(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**

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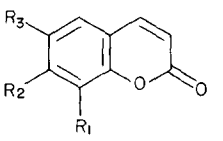
**Key Word Index**—*Diosma acmaeophylla*; Rutaceae; 7-, 6,7- and 7,8-oxygenated coumarins; chemical systematics.

**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 Screening of a number of species has revealed volatile oils, flavonoids and coumarins ([4]; Waterman, P. G., unpublished).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 $\delta$ 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.

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marin **5** is new to the Rutaceae but has previously been reported from *Artemisia apiacea* Hance [8]. The sixth coumarin analysed for $C_{10}H_8O_4$ and was phenolic. It was identified as **7** by comparison with the hydrolysis product of **5** and is presumed to be an artefact of **5**.

From the specimen Williams–2009, collected near Paleisheuwel at the northern boundary of the Berg River valley, four coumarins were obtained by prep. TLC of a petrol extract on Si gel. Three of the coumarins were identified as **2–4** and the fourth as 6-methoxy-7-(3′,3′-dimethylallyloxy)-coumarin (**8**). All were characterized by comparison of UV, IR, $^1$HNMR, EIMS and mp with published data [9, 6, 7, 10] respectively.

Compared with other tribes of the Rutaceae, little is known about the distribution of coumarins in the Diosmeae [11]. Simple coumarins, but not furano- or pyranocoumarins, have now been recorded in four genera, *Agathosma* [5, 12], *Coleonema* [13, 14], *Diosma* and *Phyllosma* [15]. In *Agathosma, Diosma* and *Phyllosma* isolated coumarins are characterized by oxygenation patterns involving C-6, C-7 and C-8. Prenylation, when it occurs, has so far been restricted to *O*-prenylation at C-7. By contrast in *Coleonema* species ([13, 14] Gray, A. I., unpublished) *C*-prenylation commonly occurs at C-6.

## EXPERIMENTAL

*Plant material.* Voucher specimens for the two samples of *Diosma acmaeophylla* examined have been lodged at the Herbarium of the Newlands Botanic Gardens, Kirstenbosch, S. Africa.

*Isolation and identification of coumarins from Williams–2400.* Powdered aerial parts (290 g) were extracted with petrol (bp 40–60°). Concn gave a solid (8 g) which was chromatographed over a column of Si gel. Elution with petrol (bp 60–80°) containing increasing amounts of EtOAc gave the following:

7-(3′,3′-*Dimethylallyloxy*)-*coumarin* (**3**), (11 mg). Mp 75–76° (lit. [5] 77–78°). Found: [M$^+$] 230.0949; $C_{14}H_{14}O_3$ requires 230.0943.

*Herniarin* (**1**), (23 mg). Mp 115–117° (lit. [16] 117–118°). Found: [M]$^+$ 176.0483; $C_{10}H_8O_3$ requires 176.0473.

7,8-*Methylenedioxy-coumarin* (**4**), (8 mg). Mp 175–177° (lit. [6] 187–189°). Found: [M]$^+$ 190.0263; $C_{10}H_6O_4$ requires 190.0266.

8-*Methoxy*-7-(3′,3′-*dimethylallyloxy*)-*coumarin* (**5**), (13 mg). Needles from petrol (bp 60–80°), mp 102–103° (lit. [8] 101°). Found: [M]$^+$ 260.1039; $C_{15}H_{16}O_4$ requires 260.1049. UV $\lambda_{max}^{EtOH}$ nm: 250sh, 257, 318. IR $\nu_{max}^{KCl}$ cm$^{-1}$: 1925. $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 1.79 (6H, *s*, 3′-$(Me)_2$), 3.99 (3H, *s*, OMe), 4.68 (2H, *d*, $J = 6$ Hz, $H_2$-1′), 5.52 (1H, *t*, $J = 6$ Hz, H-2′), 6.26, 7.62 (2H, AB*q*, $J = 10$ Hz, H-3 and H-4), 6.89, 7.14 (2H, AB*q*, $J = 9$ Hz, H-6 and H-5). EIMS *m/z* (rel. int.): 260 [M]$^+$ (14), 192 (100), 177 (39), 164 (35).

*Daphnetin 8-methyl ether* (**7**), (7 mg). Amorphous solid. Found: [M]$^+$ 192.0410; $C_{10}H_8O_4$ requires 192.0423. UV $\lambda_{max}^{EtOH}$ nm: 257, 325; (+NaOH) 280, 355. IR $\nu_{max}^{KCl}$ cm$^{-1}$: 3340, 1700. $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 4.13 (3H, *s*, OMe), 6.24 (1H, *s*, replaceable by $D_2O$, OH), 6.25, 7.64 (2H, AB*q*, $J = 10$ Hz, H-3 and H-4), 6.90, 7.14 (2H, AB*q*, $J = 9$ Hz, H-6 and H-5). EIMS *m/z* (rel. int.): 192 [M]$^+$ (100), 177 (68), 164 (58). Hydrolysis of **5** in dil. $H_2SO_4$ gave a product identical to **7**.

*Scoparone* (**2**), (17 mg). Mp 142–144° (lit. [9] 144–146°). Found: [M]$^+$ 206.0569; $C_{11}H_{10}O_4$ requires 206.0579.

*Isolation and identification of coumarins from Williams-2009.* Dried, milled aerial parts (300 g) were extracted with petrol (bp 60–80°). Concn gave a brown solid which was fractionated by prep. TLC (Si gel: solvent; $C_7H_{16}$–EtOAc, 10:3) to give **3** (10 mg), mp 74–75°; **4** (12 mg), mp 187–188°; **2** (62 mg), mp 145–146°; and 6-methoxy-7-(3′,3′-dimethylallyloxy)-coumarin (**8**), (8 mg). Mp 79–80° (lit. [10] 81–82°). Found: [M]$^+$ 260.1041; $C_{15}H_{16}O_4$ requires 260.1049.

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