Bisresorcinol Derivatives from *Grevillea glauca*

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Seven new and three known bisresorcinols, grevirobstol A (= 5,5′-((6*Z*,9*Z*)-hexadeca-6,9-diene-1,16-diyl)bisresorcinol; **8**), 5,5′-[(8*Z*)-hexadec-8-ene-1,16-diyl]bisresorcinol (**9**), and 2-methyl-5,5′-[8*Z*)-hexadec-8-ene-1,16-diyl]bisresorcinol (**10**) were isolated from the stems of *Grevillea glauca*. The new compounds were identified on the basis of spectroscopic data as (*Z*)-6,7-didehydroglaucone A (**1**), glaucones A and B (**2** and **3**, resp.), 2-(3-hydroxyisopentyl)bisnorstriatol (**4**), 2-(3-methylbut-2-en-1-yl)bisnorstriatol (**5**), 2′-methylgrebustol A (**6**), and glaucane (**7**).

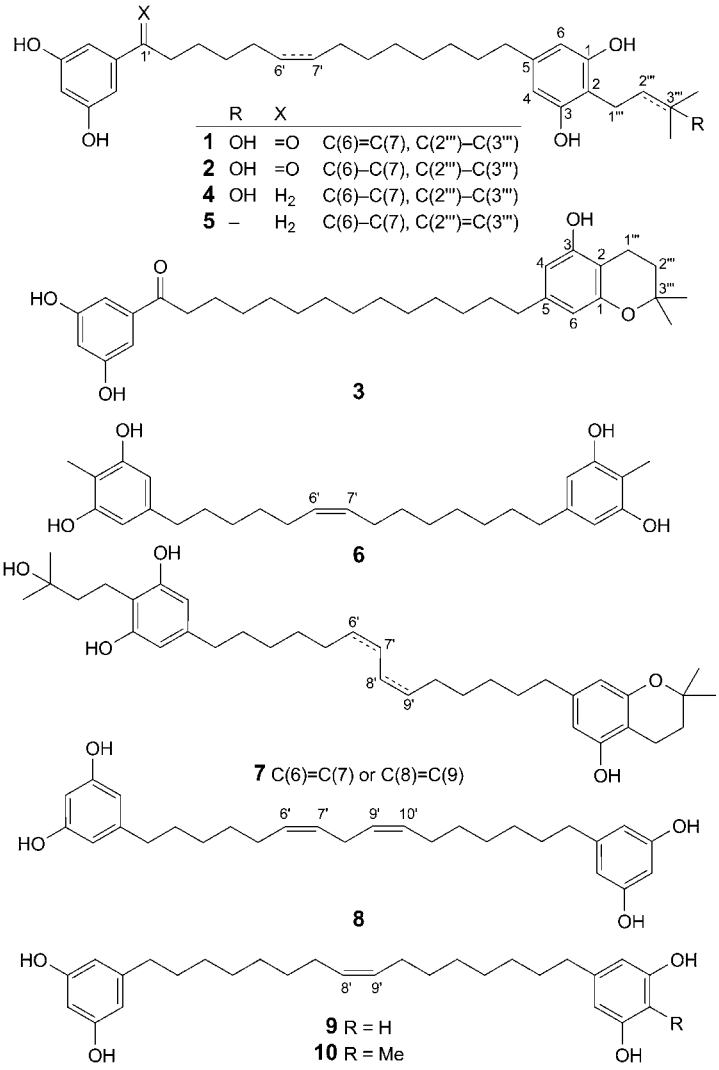
Introduction. – With over 350 species, *Grevillea* R. BR. ex KNIGHT is the largest genus in the family Proteaceae, and one of the largest plant genera in Australia [1]. Considering its size and ecological importance in Australia, information on the chemistry of this genus is surprisingly scanty. Early phytochemical work on the genus has focused on the common and widespread species *G. robusta* and *G. striata*, and most of the compounds isolated have been resorcinol derivatives [2–6].

Recently, we have undertaken a phytochemical survey of a large number of species. As part of this survey, we have explored in detail the profile of compounds present in *G. robusta* [7], *G. banksii* [8], *G. whiteana* [9], and *G. floribunda* [10]. In all of these species, the major classes of compounds were again bisresorcinols, but structural variation has been shown to be greater than previously recognised.

We now wish to report the results of an investigation of a further species, *Grevillea glauca* BANKS & SOL. ex KNIGHT, a shrub or small tree 2–8 m high, usually with a single main stem and endemic to the monsoon belt from Northern Australia in Queensland, Northern Territory, and Western Australia [1].

Results and Discussion. – A crude AcOEt extract of the woody stems of *G. glauca* was separated by HPLC to yield seven new, **1**–**7**, and three known, **8**–**10**, bisresorcinols. The latter were identified as grevirobstol A (**8**) [6], 5,5′-[(8*Z*)-hexadec-8-ene-1,16-diyl]bisresorcinol (**9**) [11], and 2-methyl-5,5′-[(8*Z*)-hexadec-8-ene-1,16-diyl]bisresorcinol (**10**) [9].

Compound **1** was assigned the molecular formula $C_{31}H_{44}O_6$ on the basis of NMR and MS data. The ^{1}H-, ^{13}C-JMOD and HSQC spectra of **1** (*Tables 1* and *2*) showed signals for two Me groups, 13 CH_2 groups, five aromatic CH groups (δ(C) 107.6 × 2,



108.1 × 2, and 108.6), two alkene CH groups (δ(C) 131.0 and 130.9), one CO group (δ(C) 203.2), one O-bearing quaternary C-atom and seven aromatic quaternary C-atoms (δ(C) 114.6, 140.5, 142.5, 157.0 × 2, and 160.3 × 2). The ^{1}H-NMR spectrum confirmed the presence of four CH_2 groups at δ(H) 1.25 – 1.35, two allylic CH_2 groups at δ(H) 2.01 – 2.04, two olefinic H-atoms at δ(H) 5.32 – 5.37, one pair of AB_2 aromatic H-atoms at δ(H) 6.48 and 6.87, and another pair of aromatic H-atoms at δ(H) 6.14.

Two symmetrical resorcinol rings, one monosubsituted and one disubstituted, were established on the basis of ^{1}H-NMR and HMBC spectra. The correlations between the CO group and the two equivalent aromatic H-atoms with a signal at δ(H) 6.87 in the

Table 1. *^{1}H-NMR Data for* **1**–**7** (CD_3OD, 500 MHz, δ in ppm, J in Hz)

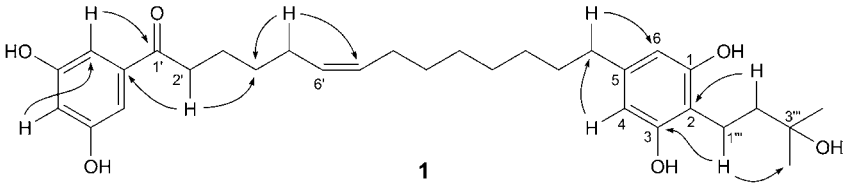
	1	**2**	**3**	**4**	**5**	**6**	**7**
Resorcinol-1							
2	6.48 (*t*, *J* = 2.2)	6.48 (*t*, *J* = 2.2)	6.48 (*d*, *J* = 2.3)	6.08 (*t*, *J* = 2.2)	6.08 (*t*, *J* = 2.2)		
4, 6	6.87 (*d*, *J* = 2.2)	6.87 (*d*, *J* = 2.2)	6.87 (*d*, *J* = 2.2)	6.13 (*d*, *J* = 2.2)	6.13 (*d*, *J* = 2.2)	6.15 (*s*)	6.14 (*s*)
Tetradecene/tetradecane							
1′				2.41 (*t*, *J* = 7.7)	2.35 – 2.45 (*m*)	2.43 (*t*, *J* = 6.0)	2.37 – 2.43 (*m*)
2′	2.88 – 2.92 (*m*)	2.91 (*t*, *J* = 7.4)	2.91 (*t*, *J* = 7.4)	1.55 (br. *s*)	1.52 – 1.57 (*m*)	1.54 – 1.60 (*m*)	1.52 – 1.57 (*m*)
3′	1.65 – 1.70 (*m*)	1.62 – 1.65 (*m*)	1.65 – 1.70 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	1.28 – 1.38 (*m*)	1.29 – 1.37 (*m*)
4′	1.25 – 1.35 (*m*)	1.26 – 1.37 (*m*)	1.28 – 1.36 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	1.28 – 1.38 (*m*)	1.29 – 1.37 (*m*)
5′	2.01 – 2.04 (*m*)	1.26 – 1.37 (*m*)	2.03 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	1.28 – 1.38 (*m*)	1.29 – 1.37 (*m*)
6′	5.32 – 5.37 (*m*)	1.26 – 1.37 (*m*)	1.28 – 1.36 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	1.28 – 1.38 (*m*)	1.29 – 1.37 (*m*)
7′	5.32 – 5.37 (*m*)	1.26 – 1.37 (*m*)	1.28 – 1.36 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	2.01 – 2.06 (*m*)	2.01 – 2.03 (*m*)
8′	2.01 – 2.04 (*m*)	1.26 – 1.37 (*m*)	1.28 – 1.36 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	5.34 (*t*, *J* = 4.7)	5.31 – 5.36 (*m*)
9′	1.25 – 1.35 (*m*)	1.26 – 1.37 (*m*)	1.28 – 1.36 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	5.34 (*t*, *J* = 4.7)	5.31 – 5.36 (*m*)
10′	1.25 – 1.35 (*m*)	1.26 – 1.37 (*m*)	1.28 – 1.36 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	2.01 – 2.06 (*m*)	2.01 – 2.03 (*m*)
11′	1.25 – 1.35 (*m*)	1.26 – 1.37 (*m*)	1.28 – 1.36 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	1.28 – 1.38 (*m*)	1.29 – 1.37 (*m*)
12′	1.25 – 1.35 (*m*)	1.26 – 1.37 (*m*)	1.28 – 1.36 (*m*)	1.28 – 1.31 (*m*)	1.28 – 1.35 (*m*)	1.28 – 1.38 (*m*)	1.29 – 1.37 (*m*)
13′	1.56 – 1.58 (*m*)	1.53 – 1.56 (*m*)	1.53 – 1.56 (*m*)	1.55 (br. *s*)	1.28 – 1.35 (*m*)	1.54 – 1.60 (*m*)	1.52 – 1.57 (*m*)
14′	2.38 – 2.42 (*m*)	2.41 (*t*, *J* = 7.3)	2.38 – 2.45 (*m*)	2.45 (*t*, *J* = 7.7)	2.35 – 2.45 (*m*)	2.43 (*t*, *J* = 6.0)	2.37 – 2.43 (*m*)
Resorcinol-2							
4″	6.14 (*s*)	6.14 (*s*)	6.16 (*d*, *J* = 1.5)	6.14 (*s*)	6.14 (*s*)	6.15 (*s*)	6.16 (*d*, *J* = 1.5)
6″	6.14 (*s*)	6.14 (*s*)	6.07 (*d*, *J* = 1.4)	6.14 (*s*)	6.14 (*s*)	6.15 (*s*)	6.07 (*d*, *J* = 1.4)
Prenyl-1 (or Me-1)							
1‴	2.62 – 2.67 (*m*)	2.64 (*t*, *J* = 8.1)	2.60 (*t*, *J* = 6.8)	2.66 (*t*, *J* = 8.2)	*3.25* (*d*, *J* = 7.0)	2.00 (*s*)	2.60 (*t*, *J* = 6.9)
2‴	1.65 – 1.70 (*m*)	1.68 (*t*, *J* = 8.1)	1.76 (*t*, *J* = 6.8)	1.68 (*t*, *J* = 8.2)	5.24 (*t*, *J* = 4.5)		1.76 (*t*, *J* = 6.8)
4‴	1.22 (*s*)	1.23 (*s*)	1.28 (*s*)	1.22 (*s*)	1.64 (*s*)		1.23 (*s*)
5‴	1.22 (*s*)	1.23 (*s*)	1.28 (*s*)	1.22 (*s*)	1.74 (*s*)		1.23 (*s*)
Prenyl-2 (or Me-2)							
1⁗						2.00 (*s*)	2.61 – 2.64 (*m*)
2⁗							1.62 – 1.68 (*m*)
4⁗							1.28 (*s*)
5⁗							1.28 (*s*)

Table 2. *^{13}C-NMR Data for* **1**–**7** (CD_3OD, 125 MHz, δ in ppm)

	1	**2**	**3**	**4**	**5**	**6**	**7**
Resorcinol-1							
1, 3	160.3 (*s*)	160.2 (*s*)	160.2 (*s*)	159.4 (*s*)	159.4 (*s*)	157.0 (*s*)	157.0 (*s*)
2	108.6 (*d*)	108.5 (*d*)	108.5 (*d*)	101.1 (*d*)	101.1 (*d*)	109.4 (*s*)	114.6 (*s*)
4, 6	107.6 (*d*)	107.6 (*d*)	107.6 (*d*)	108.1 (*d*)	108.0 (*d*)	107.9 (*d*)	108.1 (*d*)
5	140.5 (*s*)	140.5 (*s*)	140.6 (*s*)	146.5 (*s*)	146.5 (*s*)	142.2 (*s*)	142.5 (*s*)
Tetradecene/tetradecane							
1′	203.2 (*s*)	203.2 (*s*)	203.2 (*s*)	36.9 (*t*)	36.9 (*t*)	36.8 (*t*)	36.9 (*t*)
2′	39.6 (*t*)	39.8 (*t*)	39.8 (*t*)	32.5 (*t*)	32.5 (*t*)	32.6 (*t*)	32.5 (*t*)
3′	25.8 (*t*)	25.9 (*t*)	25.9 (*t*)	30.9 (*t*)	30.9 (*t*)	30.4 (*t*)	30.4 (*t*)
4′	30.8 (*t*)	30.5 (*t*)	30.4 (*t*)	30.9 (*t*)	30.9 (*t*)	30.8 (*t*)	30.8 (*t*)
5′	28.2 (*t*)	30.7 (*t*)	30.8 (*t*)	30.9 (*t*)	30.9 (*t*)	30.9 (*t*)	30.9 (*t*)
6′	131.0 (*d*)	30.9 (*t*)	30.9 (*t*)	30.8 (*t*)	30.8 (*t*)	30.9 (*t*)	30.9 (*t*)
7′	130.9 (*d*)	30.9 (*t*)	30.9 (*t*)	30.5 (*t*)	30.5 (*t*)	28.3 (*t*)	28.2 (*t*)
8′	28.2 (*t*)	30.9 (*t*)	30.9 (*t*)	30.5 (*t*)	30.5 (*t*)	130.9 (*d*)	130.9 (*d*)
9′	30.8 (*t*)	30.9 (*t*)	30.9 (*t*)	30.8 (*t*)	30.8 (*t*)	131.0 (*d*)	131.0 (*d*)
10′	30.6 (*t*)	30.8 (*t*)	30.9 (*t*)	30.9 (*t*)	30.9 (*t*)	28.3 (*t*)	28.2 (*t*)
11′	30.4 (*t*)	30.7 (*t*)	30.7 (*t*)	30.9 (*t*)	30.9 (*t*)	30.9 (*t*)	30.9 (*t*)
12′	30.3 (*t*)	30.5 (*t*)	30.5 (*t*)	30.9 (*t*)	30.9 (*t*)	30.8 (*t*)	30.8 (*t*)
13′	32.1 (*t*)	32.6 (*t*)	32.6 (*t*)	32.6 (*t*)	32.6 (*t*)	32.6 (*t*)	32.6 (*t*)
14′	36.9 (*t*)	36.9 (*t*)	36.9 (*t*)	37.1 (*t*)	37.1 (*t*)	36.9 (*t*)	36.9 (*t*)
Resorcinol-2							
1″	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)
2″	114.6 (*s*)	114.6 (*s*)	114.6 (*s*)	114.6 (*s*)	113.8 (*s*)	109.4 (*s*)	114.6 (*s*)
3″	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)	157.0 (*s*)
4″	108.1 (*d*)	108.1 (*d*)	107.4 (*d*)	108.1 (*d*)	108.1 (*d*)	107.9 (*d*)	107.5 (*d*)
5″	142.5 (*s*)	142.6 (*s*)	143.2 (*s*)	142.6 (*s*)	142.6 (*s*)	142.2 (*s*)	143.2 (*s*)
6″	108.1 (*d*)	108.1 (*d*)	109.5 (*d*)	108.1 (*d*)	108.1 (*d*)	107.9 (*d*)	109.5 (*d*)
Prenyl-1 (or Me-1)							
1‴	19.3 (*t*)	19.3 (*t*)	18.1 (*t*)	19.3 (*t*)	23.2 (*t*)	8.4 (*q*)	18.1 (*t*)
2‴	43.8 (*t*)	43.8 (*t*)	33.7 (*t*)	43.8 (*t*)	125.2 (*d*)		33.7 (*t*)
3‴	72.2 (*s*)	72.1 (*s*)	72.2 (*s*)	72.2 (*s*)	131.0 (*s*)		72.2 (*s*)
4‴	29.3 (*q*)	29.3 (*q*)	27.1 (*q*)	29.3 (*q*)	26.1 (*q*)		27.1 (*q*)
5‴	29.3 (*q*)	29.3 (*q*)	27.1 (*q*)	29.3 (*q*)	18.0 (*q*)		27.1 (*q*)
Prenyl-2 (or Me-2)							
1⁗						8.4 (*q*)	19.3 (*t*)
2⁗							43.7 (*t*)
3⁗							72.2 (*s*)
4⁗							29.3 (*q*)
5⁗							29.3 (*q*)

monosubstituted resorcinol ring indicated the presence of a CO group in 1-position of the chain, as well as one of the resorcinol substituents in 1-position (*Fig.*). The C=C bond in the CH_2 chain was located based on correlations observed in the COSY-45 and HMBC spectra (*Fig.*). The connectivity =CH (δ(C) 131.0)–CH_2 (δ(C) 28.2)–CH_2 (δ(C) 30.8)–CH_2 (δ(C) 25.8)–CH_2 (δ(C) 39.6)–C=O-resorcinol was found. The (*Z*)-configuration of the C=C bond was established by considering the chemical shifts (δ(C) 28.2×2) of the allylic C-atoms. A lower-field chemical shift would be expected for

C-atoms allylic to a C=C bond with (*E*)-geometry [6][11]. The 3-hydroxyisopentyl group was characterized by the observation of ^{1}H,^{1}H and ^{1}H,^{13}C correlations, and it could be shown that it is located at the disubstituted resorcinol between the two OH groups (*Fig.*). Consequently, this resorcinol moiety must be linked to the 1-oxoalken-1-yl chain at C(5)-position, which was confirmed by HMBCs. Hence, the structure of **1** was assigned as 2′-(3-hydroxyisopentyl)-5,5′-[(6*Z*)-1-oxotetradec-6-en-1,14-diyl]bisresorcinol.



1

Figure. *Key HMBCs of* **1**

NMR (*Tables 1* and *2*) and MS data for **2** suggested the molecular formula $C_{31}H_{46}O_6$ and revealed identical resorcinol units to those in **1**. The absence of signals for a C=C bond and a MW of 2 amu greater than that of **1** indicated that **2** was 14-[3,5-dihydroxy-4-(3-hydroxy-3-methylbutyl)phenyl]-1-(3,5-dihydroxyphenyl)tetradecan-1-one, to which the trivial name glaucone A has been assigned. Consequently, **1** can be given the trivial name 6,7-*cis*-dehydroglaucone A.

Compound **3** was assigned the molecular formula $C_{31}H_{44}O_5$ based on the HR-ESI-MS data. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*, resp.) indicated the same 1-(3,5-dihydroxyphenyl)tetradecan-1-one substructure as found in **2**. Comparison with the NMR spectra of **2** revealed several differences in the chemical shifts of the prenylated resorcinol substituent, notably in the resonance of the Me group and in the non-equivalence of the CH groups. These changes indicated that a dihydropyran ring had been formed with loss of H_2O to give 14-(3,4-dihydro-5-hydroxy-2,2-dimethyl-2*H*-chromen-7-yl)-1-(3,5-dihydroxyphenyl)tetradecan-1-one (trivial name glaucone B).

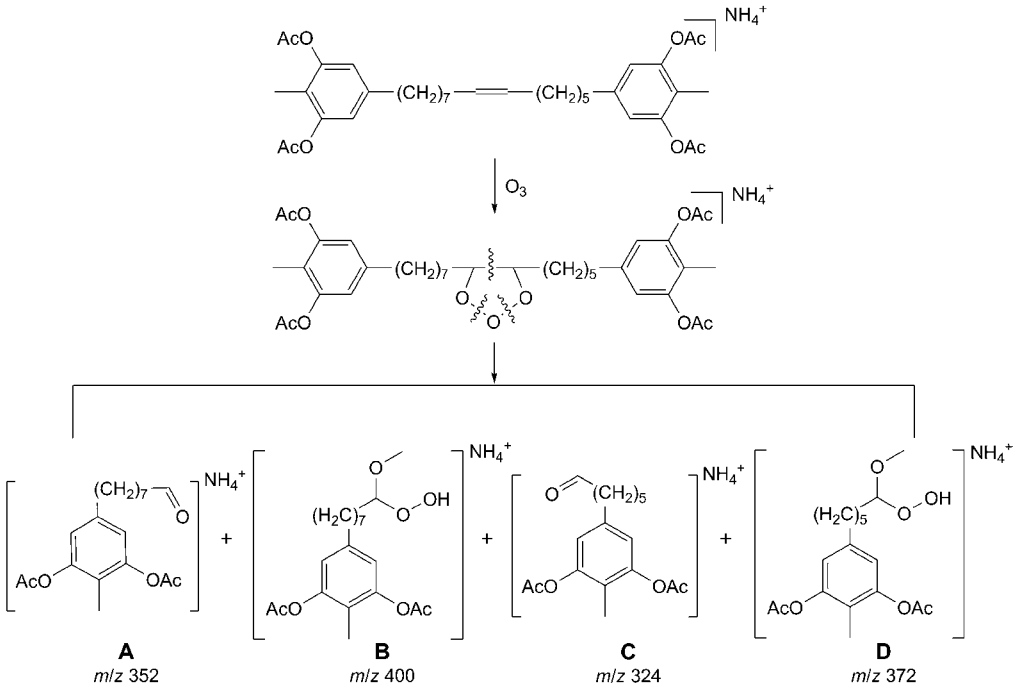
Compound **4** was assigned the molecular formula $C_{31}H_{48}O_5$ by combined analysis of the HR-ESI-MS and NMR data. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*, resp.) were comparable to those of **2**, except that the CO group at C(1) was replaced by a CH_2(1) group. On this basis, **4** was assigned as 5-[14-(3,5-dihydroxyphenyl)tetradecyl]-2-(3-hydroxy-3-methylbutyl)benzene-1,3-diol.

Compound **5** showed a molecular formula $C_{31}H_{46}O_4$, and the ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*, resp.) were analogous to those of **4**, with the exception that 3-hydroxyisopentyl substituent was replaced by a 3-methylbut-2-en-1-yl group. Thus, **5** was defined as 5-[14-(3,5-dihydroxyphenyl)tetradecyl]-2-(3-methylbut-2-en-1-yl)benzene-1,3-diol, and named 2-(3-methylbut-2-en-1-yl)bisnorstriatol.

The HR-ESI-MS of **6** indicated an empirical formula $C_{28}H_{40}O_4$. The NMR spectra of **6** (*Tables 1* and *2*, resp.) revealed signals for two Me groups attached to aromatic rings (δ(H) 8.4), twelve CH_2 groups, including two benzylic CH_2 groups (δ(C) 36.8 and 36.9), four identical aromatic CH groups (δ(C) 107.9), two alkene CH groups (δ(C) 130.9 and 131.0), four identical aromatic quaternary C-atoms (δ(C) 157.0), and two pairs of aromatic quaternary C-atoms (δ(C) 109.4 and 142.2), indicating that **6** was a

bis-5-alkylresorcinol derivative with a 2-Me substituent on both aromatic rings and one C=C bond in a tetradecyl chain. Such compounds are typical of *Grevillea* [3][4][6]. The location of the C=C bond in the CH_2 group chain was determined by MS analysis with on-line ozonolysis [12] of a sample of **6** that had previously been peracetylated (*Scheme*). The four ammoniated fragment ions at *m/z* 324, 352, 372, and 400 clearly indicated the presence of the tetradec-6-enyl chain. The (*Z*)-form was established by considering the chemical shifts (δ(C) 28.2 × 2) of the allylic C-atoms. Hence, the structure of **6** was 5,5′-(6*Z*)-tetradec-6-ene-1,14-diylbis(2-methylbenzene-1,3-diol) and named 2′-methylgrebustol A, based on grebustol A reported from [5].

Scheme. *Mass Fragmentation of Acetylated* **6** *with Online Ozonolysis*



The HR-ESI-MS spectrum of **7** was consistent with the molecular formula $C_{36}H_{54}O_5$. A comparison of the NMR spectra of **7** (*Tables 1* and *2*, resp.) with those of **2** and **3** suggested a tetradecene with (3-hydroxy-3-methylbutyl)-resorcinol and (3,4-dihydro-5-hydroxy-2,2-dimethyl-2*H*-chromen-7-yl)resorcinol as the terminal substituents. The (*Z*)-form was established by considering the chemical shifts (δ(C) 28.2 × 2) of the allylic CH groups. An online ozonolysis experiment was applied on a sample of **7** that had been peracetylated. Unfortunately, the result failed to give any useful information, and consequently the position of the C=C bond remains ambiguous. However, it can be assumed that the structure of **7** is either 5-[(6*Z*)-14-(3,4-dihydro-5-hydroxy-2,2-dimethyl-2*H*-chromen-7-yl)tetradec-6-en-1-yl]-2-(3-hydroxy-3-methylbutyl)benzene-1,3-diol or 5-[(8*Z*)-14-(3,4-dihydro-5-hydroxy-2,2-dimethyl-2*H*-chromen-7-yl)tetradec-8-en-1-yl]-2-(3-hydroxy-3-methylbutyl)benzene-1,3-diol.

The major metabolites of *G. glauca* have been demonstrated to be tetradecane bisresorcinols, which is typical for the genus. For the first time, we report the occurrence of a tetradecan-1-one chain linked to resorcinol units. Previously, CO groups in the bridging alkyl chain have been restricted to compounds with a phloroglucinol terminal group [9].

Experimental Part

General. Prep. reversed-phase HPLC: *Gilson* HPLC system with *306* pump, *UV/VIS-155* detector and *FC 204* fraction collector (collecting frequence: 0.5 min per fraction) using a *Alltina* C_{18} column (22×150 mm, 5 μm) with flow rate at 20 ml min^{-1}. Semi-prep. isolations: *Agilent 1100* system with quaternary pump and *DAD* using a *Zorbax SB* C_{18} column (9.4×250 mm, 5 μm) with flow rate at 4.0 ml min^{-1}. NMR Spectra: *Bruker AVANCE DRX-500* (^1H, 500 MHz; ^{13}C, 125.77 MHz) spectrometer using CD_3OD as solvent and the residual solvent peak as reference; all experiments were run using the standard pulse sequences in the *Bruker* library. MS: *Agilent 1100* Series LC/MSD with binary pump, DAD, MS detector featuring atmospheric pressure chemical ionization (APCI) and a *Phenomenex Aqua* C_{18} column (4.6×150 mm, 5 μm) with the flow rate at 1.0 ml min^{-1}. HR-EI-MS: *Kratos MS 25 RFA via* direct insertion at 70 eV with PFK used as reference for magnet scan accurate mass data.

Plant Material. Fresh stems of *Grevillea glauca* were collected west of Walkamin, Queensland, Australia, in August 2003, and identified by one of the authors (*P. I. F*). A voucher specimen (PIF 29565) was deposited with the Queensland Herbarium.

Extraction and Isolation. The ground, air-dried stems (867 g) were extracted with AcOEt (4×1 l) under sonication for 2 h. The AcOEt extract (3.8 g) was dissolved in 10% aq. MeOH and partitioned against hexane. The MeOH partition was applied to prep. HPLC with a solvent system of *A* (H_2O, 0.05% TFA) and *B* (MeCN, 0.05% TFA) with a gradient elution of 65 to 95% of *B* to afford 29 fractions over 18 min (sample collection started at 2 min). *Fr. 10* (29.7 mg) was subjected to semi-prep. HPLC, eluted with H_2O/MeCN 50:50, yielding **1** (1.3 mg, t_R 10.5 min). *Fr. 12* (32.4 mg) was separated by semi-prep. HPLC, eluted with H_2O/MeCN 32:68, giving **2** (3.7 mg, t_R 7.1 min), **3** (2.4 mg, t_R 8.4 min), **6** (2.1 mg, t_R 12.9 min), and **9** (2.5 mg, t_R 14.8 min). *Fr. 13* (64.8 mg) was purified by semi-prep. HPLC, eluted with H_2O/MeCN 35:65, yielding **7** (3.1 mg, t_R 6.3 min) and **10** (1.4 mg, t_R 8.9 min). *Fr. 16* (51.5 mg) was purified by semi-prep. HPLC, eluted with H_2O/MeCN 32:68, yielding **4** (1.4 mg, t_R 6.7 min) and **8** (0.7 mg, t_R 10.2 min). *Fr. 18* (17.1 mg) was subjected to semi-prep. HPLC, eluted with H_2O/MeCN 30:70, yielding **5** (1.9 mg, t_R 8.5 min).

Peracetylation. Reactant (0.5 mg) was placed in a 10-ml capped tube with 1 ml of Ac_2O and 3 ml of pyridine. The soln. was stirred at 60° for 90 min. The reaction was quenched by adding 2 ml of H_2O, and then partitioned against 2 ml of CH_2Cl_2. The CH_2Cl_2 phase was washed with H_2O (2×2 ml), then analyzed by LC-MS to check the completeness of peracetylation.

Ozonolysis of Mass Selected Ions – Ozone Induced Dissociation (OzID). Ozone Induced Dissociation (OzID) is a novel approach for the identification of the C=C bond position using mass spectrometry [12]. In OzID, ions are mass-selected and allowed to react with ozone to produce chemically induced fragment ions. The mass-to-charge ratio of these fragment ions allows the assignment of the C=C bond position. OzID was performed on a modified *ThermoFinnigan LTQ* ion-trap mass spectrometer (San Jose, CA, USA). The instrument modification involved by-passing the He splitter to make a direct connection between the He supply and the ion trap with the He flow rate controlled using a metering flow valve. High concentration O_3 was generated using a *HC-30* O_3 generator (*Ozone Solutions*, Sioux Center, Iowa, USA). Ozone was collected in a plastic syringe and introduced into the flow of He through a PEEKsil tubing restrictor (100 mm × 1/16″ OD × 0.023 mm ID, *SGE*). Samples were prepared in MeOH with 100 μM AcONa and ionized by Electrospray Ionization (ESI) with the presence of 5 mM $AcONH_4$. To acquire OzID spectra, $[M + NH_4]^+$ ions were mass-selected and trapped in the presence of O_3 for 10 per scan. At least 50 scans were acquired for each spectrum.

(Z)-6,7-Didehydroglaucone A (=2′-(3-Hydroxyisopentyl)-5,5′-[(6Z)-1-oxotetradec-6-en-1,14-diyl]bisresorcinol = (6Z)-14-[3,5-Dihydroxy-4-(3-hydroxy-3-methylbutyl)phenyl]-1-(3,5-dihydroxyphe-

nyl)tetradec-6-en-1-one; **1**). Brown gum. UV (MeOH): 268 (4.10), 322 (3.28). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 535.3032 ($[M+Na]^+$, $C_{31}H_{44}NaO_6^+$; calc. 535.3036).

Glaucone A (*=14-[3,5-Dihydroxy-4-(3-hydroxy-3-methylbutyl)phenyl]-1-(3,5-dihydroxyphenyl)tetradecan-1-one*; **2**). Brown gum. UV (MeOH): 265 (3.41), 321 (3.07). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESIMS (pos.): 537.3200 ($[M+Na]^+$, $C_{31}H_{46}NaO_6^+$; calc. 537.3192).

Glaucone B (*=14-(3,4-Dihydro-5-hydroxy-2,2-dimethyl-2*H*-chromen-7-yl)-1-(3,5-dihydroxyphenyl)tetradecan-1-one*; **3**). Brown gum. UV (MeOH): 265 (3.45), 322 (3.12). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 519.3097 ($[M+Na]^+$, $C_{31}H_{44}NaO_5^+$; calc. 519.3086).

2-(3-Hydroxyisopentyl)bisnorstriatol (*=5-[14-(3,5-Dihydroxyphenyl)tetradecyl]-2-(3-hydroxy-3-methylbutyl)benzene-1,3-diol*; **4**). Brown gum. UV (MeOH): 223 (sh, 4.27), 275 (3.11). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 523.3408 ($[M+Na]^+$, $C_{31}H_{48}NaO_5^+$; calc. 523.3399).

2-(3-Methylbut-2-en-1-yl)bisnorstriatol (*=5-[14-(3,5-Dihydroxyphenyl)tetradecyl]-2-(3-methylbut-2-en-1-yl)benzene-1,3-diol*; **5**). Brown gum. UV (MeOH): 221 (sh, 4.25), 275 (3.24). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 505.3293 ($[M+Na]^+$, $C_{31}H_{46}NaO_4^+$; calc. 505.3294).

2′-Methylgrebustol A (*=5,5′-(6*Z*)-Tetradec-6-ene-1,14-diylbis(2-methylbenzene-1,3-diol)*; **6**). Brown gum. UV (MeOH): 222 (sh, 4.22), 275 (3.31). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 463.2833 ($[M+Na]^+$, $C_{28}H_{40}NaO_4^+$; calc. 463.2824).

Glaucane (*=5-[(6*Z*)-14-(3,4-Dihydro-5-hydroxy-2,2-dimethyl-2*H*-chromen-7-yl)tetradec-6-en-1-yl]-2-(3-hydroxy-3-methylbutyl)benzene-1,3-diol or 5-[(8*Z*)-14-(3,4-Dihydro-5-hydroxy-2,2-dimethyl-2*H*-chromen-7-yl)tetradec-8-en-1-yl]-2-(3-hydroxy-3-methylbutyl)benzene-1,3-diol*; **7**). Brown gum. UV (MeOH): 225 (sh, 4.29), 276 (3.29). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 589.3867 ($[M+Na]^+$, $C_{36}H_{54}NaO_5^+$; calc. 589.3869).

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