

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}C -NMR of (5) established the stereochemistry about both double bonds as *E*. Treatment of (5) in CD_3OD with NaOMe gave the dideutero-derivative (8) (M^+ : $-m/e$ 344) the ^1H -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 C_6H_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 C_3 unit has been lost to give a C_{22} degraded terpenoid.

- 1 Acknowledgment. We thank Dr C. Evans for sponge identification, RRIMP Museum number FN1516/000.
- 2 To whom reprint requests should be addressed.
- 3 L. Minale, G. Cimino, D. de Stefano and G. Sodano, Fortschr. Chem. org. NatStoffe 33, 1 (1976).
- 4 R.J. Wells, Pure appl. Chem. 51, 1829 (1979).
- 5 W. Hofheinz, personal communication.

Synthesis of koenigicine

R. B. Sharma, R. Seth-Verma and R.S. Kapil

Central Drug Research Institute, Lucknow 226001 (India), 23 October 1979

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.

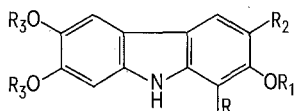
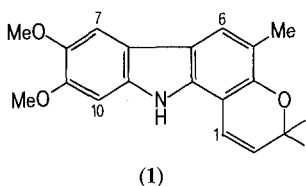
Several years ago we reported the isolation of a trioxxygenated carbazole alkaloid, koenigicine, from the leaves of *Murrya koenigii*¹ Spreng. Based on a combination of physicochemical studies and biogenetic considerations, structure (1) was proposed for this base. We now report its synthesis which conclusively 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°C furnished a mixture of compounds from which the required 3'-methyl-2-nitro-4,4',5-trimethoxybiphenyl, m.p. 139 – 140°C could be isolated in 58% yield by column chromatography over silica gel. This, on heating with triethylphosphite at 180°C , afforded a mixture of isomeric 1-methyl-2,6,7-trimethoxycarbazole (2), m.p. 208°C (20%) and 3-methyl-2,6,7-trimethoxycarbazole (3),

m.p. 240°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°C proved abortive. We then focussed our attention on the DDQ oxidation² of methylcarbazoles - a reaction described earlier by us. In a modified procedure the (6), m.p. 211 – 212°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°C (d) [NMR ($\text{DMSO}-d_6$): τ 6.15 (s, 6, 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, CHO)] in 50% yield which on hydrogenolysis over Pd/C (10%) afforded the phenol (4), m.p. 228°C (80%) [NMR (CD_3COCD_3): τ 7.72 (s, 3, ArCH_3), 6.23 (s, 3, ArOCH_3), 6.20 (s, 3, ArOCH_3), 3.15 (s, 1, H-8), 3.09 (s, 1, H-1), 2.58 (bs, 1, NH), 2.55 (s, 1, H-5), 2.42 (s, 1, H-4) and 0.58 (bs, 1, OH)].

Finally, condensation of (4) with 3-hydroxyisovaleraldehyde dimethylacetal³ in pyridine at 135°C followed by PLC of the reaction mixture over silica gel gave (1), m.p. 224°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 mass⁴.



- (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) $\text{R} = \text{R}_1 = \text{H}$, $\text{R}_2 = \text{CHO}$, $\text{R}_3 = \text{Me}$

- 1 S.P. Kureel, R.S. Kapil and S.P. Popli, Experientia 25, 790 (1969).
- 2 F. Anwer, A.S. Masaldan, R.S. Kapil and S.P. Popli, Indian J. Chem. 11, 1314 (1973).
- 3 S.P. Kureel, R.S. Kapil and S.P. Popli, Chem Ind. 1970, 1262.
- 4 CDRI Communication No. 2634.