

## STUDIES IN TERPENOID-XXII. SYNTHESIS OF MANSONONE G

By V. VISWANATHA AND G. S. KRISHNA RAO

(Department of Organic Chemistry, Indian Institute of Science, Bangalore-12, India)

(Received: May 25, 1972)

### ABSTRACT

The synthesis of 3,8-dimethyl-5-isopropyl-6-hydroxytetralone (7a) and its oxidation by selenium dioxide to mansonone G (4a) are reported, the sequence constituting the first successful synthesis of this naturally occurring hydroxy-o-naphthaquinone.

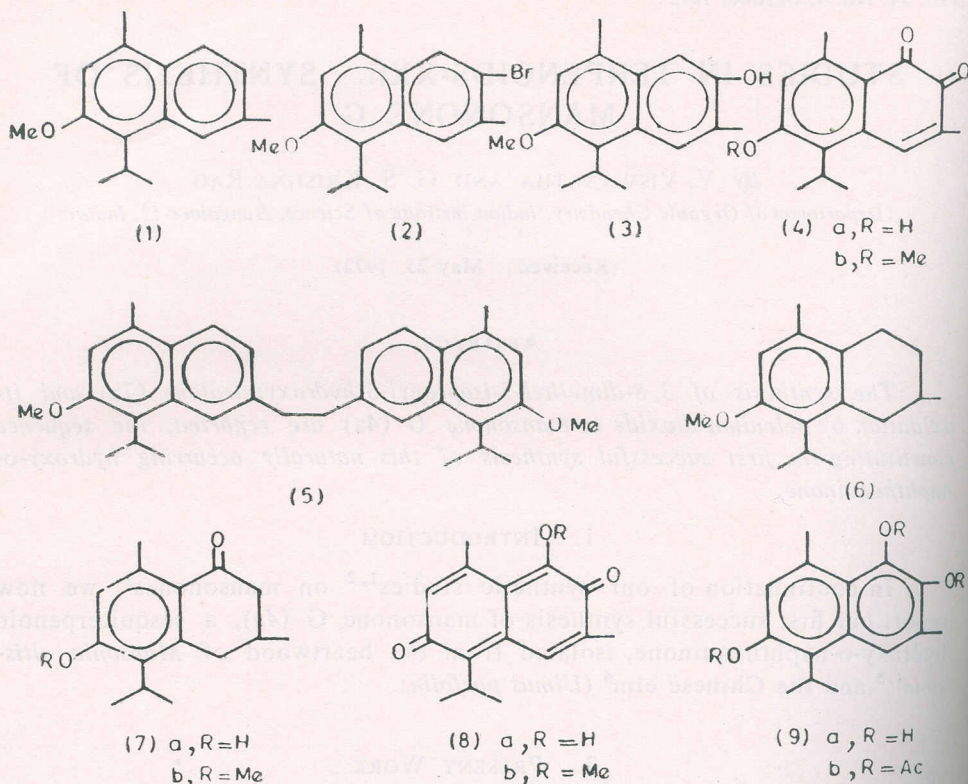
### 1. INTRODUCTION

In continuation of our synthetic studies<sup>1,2</sup> on mansonones<sup>3</sup>, we now report our first successful synthesis of mansonone G (4a), a sesquiterpenoid hydroxy-o-naphthaquinone, isolated from the heartwood of *Mansonia altissima*<sup>4,5</sup> and the Chinese elm<sup>6</sup> (*Ulmus parfolia*).

### 2. PRESENT WORK

3-Methoxycadalene<sup>7</sup> (1) was brominated (Br<sub>2</sub>-AcOH) to the bromo methoxycadalene<sup>8</sup> (2), m.p. 105-106°, intended for conversion by copper-bronze-caustic alkali treatment<sup>9</sup> to the hydroxy methoxycadalene (3) to be oxidised to o-methyl-mansonone G (4b) by Fremy's salt<sup>1,10</sup>. The realisation of 3 and with it the subsequent plan were thwarted, when a dimer (5), m.p.180-181° (mass and NMR spectra) resulted, instead of the hoped for Br → OH transformation (see Scheme).

In the alternate successful route, 3,8-dimethyl-5-isopropyl-6-methoxytetralone (7b), m.p.83°, the chromic acid oxidation<sup>11</sup> product of 2,5-dimethyl-7-methoxy-8-isopropyltetralin<sup>12</sup> (6), was the starting material. Selenium dioxide oxidation<sup>12</sup> of 7b gave, as expected, a methoxyquinone (4b), m.p.161-162°, its analysis and spectral (UV, IR, in particular NMR) data fully supporting the structure<sup>13</sup>. However, there was a minor set back, when the methyl ether (4b) failed to undergo clean demethylation when heated with pyridinehydrochloride. Only an intractable black mass was obtained. This difficulty was circumvented by effecting the selenium dioxide oxidation on the hydroxytetralone (7a), when an orange crystalline specimen



## SCHEME

of mansnone G\* (4a), m.p.198-200°, was obtained which was identical in all respects with the natural specimen<sup>6,14</sup> (UV, IR, NMR and identical  $R_f$  values on TLC with two different solvent systems). The Japanese workers<sup>4</sup> record a m.p.210-213° for mansnone G, while the Italian group<sup>5</sup> report a m.p.201-203° for their natural sample<sup>3</sup>. The m.m.p. of our synthetic sample with the natural specimen<sup>6,14</sup> was undepressed.

The synthetic mansnone G (4a) readily (2 mins) absorbed hydrogen (Pt/H<sub>2</sub>) to give the colourless hydroquinone (9a), which as readily underwent aerial oxidation to revert to the orange quinone (4a). With *o*-phenylenediamine it gave a yellow crystalline quinoxaline derivative, m.p.211-212°. On reductive acetylation (Zn-Ac<sub>2</sub>O) of 4a, the corresponding leucotriacetate (9b), m.p.188-189° (Rep.<sup>4</sup> m.p.188-189°) was obtained.

We thank the C.S.I.R. for a Junior Research Fellowship (to V.V.).

\* This and other new compounds reported in this communication gave correct elemental analysis and spectroscopic data.

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 We prepared the cadalene by dehydrogenation of the tetralol, m.p.89-90°, resulting from the sodium borohydride reduction product of 2,5-dimethyl-7-methoxy-8-isopropyltetralone<sup>12</sup>
8. The position of Br in 2 was inferred from the known electrophilic substitution pattern of 1-alkyl-2-methoxynaphthalene (cf. G.A.Olah, "Friedel-Crafts and Related Reactions", Interscience, London, 1964, Vol. III, Part I, Pp.261, 647 and 720) and was supported by its NMR spectrum.
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13. Tanaka *et al.*<sup>4</sup> report the *o*-methylmansonone G obtained on methylation of 4a [(CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>CO<sub>3</sub>-acetone] as a liquid. It is possible that their liquid methyl ether is that of 8-hydroxy-3, 7-naphthaquinone (8a), tautomeric with 4a. It is proposed to clear up this point [4b (solid) versus 8b (liquid)] in the full paper.
14. We express our grateful thanks to Prof. Fa-ching Chen for kindly sending us an authentic sample of naturally occurring mansonone G and a copy of its NMR spectrum.