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STRUCTURES OF UNUSUALLY PRENYLATED NAPHTHOQUINONES OF STREPTOCARPUS DUNNII AND ITS CELL CULTURES

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From Streptocarpus dunnii and its cell cultures, five unusually prenylated naphthoquinones and one anthraquinone were newly isolated together with two quinonoids already reported. Furthermore, the structures of four new naphthoquinones were elucidated.

KEYWORDS —Streptocarpus dunnii; Gesneriaceae; dunnione derivatives; 1-hydroxy-2-methylanthraquinone; cell cultures

Dunnione (**1**),[1] an unusually prenylated 1,2-naphthoquinone, was isolated from the leaves of Streptocarpus dunnii Mast. (Gesneriaceae); 1-hydroxy-2-hydroxymethylanthraquinone (**2**),[2] an anthraquinone structurally related to the quinones of the plants of Rubiaceae, was isolated from the roots thereof. Prior to studying the biosynthesis of quinones **1** and **2**, we reinvestigated the quinonoid constituents of this plant and further examined those of its cell cultures.

The benzene extract of the aerial parts of this plant was fractionated by column chromatography and preparative layer chromatography using silica gel, giving the major quinone **1** and six minor quinones: **2**, α-dunnione (**3**), dehydrodunnione (**4**), streptocarpone (**5**), 7-hydroxydunnione (**6**) and 1-hydroxy-2-methylanthraquinone (**7**). Likewise, the benzene extract of the roots gave quinone **2** as a sole quinone, as reported, while both extracts of the aseptically cultured plantlets and the cells coexisting with half-differentiated plantlets[3] afforded the five quinonoids **1**, **2**, **4**, **7** and 8-hydroxydunnione (**8**) besides the major quinone **3**. The structure eludication of the new quinones is described below.

Dehydrodunnione (**4**), orange-red needles, $C_{15}H_{12}O_3$, mp 96-97°C. Its spectral data are as follows: UV λ_{max}^{MeOH} nm (log ε): 260 (4.33), 267 (inf) (4.28), 311 (3.74) and 440 (3.37); IR ν_{max}^{KBr} cm^{-1}: 1685, 1650, 1615 and 1570; ^1H NMR ($CDCl_3$) δ: 1.56 (6H, s, 4'- and 5'-H_3), 4.51 and 4.95 (2H, each d, J=3.4 Hz, 3'-H_2), 7.52-7.83 (3H, m, 5, 6 and 7-H) and 8.05-8.14 (1H, m, 8-H). On the basis of these data and the ^{13}C NMR signals (Table I), the structure **4** was assigned to this quinone, which was confirmed through Pt-catalyzed hydrogenation of it to dunnione (**1**).

Streptocarpone (**5**), yellow needles, $C_{15}H_{14}O_4$, mp 120-121°C. Its spectral data are as follows: UV λ_{max}^{MeOH} nm (log ε): 246 (sh) (4.14), 252 (4.18), 275 (4.19), 329 (3.36) and 460 (3.09); IR ν_{max}^{KBr} cm^{-1}: 3450, 1665, 1650, 1615, 1590; ^1H NMR ($CDCl_3$) δ: 1.54 (4.3H, s, 4'- and 5'-H_3), 2.18 (2.1H, s, 3'-H_3), 7.60-7.83 and 7.97-8.12 (4H, A_2B_2 pattern, 5-, 6-, 7- and 8-H); MS m/z: 258 (M^+, 6.3%), 216 (base peak). From these data coupled with the ^{13}C NMR spectral findings (Table I), this quinone was presumed to have the structure **5**. Its ^1H NMR spectrum showed, besides the above signals, weak singlets at δ 1.34, 1.52 and 1.70, which were attributable to a gem. dimethyl group and to a methyl group of a hemiketal structure. On the other hand, its ^{13}C NMR spectrum showed weak signals at δ 19.0 (q), 21.9 (q), 25.4 (q), 50.1 (s) and 115.3 (s), which were respectively assignable to 4' (or 5'), 5' (or 4'), 3', 1' and 2' carbons of the hemiketal form (**5a**). These observations suggested that streptocarpone (**5**) is present in a solution as an equilibrium mixture of the ketophenol (**5**) and the tautomeric hemiketal (**5a**) (in a ratio of 5:2).

7-Hydroxydunnione (**6**), dark-red needles, $C_{15}H_{14}O_5$, mp 217-219°C, $[\alpha]_D$ +350° ($CHCl_3$).[4] Its spectral data are as follows: UV λ_{max}^{MeOH} nm (log ε): 270 (4.52), 277 (4.55), 306 (3.83) and 495 (3.31); IR ν_{max}^{KBr} cm^{-1}: 3100, 2950, 1690, 1600 and 1550; ^1H NMR ($CDCl_3$) δ: 1.25 and 1.44 (6H, each s, 4'- and 5'-H_3), 1.46 (3H, d, J=7.0 Hz, 3'-H_3), 4.66 (1H, q, J=7.0 Hz, 2'-H), 7.12 (1H, br d, J=8.0 Hz, 6-H), 7.51 (1H, d, J=8.0 Hz, 5-H), 7.61 (1H, br s, 8-H) and 7.40-8.20 (1H, br signal, OH). The ^1H NMR signal pattern in the aromatic region indicated the location of the hydroxy group at the C-7. The pattern in other regions was the same as that of dunnione (**1**). Thus, the structure **6** was assigned to this quinone.

8-Hydroxydunnione (**8**), optically inactive red needles, $C_{15}H_{14}O_4$, mp 151-152°C. Its spectral data are as follows: UV λ_{max}^{MeOH} nm (log ε): 242 (sh) (4.35), 260 (4.40), 294 (3.89) and 412 (3.84); IR ν_{max}^{KBr} cm^{-1}: 3200, 1690, 1640, 1610 and 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.26 and 1.44 (6H, each s, 4'- and 5'-H), 1.46 (3H, d, J=6.6 Hz, 3'-H_3), 4.64 (1H, q, J=6.6 Hz, 2'-H), 7.10 (1H, dd, J=1.0 and 8.8 Hz, 7-H), 7.19 (1H, dd, J=1.0 and 7.3 Hz, 5-H), 7.53 (1H, dd, J=7.3 and 8.8 Hz, 6-H) and 11.92 (1H, s, chelated OH). From the above data coupled with the ^{13}C NMR findings (Table I), this quinone was presumed to be racemic 8-hydroxydunnione (**8**).

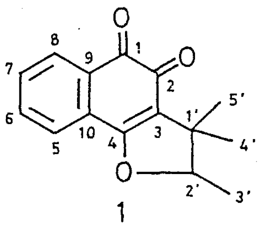
Finally, it is noteworthy that the optical purities of these dunnione derivatives varied depending on their origins. The optically pure dunnione (**1**)[5] isolated from the leaves had an $[\alpha]_D$ value of +307° ($CHCl_3$), while **1** from the plantlets possessed a value of +16.4°. α-Dunnione (**3**) from the leaves possessed $[\alpha]_D$ -9.9° ($CHCl_3$); and **3** from both plantlets and cells coincidently had identical values of +9.5°, while the optically pure α-dunnione (**3**)[1,5] derived from optically pure (+)-dunnione (**1**) had a value of +91.7°. 8-Hydroxydunnione (**8**) isolated from the plantlets as

Table I. ^{13}C NMR Spectral Data of Naphthoquinones isolated from *S. dunnii*[a)]

C No. / Compd.	1	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'
1	180.9 (s)	175.0 (s)	123.0 (s)	167.7 (s)	124.2 (d)	131.3 (d)	134.2 (d)	128.7 (d)	130.4 (s)	127.6 (s)	44.0 (s)	92.6 (d)	25.7 (q)	20.3 (q)	14.5 (q)
3	178.1 (s)	158.2 (s)	130.7 (s)	181.8 (s)	125.6 (d)	133.8 (d)	132.4 (d)	125.7 (d)	131.1 (s)	133.2 (s)	45.1 (s)	91.4 (d)	25.8 (q)	20.6 (q)	14.2 (q)
4	180.2 (s)	170.7 (s)	122.9 (s)	164.8 (s)	124.2 (d)	131.6 (d)	134.7 (d)	129.4 (d)	130.6 (s)	126.6 (s)	44.2 (s)	126.0 (s)	86.8 (t)	27.7 (q)	27.7 (q)
5[b)]	181.3 (s)	153.3 (s)	128.6 (s)	184.2 (s)	126.0 (d)	135.0 (d)	132.8 (d)	126.9 (d)	132.8 (s)	134.1 (s)	50.4 (s)	209.8 (s)	25.5 (q)	24.5 (q)	24.5 (q)
6	181.8 (s)	175.5 (s)	120.3 (s)	164.5 (s)	126.8 (d)	120.9 (d)	159.5 (s)	117.0 (d)	132.8 (s)	121.3 (s)	43.9 (s)	93.1 (d)	25.9 (q)	20.4 (q)	14.6 (q)
8	185.0 (s)	174.9 (s)	123.4 (s)	167.6 (s)	122.9 (d)	137.5 (d)	117.3 (d)	164.4 (s)	113.6 (s)	127.9 (s)	44.2 (s)	92.8 (d)	25.8 (q)	20.3 (q)	14.6 (q)

a) Measured at 50.10 MHz in $CDCl_3$. Chemical shifts in ppm from Me_4Si.

b) Signals originating only from the tautomeric **5a** are not shown.



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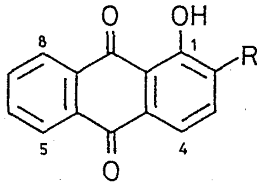
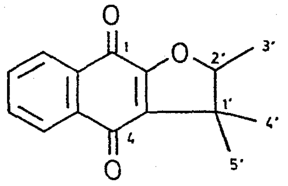


2 R = CH_2OH

7 R = CH_3



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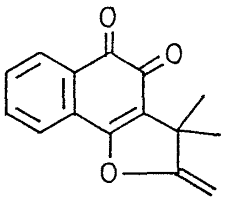

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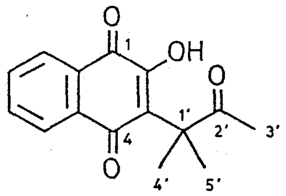

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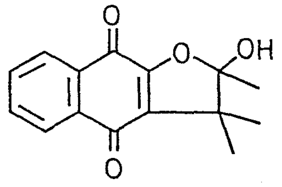
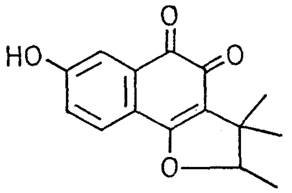


5a



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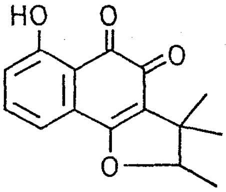

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well as the cell cultures was found to be racemic.

The absolute structures of dunnione derivatives are under investigation.

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REFERENCES AND NOTES

1) J. R. Price and R. Robinson, J. Chem. Soc., 1939, 1522. This quinone was also isolated from Calceolaria integrifolia (Scrophulariaceae). cf. P. Rüedi, C. H. Eugster, Helv. Chim. Acta, 60, 945 (1977).

2) J. Stöckigt, U. Srocka and M. H. Zenk, Phytochemistry, 12, 2389 (1973).

3) Callus tissues induced from the aseptically cultivated plantlets were transferred to the Linsmaier-Skoog medium supplemented with 10^{-5}M IAA and 10^{-6}M kinetin and subcultured to give cells coexisting with half-differentiated plantlets.

4) The figure represents the value of the quinone (**6**) isolated from the mature plants. The value of **6** isolated from the plantlets was not obtainable because of the scarcity of the substance.

5) The optical purity was ascertained through the ^{1}H NMR measurements in the presence of the chiral shift reagent Eu(TFC)$_3$.

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