

Results of calculations of the critical rotational parameter  $\epsilon$  are presented in the figure. Also presented is the curve of the radii of cylinders at critical rotation.

The maximal (critical) value of rotational parameter  $\epsilon_{\max}$  increases with increasing  $y_0^{-2}$ , that is with the transition

from relativistic cylinders to non-relativistic ones. As to the dimensionless radius  $\eta_1$  of the cylinders, the function  $\eta_1(y_0^{-2})$  has the minimum at  $y_0^{-2} \approx 0.35$  while for the degenerate gravitating non-rotating spheres corresponding minimum occurs at  $y_0^{-2} \approx 0.45$ .

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## Furodendin, a $C_{22}$ degraded terpene from the sponge *Phyllospongia dendyi*

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**Summary.** The structure of furodendin (5), a minor secondary metabolite of the sponge *Phyllospongia dendyi*, has been solved by spectral methods. Furodendin is probably derived, biosynthetically, by elimination of a  $C_3$  unit from a  $C_{25}$  geranyl-farnesol precursor.

Many species of the sponge genus *Spongia* have been found to contain the biosynthetically intriguing  $C_{21}$  difuranoterpenes<sup>3</sup> (eg. 1) probably derived from linear sesterterpene tetronic acids<sup>3</sup> (eg. 2) found in sponges of the genus *Ircinia*<sup>2</sup>. The sponge genus *Phyllospongia* has yielded a series of  $C_{26}$  and  $C_{27}$  tetracyclic 'sesterterpenes' (eg. 3) related to scalarin but with additional methyl groups at C24 for the  $C_{26}$  compounds and at C19 and C24 for  $C_{27}$  representatives<sup>4,5</sup>.

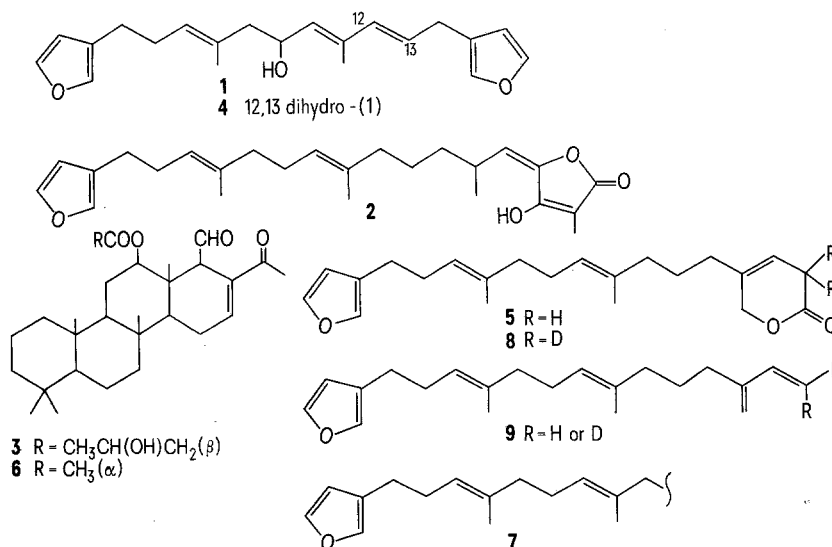
We have found that *Phyllospongia* species also contain truncated furanoterpenes. Thus *P. foliascens* collected near Cairns on the Great Barrier Reef was found to contain, in addition to  $C_{27}$  tetracyclic terpenes, the previously unreported didehydrofuranospongini-1 (4). We have also isolated a novel  $C_{22}$  furanoterpene (5) for which we propose the name furodendin, from *P. dendyi*.

Furodendin (5) was isolated as an oil together with the previously reported  $C_{26}$  tetracyclic sesterterpenes (3) and (6)<sup>4</sup> from the dichloromethane extract of the freeze-dried sponge by silica gel chromatography. The formula

$C_{22}H_{30}O_3$  was established by high resolution mass spectrometry. The IR-spectrum ( $\nu_{\max}$  1743  $\text{cm}^{-1}$ ) suggested the presence of an ester or 6-membered ring lactone carbonyl and this was supported by the presence of a singlet at 169.4 in the  $^{13}\text{C}$ -NMR-spectrum.

The  $^1\text{H}$ -NMR-spectrum of (5) showed resonances typical of a  $\beta$ -substituted furan [ $\delta$ 7.36 (1H, bs); 7.20 (1H, bs); 6.30 (1H, bs)] and two  $\text{CH}_2\text{-CH}=\text{C}(\text{CH}_3)$ -groups [ $\delta$ 5.20 (1H, bt); 5.12 (1H, bt) and 1.60 (6H, bs)]. The remainder of the spectrum comprised a 2 proton multiplet at  $\delta$ 1.54, signals due to 6 allylic  $\text{CH}_2$  groups between  $\delta$ 2.6 and 1.9, a 2 proton broad singlet at  $\delta$ 3.08, a 2 proton broad signal at  $\delta$ 4.62 and a broad resonance at  $\delta$ 5.56 (1H).

Irradiation at  $\delta$ 3.08 sharpened the  $\delta$ 5.56 and 4.62 signals considerably and irradiation at  $\delta$ 5.56 gave the  $\delta$ 4.62 resonance as a dd ( $J=2.5, 2.5$  Hz) and the signal at  $\delta$ 3.08 as a finely coupled multiplet. The  $^{13}\text{C}$ -NMR [ $\delta$ 169.4(s), 142.6(d), 138.8(d), 135.6(s), 135.3(s), 134.2(s), 134.0(d), 125.4(d), 125.3(d), 115.4(s), 111.0(d), 71.0(t), 30.0(t), 28.4(t), 26.5(t), 25.5(t), 25.1(t), 16.0 (q, 2C)] indicated a carbonyl



group and 5 double bonds (4 trisubstituted and 1 disubstituted). Furodendin was therefore bicyclic. The partial structure (7) was supported by NMR evidence and also by prominent fragment ions at  $m/e$  81 (base peak), 95, 135, 149 and 217 in the mass spectrum of (5). The appearance of the methyl carbons at  $\delta 16.0$  in the  $^{13}\text{C}$ -NMR of (5) established the stereochemistry about both double bonds as *E*. Treatment of (5) in  $\text{CD}_3\text{OD}$  with  $\text{NaOMe}$  gave the dideutero-derivative (8) ( $M^+ - m/e$  344) the  $^1\text{H}$ -NMR of which showed no resonance at  $\delta 3.08$  and much sharpened signals at  $\delta 5.56$  and  $4.62$ .

The mass spectrum of furodendin (5) showed no ions corresponding to the unsaturated lactone portion of the molecule, which was not surprising in that extrusion of carbon dioxide to give the ion (9) would be anticipated to be a facile process. Expected cleavage of this ion would give rise to ions at  $m/e$  67, 81 and 135 from either end of the molecule. Indeed high resolution observation of ions at

$m/e$  81 showed that both  $\text{C}_6\text{H}_9$  and  $\text{C}_5\text{H}_5\text{O}$  ions were present. The mass spectrum of the dideutero-derivative (8) showed ions at  $m/e$  67 ( $\text{C}_4\text{H}_3\text{O}$ ), 69 ( $\text{C}_5\text{H}_5\text{D}_2$ ), 81 ( $\text{C}_5\text{H}_5\text{O}$ ), 83 ( $\text{C}_6\text{H}_7\text{D}_2$ ), 135 ( $\text{C}_9\text{H}_{11}\text{O}$ ) and 137 ( $\text{C}_{10}\text{H}_{13}\text{D}_2$ ) which was fully in accord with the proposed structure of furodendin (5). Hydrogenation of (5) with 5% palladium on carbon gave a hexahydroderivative.

Furodendin is the 1st example of a compound, presumably derived from a geranyl-farnesol precursor, in which a  $\text{C}_3$  unit has been lost to give a  $\text{C}_{22}$  degraded terpenoid.

- 1 Acknowledgment. We thank Dr C. Evans for sponge identification, RRIMP Museum number FN1516/000.
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## Synthesis of koenigicine

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**Summary.** The structure of koenigicine as 8,9-dimethoxy-3,3,5-trimethyl-3,11-dihydropyrano-[3,2-a] carbazole (1) has been confirmed by synthesis.

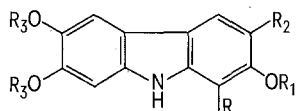
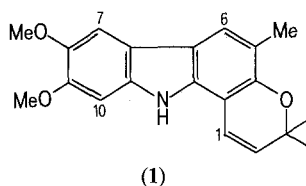
Several years ago we reported the isolation of a trioxxygenated carbazole alkaloid, koenigicine, from the leaves of *Murrya koenigii*<sup>1</sup> Spreng. Based on a combination of physicochemical studies and biogenetic considerations, structure (1) was proposed for this base. We now report its synthesis which conclusively confirms the structure assigned earlier. Ullmann condensation of 5-iodo-2-methoxytoluene with 2-bromo-4,5-dimethoxynitrobenzene in the presence of copper bronze at  $220^\circ\text{C}$  furnished a mixture of compounds from which the required 3'-methyl-2-nitro-4,4',5-trimethoxybiphenyl, m.p.  $139\text{--}140^\circ\text{C}$  could be isolated in 58% yield by column chromatography over silica gel. This, on heating with triethylphosphite at  $180^\circ\text{C}$ , afforded a mixture of isomeric 1-methyl-2,6,7-trimethoxycarbazole (2), m.p.  $208^\circ\text{C}$  (20%) and 3-methyl-2,6,7-trimethoxycarbazole (3),

m.p.  $240^\circ\text{C}$  (35%) which were separated and characterized by full spectroscopic studies.

Our initial attempts to demethylate selectively (3) so as to obtain the desired phenol (4), or a preferential functionalization of the hydroxy group in 3-methyl-2,6,7-trihydroxycarbazole (5), m.p.  $240^\circ\text{C}$  proved abortive. We then focussed our attention on the DDQ oxidation<sup>2</sup> of methylcarbazoles - a reaction described earlier by us. In a modified procedure the (6), m.p.  $211\text{--}212^\circ\text{C}$  was obtained by DDQ oxidation of (3) in over 50% yield.

Boron trichloride catalyzed demethylation of (6) in dichloromethane for 3 min furnished (7), m.p.  $223^\circ\text{C}$  (d) [NMR ( $\text{DMSO}-d_6$ ):  $\tau$  6.15 (s, 6,  $\text{ArOCH}_3$ ), 3.15 (s, 1, H-8), 2.99 (s, 1, H-1), 2.32 (s, 1, H-5), 1.69 (s, 1, H-4) and  $-0.11$  (s, 1,  $\text{CHO}$ )] in 50% yield which on hydrogenolysis over  $\text{Pd/C}$  (10%) afforded the phenol (4), m.p.  $228^\circ\text{C}$  (80%) [NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\tau$  7.72 (s, 3,  $\text{ArCH}_3$ ), 6.23 (s, 3,  $\text{ArOCH}_3$ ), 6.20 (s, 3,  $\text{ArOCH}_3$ ), 3.15 (s, 1, H-8), 3.09 (s, 1, H-1), 2.58 (bs, 1,  $\text{NH}$ ), 2.55 (s, 1, H-5), 2.42 (s, 1, H-4) and 0.58 (bs, 1,  $\text{OH}$ )].

Finally, condensation of (4) with 3-hydroxyisovaleraldehyde dimethylacetal<sup>3</sup> in pyridine at  $135^\circ\text{C}$  followed by PLC of the reaction mixture over silica gel gave (1), m.p.  $224^\circ\text{C}$  in 35% yield. This product was found to be identical with the natural koenigicine by several criteria, such as, m.p., m.m.p., Co-TLC, UV, IR, NMR and mass<sup>4</sup>.



- (2)  $\text{R} = \text{R}_1 = \text{R}_3 = \text{Me}$ ,  $\text{R}_2 = \text{H}$
- (3)  $\text{R} = \text{H}$ ,  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{Me}$
- (4)  $\text{R} = \text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{R}_3 = \text{Me}$
- (5)  $\text{R} = \text{R}_1 = \text{R}_3 = \text{H}$ ,  $\text{R}_2 = \text{Me}$
- (6)  $\text{R} = \text{H}$ ,  $\text{R}_1 = \text{R}_3 = \text{Me}$ ,  $\text{R}_2 = \text{CHO}$
- (7)  $\text{R} = \text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{CHO}$ ,  $\text{R}_3 = \text{Me}$

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