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A NEW QUINONE FROM THE HEARTWOOD OF MANSONIA ALTISSIMA CHEV : MANSONONE L.

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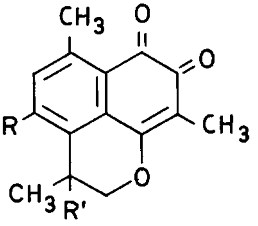
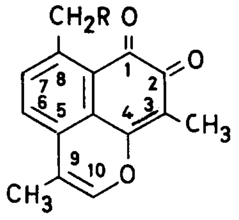
In previous papers (1, 2, 3) we have reported the isolation and the structure of eight sesquiterpene quinones isolated from the wood of Mansonia Altissima named respectively Mansonones A,B, C, D, E, F, G, and H

These Mansonones except B and D were also described by Tanaka, Yasue and Imamura (4) who have recently reported a new quinone, Mansonone I (5)

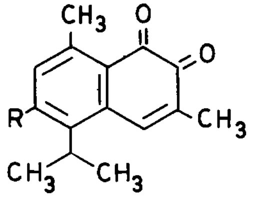
We are now reporting the isolation of another new quinone, Mansonone L. The quinone was isolated from the chloroform extract containing Mansonones F, G, and H by Al_2O_3 (IV)column chromatography (solvent benzene-chloroform -8:2) (violet crystals from ethyl acetate, melting point 165-7°). The mass spectrum shows the molecular ion at m/e = 256 (base peak), corresponding to the formula $C_{15}H_{12}O_4$.



Mans.I R : H ; R': OH
Mans.E R : H ; R': H
Mans.H R : OH; R': H



Mans. F R : H
Mans. L R : OH



Mans. C R : H
Mans. G R : OH

The UV spectrum of Mansonone L shows a maximum at 234 nm, with a shoulder at 255 nm and in the visible at 555 nm, as in Mansonone F ($C_{15}H_{12}O_3$) which suggests an oxaphenalene structure. We may therefore consider Mansonone L, which contains one oxygen atom more than Mansonone F, as a hydroxy Mansonone F. This is confirmed by the fact that Mansonone L is easily acetylated with pyridine and acetic anhydride. The more probable position of the hydroxy group, 6, can be excluded. In effect, the introduction of an hydroxy group in 6 modifies the UV spectra of Mansonones C and E respectively as it appears in Mansonone G (6-hydroxy-Mansonone C) and H (6-hydroxy-Mansonone E), whereas the spectrum of Mansonone L, as above reported, is closely related to that of Mansonone F (1) Spectra cannot be measured in alkaline solution because of the great sensitivity of the product.

The NMR spectrum of Mansonone L was measured with less than 1 mg substance with the time averaging device on a Varian HA 100 instrument. The spectrum in deuterated pyridine after 30 scans between 1 and 3.5 ppm, in comparison to that of Mansonone F in the same solvent, shows a singlet corresponding to one methyl at 1.97 ppm (1.93 ppm for the CH_3 group in the quinone ring of Mansonone F) and a doublet corresponding to a weakly coupled (J=1.5 cps) methyl at 1.92 ppm which appears at 1.86 ppm in Mansonone F. The signal of the methyl peri to the carbonyl (which in Mansonone F is at 2.57 ppm) is absent in Mansonone L. This fact suggests the presence of an oxygen atom in the form of hydroxymethyl group CH_2OH.

The NMR spectrum in deuterated acetone after 50 scans between 6.20 and 8.70 ppm shows a broad signal at 7.35 ppm compared to that of Mansonone F where a scarcely resolved quartet is present at 7.20 ppm. These signals are assigned in both quinones to the olefinic hydrogen coupled with the above mentioned methyl group which appears as a doublet (J=1.5 cps) at 1.92 and 1.86 ppm respectively. The two aromatic ortho hydrogens which appeared in Mansonone F as an AB quartet with chemical shift values very near (7.41 and 7.48 ppm) are in Mansonone L practically coincident (7.84 ppm). Moreover the mass spectrum shows a peak at M^+-17 (16% of the base peak).

Therefore the presence of a CH_2OH in peri position to the carbonyl, is strongly supported by these facts.

Moreover, the observed increase of chemical shifts in aromatic protons of Mansonone L respect to Mansonone F (7.84 respect to 7.41 and 7.48 ppm) is in agreement with the presence of a hydroxymethyl instead of that of a methyl group (6).

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