

STUDIES IN TERPENOIDS - XXXIII. SYNTHESIS OF MANSONONE D

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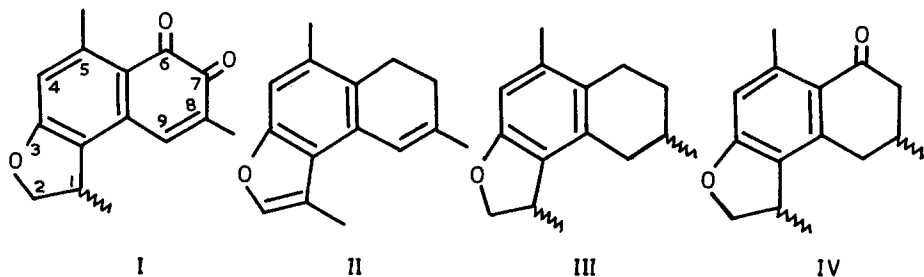
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In continuation of our work¹ on mansonones², comprising the group of naturally occurring cadalenic *o*-naphthoquinones, we report here the first synthesis of mansonone D (I), a furano-*o*-naphthaquinone isolated from Mansonia altissima³. The striking structural similarity of this quinone and pyrocurzerenone (II), a naphthofuran isolated from Curcuma zedoaria⁴ and synthesized by us recently⁵ prompted us to attempt the transformation, II \rightarrow I, which was successfully achieved as follows.

Synthetic pyrocurzerenone⁵ (II) was hydrogenated (PtO₂/MeOH) at atm. press. till it absorbed two moles of hydrogen to give the stereoisomeric mixture of tetrahydropyrocurzerenones (III). Oxidation of this mixture with chromic acid in acetic acid-propionic acid, a reagent of proven utility in the oxidation of similar 6-oxytetralin systems^{1b,c} to 6-oxytetralones, gave the corresponding stereoisomeric mixture of the furanotetralones (IV), contaminated with γ -lactonic (i.r.) impurity which probably arose from the oxidation (-OCH₂- \rightarrow -O-CO-) of the dihydrofuran moiety. However, by treatment with alkali this was eliminated and the residual oxo compound revealed in the n.m.r. (i) a methylene attached to oxygen, (ii) two secondary methyls and (iii) a deshielded aromatic methyl, though these signals had the expected complexity because of the presence of diastereoisomers in the product (IV).

The furanotetralone (IV) was oxidized by refluxing with selenium dioxide^{1b,c} for 4 hr in ethanol. The product was chromatographed (t.l.c., silica gel, chloroform), when the polar orange yellow band on the chromatogram gave on elution mansonone D (I), m.p. 173-175° (light petroleum) (Rep.³ 173-175°); M^+ 242; λ_{max} (ethanol) 220 (17980), 242 (12910), 279 (12790) and 405 nm (ϵ 7950) and had i.r. spectrum superimposable with that of the natural sample. In the n.m.r. spectrum it exhibited C₁-Me at δ 1.37 (3H, d, J 7 Hz), C₈-Me at 2.05 (3H, d, J 1.5 Hz), C₅-Me at 2.63 (3H, s), C₁-H at 3.63 (1H, m, X of ABX),



C_2 -H at 4.55 (2H, ABX pattern), C_4 -H at 6.58 (1H, s) and C_9 -H at 7.18 (1H, q, J 1.5 Hz). A notable feature of the selenium dioxide oxidation of the furano-tetralone (IV) is the resistance of the dihydrobenzofuran moiety to undergo dehydrogenation. Cases are known from literature where reagents like selenium dioxide, lead tetraacetate and chloranil failed to dehydrogenate dihydrofurans⁶.

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