africa; †Phytochemistry Research Laboratory, Department of Pharmaceutical Chemistry, University of Strathclyde, Glasgow G1 1XW, U.K.

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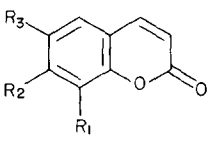
Key Word Index—*Diosma acmaeophylla*; Rutaceae; 7-, 6,7- and 7,8-oxygenated coumarins; chemical systematics.

Abstract—Investigation of two collections of *Diosma acmaeophylla* afforded seven simple coumarins, three of which were common to both samples. The chemotaxonomic significance of the isolated coumarins is discussed.

INTRODUCTION

Diosma L. (Rutaceae–Diosmeae) is a genus of *ca* 30 species, occurring only in South Africa and with most species of limited distribution [1–3]. Screening of a number of species has revealed volatile oils, flavonoids and coumarins ([4]; Waterman, P. G., unpublished). Here we report on the coumarins of the aerial parts of two samples of *D. acmaeophylla* E. and Z., a sclerophyllous shrub of widespread but localized distribution in Cape Province.

From the specimen Williams-2400, collected at Stagmanskop, 11.5 km north of the summit of Pikenienskraal Pass, six coumarins were obtained by CC of a petrol extract over Si gel. Two were identified as herniarin (**1**) and scoparone (**2**) by direct comparison with authentic samples and a further two, 7-(3′,3′-dimethylallyloxy)-coumarin (**3**) and 7,8-methylenedioxycoumarin (**4**), by comparison of physico-chemical data with that published [5, 6]. A fifth coumarin analysed for $C_{15}H_{16}O_4$. Signals in the ^1H NMR spectrum at δ 1.79, 4.68 and 5.52 and facile loss of *m/z* 69 $[C_5H_9]^+$ in the EIMS indicated a 3′,3′-dimethylallyloxy substituent. The remaining seven protons gave ^1H NMR resonances for a methoxyl substituent and two pairs of *ortho*-coupled protons. These data are compatible with a 7, 8-oxygenated coumarin but fail to distinguish between structures **5** and **6**. The coumarin was identified as **5** on the basis of a ^1H NMR shift experiment using Eu(fod)$_3$. Two complexing sites occur in **5** and **6**, between C-7 and C-8 and at C-2. Complexation between C-7 and C-8 will affect both OCH_2– and OMe approximately equally, but complexation at C-2 will affect the C-8 substituent preferentially [7]. The shifts observed for OMe and OCH_2– were 0.41 and 0.26 of that observed for H-3, clearly placing the methoxyl at C-8. Cou-



	R_1	R_2	R_3
1	H	OMe	H
2	H	OMe	OMe
3	H	$OCH_2CH{=}C(Me)_2$	H
4	$O\text{-}CH_2\text{-}O$		H
5	OMe	$OCH_2CH{=}C(Me)_2$	H
6	$OCH_2CH{=}C(Me)_2$	OMe	H
7	OMe	OH	H
8	H	$OCH_2CH{=}C(Me)_2$	OMe

*Part 14 in the series "Chemosystematics in the Rutaceae". For Part 13 see Khalid, S. A. and Waterman, P. G. (1981) *Phytochemistry* **20**, 2761.

‡Author to whom correspondence should be addressed.