6-(3-Methylbuta-1,3-dienyl)indole from Monodora tenuifolia

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Summary The title compound has been isolated from the seed of Monodora tenuifolia, and identified by analysis and by comparison of the spectra with those of the isomeric monomethyl indoles.

THE seed of Monodora tenuifolia (Benth.), Annonaceae, are mildly fragrant, and used as a food flavouring in West Africa. The main petroleum extract (ca. 0.3%) was a crystalline solid, C_{13}H_{13}N,† m.p. 124—127°; λ_{max} 225 (infl.), 264, and 310 nm (ϵ 10,100, 16,100, and 19,000). The n.m.r. spectrum showed bands attributable to an isoprenyl residue: δ 1.96 (3H, s, Me), 5.06 (2H, m, =CH₂), 6.70 and 6.80 (2H, vinyl-H, multiplicity undetermined), and aromatic resonances: 7.57 (1H, d, J 9 Hz), ca. 7 (3H, complex), and ca. 6.47 p.p.m. (1H, complex). Hydrogenation in ethanol over palladium gave a liquid tetrahydro-derivative, in which the isoprenyl bands had disappeared and were replaced by isopentyl bands: $\delta 0.92$ (6H, d, J 5 Hz, 2×Me), 1.53 (3H, m), and 2.72 p.p.m. (2H, m, Ar-CH₂). The aromatic hydrogen resonances in the tetrahydro-derivative formed a pattern closely similar to that of a synthetic sample of 6-methylindole, but different from that of any of the other monomethyl-indoles; the natural product is therefore 6-(3methylbuta-1,3-dienyl)indole (1). The recognition as a 6-substituted indole was aided by the i.r. absorption

¹ H. Plieninger, R. Fischer, and V. Liede, Annalen, 1964, 672, 223.

frequency of the aromatic hydrogens (805 and 765 cm⁻¹, 2 adjacent H). Further, a synthetic sample of 4-methylindole lacks the downfield resonance at δ ca. 7.5 p.p.m. Since this is present in the spectra of all the other mono-



methyl-indoles, it is presumably due to 4-H, and since it is a clear doublet (J 9 Hz) in the natural product, it follows that C-6 must be substituted.

So far as we are aware, this is the first isoprenyl-indole to be reported, although similar derivatives of oxygen heterocycles are well known. The biosynthesis may possibly follow the pattern suggested by Plieninger¹ for 4-dimethylallyltryptophan, an intermediate in lysergic acid biosynthesis. Alternatively, it may be a product of substitution of indole by dimethylallyl pyrophosphate or a similar reagent, or the isoprenyl group may be introduced before the hetero-ring is formed.

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[†] Satisfactory analyses for C, H, and N were obtained.