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QUINONES OF *STREPTOCARPUS DUNNII**

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Key Word Index—*Streptocarpus dunnii*; Gesneriaceae; mature plant; plantlet; cell culture; structure elucidation; unusually prenylated naphthoquinones; anthraquinones; ^{13}C NMR.

Abstract—From the mature plants, plantlets and cultured cells coexisting with half differentiated plantlets of *Streptocarpus dunnii*, five unusually prenylated naphthoquinones and one anthraquinone were newly isolated along with both dunnione and 1-hydroxy-2-hydroxymethylanthraquinone, which had already been found in this plant. Furthermore, the structures of four new naphthoquinones, dehydrodunnione, streptocarpone, 7-hydroxydunnione and 8-hydroxydunnione, were elucidated. The optical purities of dunnione derivatives are discussed.

INTRODUCTION

Dunnione (**1**), an unusually prenylated *o*-naphthoquinone, was first isolated from the leaves of *Streptocarpus dunnii* Mast. [1–3]‡. Recently, 1-hydroxy-2-hydroxymethylanthraquinone (**2**) was isolated from the roots of this plant [6]. As a part of our biosynthetic studies on these quinones, we have reinvestigated the quinones of the mature plants of *S. dunnii*. We have also examined those of its plantlets and cultured cells coexisting with half-differentiated plantlets and isolated, in addition to both quinones described above, one anthraquinone, 1-hydroxy-2-methylanthraquinone (**3**) as well as five naphthoquinones α-dunnione (**4**), dehydrodunnione (**5**), streptocarpone (**6**), 7-hydroxydunnione (**7**) and 8-hydroxydunnione (**8**). The latter four were new substances. This paper deals with the isolation and structure elucidation of these quinones.

RESULTS AND DISCUSSION

Isolation of quinones

The benzene extract of the leaves of mature *S. dunnii* plants was subjected to CC on Si gel to give 1-hydroxy-2-methylanthraquinone (**3**), α-dunnione (**4**), dehydrodunnione (**5**), dunnione (**1**), a mixture of 1-hydroxy-2-hydroxymethylanthraquinone (**2**) and streptocarpone (**6**), and 7-hydroxydunnione (**7**) in order of elution. Quinones **2** and **6** were separated by making use of the difference in their solubility in aqueous sodium carbonate. The benzene extract of the roots gave 1-hydroxy-2-hydroxymethylanthraquinone (**2**) as the sole quinone. Furthermore, the extract of the aseptically cultured plantlets in the same solvent gave quinones **1**–**5** and **8** along with a trace of **7**.

Callus tissues were induced from the leaves of the plantlets and subcultured on Linsmaier–Skoog solid medium (L–S solid medium) supplemented with kinetin and IAA for more than two years. Throughout the period of subculturing, the cultured cells tended to form poorly differentiated plantlets either on the solid medium or in the corresponding liquid medium. The benzene extract of both the free cells and coexisting half-differentiated plantlets, which were present on a fr. wt basis in a ratio of *ca* 4:6, also gave quinones **1**–**5** and **8**.

GC estimation of the quinones was carried out on each part of a mature plant including flower and pedicel (available only in a very small amount), as well as on plantlets and cells coexisting with the half-differentiated plantlets (Table 1). 7-Hydroxydunnione (**7**) isolated from the leaves of the fully grown plants and plantlets was not detectable by GC under the conditions given below because of its high polarity.

Structures of new quinones

Dehydrodunnione (**5**) was obtained as orange-red needles, $C_{15}H_{12}O_3$, mp 96–97°. Its UV and visible spectra (MeOH) showed absorptions at 260, 267 (inf.), 311 and 440 nm ($\log\varepsilon$ 4.33, 4.28, 3.74 and 3.37) and in its IR spectrum (KBr) there were bands at 1685, 1650, 1615 and 1570 cm^{-1}. From these data, **5** was assumed to be a 1,2-naphthoquinone. The ^{1}H NMR spectrum showed a singlet from a gem-dimethyl group at δ 1.55, a pair of doublets (J = 4.0 Hz) due to two exocyclic methylene protons at δ 4.46 and 4.93, and aromatic proton signals analogous to those of **1**. Furthermore, the ^{13}C NMR spectrum of **5** coincided with that of **1** except for the signals of an exocyclic methylene carbon (C-3′) at δ 86.8 (*t*) and an exo-methylene-bearing carbon (C-2′) at δ 126.0 (*s*) (Table 2). These findings suggested that this substance had the structure of dehydrodunnione (**5**). This was confirmed by conversion of dehydrodunnione (**5**) into dunnione (**1**) by catalytic hydrogenation on platinum.

Streptocarpone (**6**) was obtained as yellow needles,

*Part 18 in the series "Quinones and Related Compounds in Higher Plants". For Part 17, see Inoue, K., Inouye, H. and Chen, C.-C. (1981) *Phytochemistry* **20**, 2271. A part of this work has been published in a preliminary form: Inoue, K., Nayeshiro, H. and Inouye, H. (1982) *Chem. Pharm. Bull.* **30**, 2265.

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‡This quinone has been detected in *S. pole-evansii* (Gesneriaceae) [4] and has also been isolated from *Calceolaria integrifolia* Murr (Scrophulariaceae) [5].

Table 1. GC analysis of quinones in mature plants, plantlets and cell cultures*

Compound	R_t (min)	Mature plant			Normal plantlet	Suspension culture	
		Leaf	Flower	Root		Cell	Plantlet
1	8.2	85.0	84.1	—	4.9	2.1	1.6
2	18.5	1.1	—	100	10.1	67.0	26.8
3	10.1	2.8	1.2	—	4.6	0.4	0.7
4	5.2	0.6	0.8	—	67.9	18.1	68.3
5	3.1	5.1	11.0	—	1.6	0.1	0.3
6	8.0	5.4	2.9	—	—	—	—
8	7.8	—	—	—	10.9	12.3	2.3

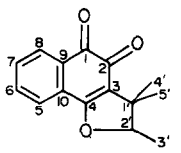
*The values represent the ratio (%) of each quinone to the sum of the seven quinones (**1**–**6** and **8**).

Table 2. ^{13}C NMR spectral data of naphthoquinones (TMS as int. standard) for compounds **1** and **4**–**8**

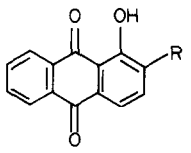
C No.	**1**	**4**	**5**	**6***	**7**	**8**
1	180.9 (*s*)	178.1 (*s*)	180.2 (*s*)	181.3 (*s*)	181.8 (*s*)	185.0 (*s*)
2	175.0 (*s*)	158.2 (*s*)	170.7 (*s*)	153.3 (*s*)	175.5 (*s*)	174.9 (*s*)
3	123.0 (*s*)	130.7 (*s*)	122.9 (*s*)	128.6 (*s*)	120.3 (*s*)	123.4 (*s*)
4	167.7 (*s*)	181.8 (*s*)	164.8 (*s*)	184.2 (*s*)	164.5 (*s*)	167.6 (*s*)
5	124.2 (*d*)	125.6 (*d*)	124.2 (*d*)	126.0 (*d*)	126.8 (*d*)	122.9 (*d*)
6	131.3 (*d*)	133.8 (*d*)	131.6 (*d*)	135.0 (*d*)	120.9 (*d*)	137.5 (*d*)
7	134.2 (*d*)	132.4 (*d*)	134.7 (*d*)	132.8 (*d*)	159.5 (*s*)	117.5 (*d*)
8	128.7 (*d*)	125.7 (*d*)	129.4 (*d*)	126.9 (*d*)	117.0 (*d*)	164.4 (*s*)
9	130.4 (*s*)	131.1 (*s*)	130.6 (*s*)	132.8 (*s*)	132.8 (*s*)	113.6 (*s*)
10	127.6 (*s*)	133.2 (*s*)	126.6 (*s*)	134.1 (*s*)	121.3 (*s*)	127.9 (*s*)
1′	44.0 (*s*)	45.1 (*s*)	44.2 (*s*)	50.4 (*s*)	43.9 (*s*)	44.2 (*s*)
2′	92.6 (*d*)	91.4 (*d*)	126.0 (*s*)	209.8 (*s*)	93.1 (*d*)	92.8 (*d*)
3′	25.7 (*q*)	25.8 (*q*)	86.8 (*t*)	25.5 (*q*)	25.9 (*q*)	25.8 (*q*)
4′	20.3 (*q*)	20.6 (*q*)	27.7 (*q*)	24.5 (*q*)	20.4 (*q*)	20.3 (*q*)
5′	14.5 (*q*)	14.2 (*q*)	27.7 (*q*)	24.5 (*q*)	14.6 (*q*)	14.6 (*q*)

*Signals originating only from the tautomeric **6a** are omitted.

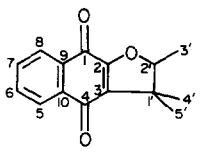
$C_{15}H_{14}O_4$, mp 120–121°. Its UV and visible spectra (MeOH) showed absorptions at 246 (sh), 252, 275, 329 and 460 nm ($\log \varepsilon$ 4.14, 4.18, 4.19, 3.36 and 3.09) and in its IR spectrum (KBr) bands were present at 3450, 1665, 1650, 1615 and 1590 cm^{-1}, indicating it to be a 1,4-naphthoquinone. The bathochromic shift of the UV absorptions with alkali and the presence of an IR band at 3450 cm^{-1} suggested that it was a lapachol-type naphthoquinone. The ^1H NMR spectrum of **6** showed a singlet from the protons of a gem-dimethyl group at δ 1.54, a



1



2 R=CH_2OH
3 R=Me



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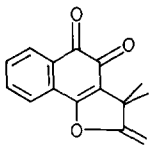

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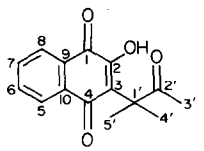

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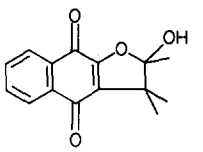
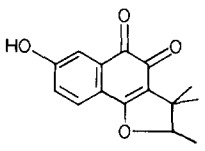


6a



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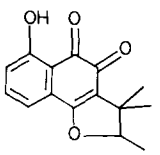

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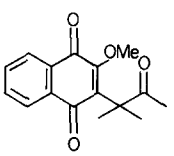

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singlet from an acetyl group at δ 2.18 and a multiplet of four aromatic protons at δ 7.60–7.83 and 7.97–8.12 (A_2B_2 pattern). In the ^{13}C NMR spectrum, it showed signals from quinone carbonyl carbons at δ 181.3 and 182.4 and a signal from a non-conjugated ketone at δ 209.7. Furthermore, in the mass spectrum, it showed a molecular ion at *m/z* 258 and a base peak at 216 $[M-42]^+$, suggesting the presence of an acetyl group in the molecule. From these spectral data the structure of this substance was presumed to be 2-hydroxy-3-(1,1-dimethyl-2-oxopropanyl)-1,4-naphthoquinone (**6**). This was confirmed by the fact that an attempted hydrogenation of **5** over Pd–C afforded **6** along with a small amount of the desired compound **1**. The formation of **6** would be explained by ketonization of the enol formed from **5** through splitting of the ether ring following hydration under acidic conditions. In the ^1H NMR spectrum of **6**, besides the above-mentioned signals, relatively small signals for methyl groups were observed at δ 1.34, 1.52 and 1.70. INDOR experiments revealed that the former two signals correspond to those for the gem-methyl group at δ 1.54 and the latter to that for the acetyl group at δ 2.18. Furthermore, in the ^{13}C NMR spectrum, relatively small signals were observed at δ 19.0 (*q*), 21.9 (*q*), 25.4 (*q*), 50.1 (*s*) and 115.3 (*s*). These signals were assignable to C-4′ (or C-5′), 5′ (or 4′), 3′, 1′ and 2′ carbons of hemiketal form (**6a**). These findings suggested that compound **6** exists as an equilibrium mixture with hemiketal (**6a**) at least in a solution. The intensity of the ^1H NMR signals concerned further indicated that the ratio of **6**–**6a** in the equilibrium mixture was *ca* 5:2. Treatment of **6** with diazomethane gave the methyl ether **9**.

7-Hydroxydunnione (**7**) was obtained as dark-red needles, $C_{15}H_{14}O_5$, mp 217–219°, $[\alpha]_D$ +350° ($CHCl_3$; *c* 0.1). Its UV and visible spectra (MeOH) showed absorptions at 270, 277, 306 and 480–510 nm (log ε 4.52, 4.55, 3.83 and 3.31) and its IR spectrum (KBr) contained bands at 3100, 2950, 1690, 1600 and 1550 cm^{-1}, suggesting that **7** was a 1,2-naphthoquinone. The ^1H NMR spectrum showed a broad doublet (J = 8.0 Hz, H-6) at δ 7.12, a doublet (J = 8.0 Hz, H-5) at δ 7.51 and a broad singlet at δ 7.61 (H-8) in the aromatic region. The signal pattern of the other region coincided with that of dunnione (**1**). Furthermore, the ^{13}C NMR spectrum was nearly in accord with the spectrum of **1** except for the low field shift of the signal of C-7 (bearing the hydroxyl group) to δ 159.5 and the respective high field shifts of the signals of the neighbouring C-6 and C-8 to δ 120.9 and 117.0. From these data, **7** was presumed to be 7-hydroxydunnione.

8-Hydroxydunnione (**8**) was obtained as optically inactive red needles, $C_{15}H_{14}O_5$, mp 151–152°. Its UV and visible spectra (MeOH) showed absorptions at 242 (sh), 260, 294 and 412 nm (log ε 4.35, 4.40, 3.89 and 3.84) and its IR spectrum (KBr) contained bands at 3200, 1690, 1640, 1610 and 1585 cm^{-1}, suggesting a 1,2-naphthoquinone structure. Its ^1H NMR spectrum ($CDCl_3$) showed, along with the singlet of a hydrogen-bonded hydroxy group at δ 11.91, three neighbouring aromatic proton signals, whose pattern was different from that of **7**. Moreover, its ^{13}C NMR spectrum was almost in accord with the spectrum of **1** except for the shifts caused by the hydroxylation of the C-8. These data led us to a conclusion that **8** was 8-hydroxydunnione.

Optical purity of dunnione derivatives

Dunnione (**1**), α-dunnione (**4**), 7-hydroxy- (**7**) and 8-hydroxydunnione (**8**) each have a chiral centre at the C-2′ position. The optical purities of these quinones were found to fluctuate depending on whether they were isolated from grown plants, plantlets or cultured cells.

Dunnione (**1**), isolated from mature plants, possessing $[\alpha]_D$ +307° ($CHCl_3$; *c* 1.2), was proved to be absolutely optically pure through ^1H NMR measurement in the presence of the chiral shift reagent, tris(trifluoroacetyl-*d*-camphorato)Eu (III) [Eu(TFC)$_3$]. But, the same quinone (**1**), isolated from the cultured cells (coexisting with plantlets), possessed a value of +16.4° ($CHCl_3$; *c* 2.7), the

calculated ratio between *d*- and *l*-enantiomers being 53:47.

The above-metnioned optically pure dunnione (**1**) gave on treatment with alkali α-dunnione (**4**), $[\alpha]_D + 91.7°$ ($CHCl_3$; *c* 1.1), which was also found to be optically pure through ^1H NMR measurement in the presence of the chiral shift reagent.*

On the other hand, α-dunnione (**4**) isolated from mature plants had $[\alpha]_D - 9.9°$ ($CHCl_3$; *c* 0.3), while the quinone (**4**) isolated from plantlets, as well as cultured cells and coexisting plantlets, coincidently possessed identical values of $+9.5°$ ($CHCl_3$; *c* 1.1). From these values, it was estimated that α-dunnione (**4**) from the mature plant is a mixture of *d*- and *l*-enantiomers in a ratio of 45:55, whereas **4** from the plantlets, as well as cell cultures coexisting with differentiating plantlets, is a mixture of both enantiomers in a ratio of 55:45. In accord with this assumption, the ^1H NMR spectrum of the *d,l*-mixture, originating from the mature plant measured in the presence of the chiral shift reagent [$Eu(TFC)_3$] (molar ratio between **4** and the reagent: 1:0.5), showed split singlets (δ 1.46 and 1.50) due to the gem-dimethyl group, which usually appears as a singlet at δ 1.29.

7-Hydroxydunnione (**7**), from mature plants, with a high rotation value seems to be optically pure. However, 8-hydroxydunnione (**8**) isolated from the plantlets, as well as from cultured cells, was found to be racemic.

It is intriguing that even compounds of the same class, occurring in the same part of the same plant, have different optical purities and that even the same compounds show different optical rotations depending on their origin, such as the grown plant, plantlet or cultured cell. Considering the diversity in the proportion of enantiomers in these quinones, this irregularity seems not to be ascribable to the partial racemization caused by the isolation procedure.

It is noteworthy that dunnione (**1**) isolated from *Calceolaria integrifolia* had a $[\alpha]_D$ of $-45.5°$, indicating it to be a mixture of *d*- and *l*-enantiomers in a ratio of 43:57. [5]. The occurrence of naphthoquinones as mixtures of enantiomers in various proportions was also observed in *Radermachera sinica* Hemsl. (Bignoniaceae). [7].

The problem of the biosynthesis of napthoquinones in *S. dunnii* involving the stereochemical process, as well as the absolute configuration of quinones **1**, **4** and **7**, remains to be examined.

EXPERIMENTAL

General procedures. Mps were uncorr. ^1H NMR: 200 MHz; ^{13}C NMR: 50.10 MHz in $CDCl_3$ with TMS as int. standard; MS: D.I. method; GC was carried out on a C_6H_6 extract (30 ml × 3) of fresh plant material (*ca* 0.3 g) using a glass column (2 m × 3 mm) packed with 3% OV-1 on 100–200 mesh Gas Chrom Q, with N_2 as carrier gas (60 ml/min); TLC: Si gel GF_{254}, bands were visualized, when necessary, by exposure to I_2 or irradiation under UV; TLC: Si gel PF_{254}, bands were visualized, when necessary, by irradiation under UV; CC: Si gel.

Plant material. The plant material used for this study was grown from sterile cultured plantlets supplied by Professor M. H. Zenk, Universität München. A voucher specimen (H. Inouye No. 4) has been deposited in the Herbarium of the Department of Botany, Faculty of Science, Kyoto University.

Induction, cultivation and redifferentiation of the callus tissues. The leaves of the sterile cultured plantlets of *S. dunnii* were placed on L–S solid medium supplemented with 10^{-6} M 2,4-D and incubated at 25° in the dark. Light grey callus tissues formed within 4 weeks were transferred to L–S solid medium supplemented with 10^{-5} M IAA and 10^{-6} M kinetin at 25° in the dark and subcultured every 4 weeks for more than 2 years. Throughout this period, the cells tended to regenerate half-differentiated plantlets. The cells and coexisting half-differentiated plantlets were then transferred to Sakaguchi flasks containing liquid medium of the same composition as above. After agitating at 25° in the dark on a reciprocating shaker for 2 months, constituents of the cells and coexisting half-differentiatiated plantlets were examined.

The half-differentiated plantlets grown on L–S solid medium were cultured under white light (6000 lx) for 2 months to stimulate further differentiation into green plantlets. The completely differentiated plantlets were then cultured on Murashige–Skoog solid medium supplemented with 2×10^{-5} M IAA and 10^{-5} M kinetin for 2 months under the same irradiation condition to form multi-tiller plantlets. They were then transplanted into pots and grown in a greenhouse at 25° and flowered after 1 year.

Isolation of the quinones from leaves of mature plants. Mature leaves (57 g) of *S. dunnii* were cut into pieces and extracted with C_6H_6 (500 ml × 2) and the extract was concd *in vacuo* to give a dark red residue (835 mg), which was subjected to CC on Si gel (100 g) first with C_6H_6–EtOAc (99:1) (fr. 1–20) and then with C_6H_6–EtOAc (1:1) (fr. 21–30) as eluents, collecting 100-ml fractions. Fraction 4 on concn gave a yellow crystalline residue (13.3 mg), which was recrystallized from MeOH to give 1-hydroxy-2-methylanthraquinone (**3**) (12 mg) as yellow needles. Fraction 9 was concd to give a dark green residue (51.6 mg), which was further subjected to TLC with C_6H_6 as eluent. The main yellow band (R_f 0.25) gave, on extraction with $CHCl_3$ followed by concn *in vacuo*, a yellow residue (18 mg), which was recrystallized from petrol (bp 40–60°) to give α-dunnione (**4**) (10 mg) as yellow plates. Fraction 10 was concd to give an orange-red residue (21.2 mg), which was recrystallized from petrol to give dehydrodunnione (**5**) (10 mg) as orange-red needles. Combined fr. 12 and 13 on concn gave a red residue (312.1 mg), which was recrystallized from petrol to give dunnione (**1**) (300 mg) as red needles. Combined fr. 16–19 on concn *in vacuo* gave rise to a yellow crystalline residue (36.4 mg), which was dissolved in $CHCl_3$ (20 ml) and shaken with 5% aq. Na_2CO_3 (20 ml × 3). The $CHCl_3$ layer was washed with H_2O, dried ($MgSO_4$) and concd *in vacuo*. The resulting yellow residue (20 mg) was recrystallized from MeOH to give 1-hydroxy-2-hydroxymethylanthraquinone (**2**) (18 mg) as yellow needles, whereas the Na_2CO_3 layer was acidified with 5% HCl to pH 2–3 and extracted with $CHCl_3$ (30 ml × 3). The $CHCl_3$ layer was washed with H_2O, dried and concd *in vacuo* to give a yellow residue (16 mg), which was recrystallized from petrol to give streptocarpone (**6**) (12 mg) as yellow needles. Finally, fr. 30 on concn *in vacuo* gave a red residue (0.5 mg). This was combined with the corresponding part obtained from another lot of the extract of the plant material (200 g) and recrystallized from *n*-hexane to give 7-hydroxydunnione (**7**) as dark red needles (3 mg).

Isolation of the quinones from the roots, aseptically cultured green plantlets and cell suspension cultures consisting of cells and half-differentiated plantlets. The roots (7.2 g) and green plantlets (87.9 g) were extracted with C_6H_6 and concd *in vacuo* to give the residues, S–r (23 mg) and S–p (175.5 mg), respectively.

*The mechanism suggested for this conversion [2] is not appropriate, since it has recently been found that two exogenous oxygen atoms were introduced into the molecule during this reaction [unpublished results].

S–r was recrystallized from MeOH to give 1-hydroxy-2-hydroxymethylanthraquinone (**2**) as yellow needles (18 mg). S–p was subjected to TLC (C_6H_6–EtOAc, 4:1) and the four coloured bands were eluted with $CHCl_3$ and concd *in vacuo*. The residues were worked-up in the same way as the leaves to give **1** (R_f 0.49, 6 mg), **2** (R_f 0.31, 8 mg), **3** (R_f 0.65, 0.3 mg), **4** (R_f 0.60, 13 mg), **5** (R_f 0.54, 0.3 mg) and **8** (R_f 0.46, 10 mg). The last one on recrystallization from petrol gave 8-hydroxydunnione (**8**) as red needles (3.2 mg). The cell suspension cultures, after division into cells and differentiated plantlets (52 mg), as well as medium (870 ml), were extracted with C_6H_6 and concd *in vacuo*. The residues (each 84 and 28 mg), showing the same spots on TLC, were combined and subjected to TLC. On work-up in the usual way, **1** (3.5 mg), **2** (18 mg), **3** (1.2 mg), **4** (10 mg), **5** (0.7 mg) and **8** (3.3 mg) were obtained.

The properties of dunnione (**1**) and 1-hydroxy-2-hydroxymethylanthraquinone (**2**) thus isolated coincided with the data reported, except for the optical rotation of **1** isolated from the cultured cells [1–6].

1-Hydroxy-2-methylanthraquinone (**3**). Yellow needles, mp 183–184°; UV λ_{max}^{MeOH} nm (log ε): 226 (4.24), 247 (4.40), 254 (4.42), 279 (4.02), 325 (3.43) and 408 (3.74); IR ν_{max}^{KBr} cm^{-1}: 1660, 1625 and 1580; ^1H NMR: δ 2.37 (3H, *s*, Ar-methyl), 7.51 (1H, *d*, *J* = 8.0 Hz, H-3), 7.74 (1H, *d*, *J* = 8.0 Hz, H-4), 7.73–7.86 (2H, *m*, H-6, H-7), 8.20–8.35 (2H, *m*, H-5, H-8) and 12.93 (1H, *s*, chelated OH). (Found: C, 75.41; H, 4.07. Calc. for $C_{15}H_{10}O_3$: C, 75.63; H, 4.23%.)

α-Dunnione (**4**). Yellow plates, mp 111–112°; UV λ_{max}^{MeOH} nm (log ε): 248 (sh) (4.13), 253 (4.17), 288 (3.91), 335 (3.27) and 350 (2.97); IR ν_{max}^{KBr} cm^{-1}: 1670, 1640, 1610 and 1590; ^1H NMR: δ 1.29 and 1.46 (each 3H, *s*, H_3-4′, H_3-5′), 1.40 (3H, *d*, *J* = 7.0 Hz, H_3-3′), 4.52 (1H, *q*, *J* = 7.0 Hz, H-2′), 7.53, 7.75 (2H, *m*, H-6, H-7), 7.85–8.07 (2H, *m*, H-5, H-8); MS *m/z*: 242 $[M]^+$ (55.2), 227 (base peak), 214 (2.9), 199 (9.9), 171 (8.3). (Found: C, 74.52; H, 5.78. Calc. for $C_{15}H_{14}O_3$: C, 74.37; H, 5.82%.)

Dehydrodunnione (**5**). ^1H NMR: δ 1.55 (6H, *s*, H_3-4′, H_3-5′), 4.46 and 4.93 (each 1H, *d*, *J* = 4.0 Hz, H_2-3′), 7.48–7.77 (3H, *m*, H-5–H-7) and 7.96–8.15 (1 H, *m*, H-8); MS *m/z*: 240 $[M]^+$ (46.2), 225 (base peak), 212 (12.7), 198 (14), 197 (95.2), 173 (10.8). (Found: C, 74.69; H, 5.11. $C_{15}H_{12}O_3$ requires: C, 74.99; H, 5.03%.)

Streptocarpone (**6**). MS *m/z*: 258 $[M]^+$ (6.3), 216 (base peak), 201 (4.7), 197 (9.9), 187 (7.1), 183 (6.2). (Found: C, 69.54; H, 5.55. $C_{15}H_{14}O_4$ requires: C, 69.75; H, 5.46%.)

7-Hydroxydunnione (**7**). ^1H NMR: δ 1.25 and 1.44 (each 3H, *s*, H_3-4′, H_3-5′), 1.46 (3H, *d*, *J* = 7.0 Hz, H_3-3′), 4.66 (1H, *q*, *J* = 7.0 Hz, H-2′), 7.4–8.2 (1H, *br* OH). (Found: M^+ 258.0900. $C_{15}H_{14}O_4$ requires: 258.0891.)

8-Hydroxydunnione (**8**). ^1H NMR: δ 1.26 and 1.44 (each 3H, *s*, H_3-4′, H_3-5′), 1.46 (3H, *d*, *J* = 6.6 Hz, H_3-3′), 4.64 (1H, *q*, *J* = 6.6 Hz, H-2′), 7.10 (1H, *dd*, *J* = 1.0, 8.8 Hz, H-7), 7.19 (1H, *dd*, *J* = 1.0, 7.3 Hz, H-6), 7.53 (1H, *dd*, *J* = 7.3, 8.8 Hz, H-5), 11.92 (1H, *s*, chelated OH). MS *m/z*: 258 $[M]^+$ (10), 243 (62.3), 230 (38.4), 215 (base peak). (Found: M^+ 258.0886. $C_{15}H_{14}O_4$ requires: 258.0891.)

Conversion of (+)-dunnione (**1**) *into (+)-α-dunnione* (**4**). A suspension of (+)-**1** (40 mg) in 5% aq. NaOH (10 ml) was stirred at room temp. for 70 min. The resulting yellow ppt was collected by filtration and washed with H_2O until neutral. After drying, the yellow ppt (29 mg) was recrystallized from petrol to give α-dunnione (**4**) (24 mg) as yellow plates. Mp 120–121° (lit. [2] mp 121–122°), $[\alpha]_D^{30}$ +91.7° ($CHCl_3$; *c* 1.1) (lit. [2] $[\alpha]_D^{19}$ +104° ($CHCl_3$; *c* 0.77)). Its UV, IR and ^1H NMR data were in accord with those of α-dunnione directly isolated from mature plants as well as cell cultures of *S. dunnii*. (Found: C, 74.42; H, 5.80. Calc. for $C_{15}H_{14}O_3$: C, 74.37; H, 5.82%.)

Catalytic hydrogenation of dehydrodunnione (**5**). A soln of **5** (27 mg) in MeOH (10 ml) was hydrogenated over Pt (27 mg). After removal of the catalyst, the soln was concd *in vacuo* and the residue was subjected to TLC (C_6H_6–EtOAc, 9:1). The band at *ca* R_f 0.52 gave, on usual work-up, red needles (7.2 mg) which were identified as **1** (IR and ^1H NMR), while the band at *ca* R_f 0.49 gave the unchanged starting material (19 mg).

Conversion of dehydrodunnione (**5**) *into streptocarpone*. In an attempt to get dunnione (**1**), a soln of **5** (15 mg) in HOAc (5 ml) was hydrogenated over 10% Pd–C (5 mg) for 17 hr. After removal of the catalyst, the filtrate was concd *in vacuo*. The resulting residue gave on TLC (C_6H_6–EtOAc, 4:1) two bands at *ca* R_f 0.20 (major) and 0.49 (minor). The major one, on usual work-up followed by recrystallization from petrol, gave yellow needles (9 mg), which were identified as streptocarpone (**6**) (mmp, IR and ^1H NMR). The minor band gave **1**.

Methylation of streptocarpone (**6**). Compound **6** (5 mg) was treated with excess CH_2N_2–Et_2O. After evaporation of the solvent, streptocarpone methyl ether (**9**) (5 mg) was obtained as a yellow oil. UV λ_{max}^{MeOH} nm (log ε): 245 (4.06), 250 (4.05), 275 (3.85), 327 (3.27); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1670, 1650, 1590; ^1H NMR (60 MHz): δ 1.50 (6H, *s*, H_3-4′, H_3-5′), 2.15 (3H, *s*, –COMe), 4.05 (3H, *s*, OMe), 7.57–7.78 (2H, *m*, H-6, H-7) and 7.85–8.07 (2H, *m*, H-5, H-8). (Found: M^+ 304.0945. $C_{16}H_{16}O_6$ requires: 304.0946.)

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