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THE QUINONOID PIGMENTS OF MANSONIA ALTISSIMA WOOD.

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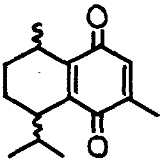
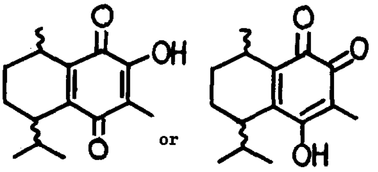
In 1959, Sandermann and coworker[1)] reported that wood sawdust of Mansonia altissima Chev. causes an allergic sensitiveness and a violent sneezing, and the heartwood contains two pigments.

Marini Bettòlo and coworkers[2)] recently recognized six pigments in the above heartwood and discussed the respective structures of pigments; Mansonone A $C_{15}H_{20}O_2$ m.p.117-8(I), Mansonone B $C_{15}H_{20}O_3$ m.p.68-9(II), Mansonone C $C_{15}H_{16}O_2$ m.p.134-8(III), Mansonone D $C_{15}H_{14}O_3$ m.p.173-5(IV), Mansonone E $C_{15}H_{14}O_3$ m.p.148-9(V) and Mansonone F $C_{15}H_{12}O_3$ m.p.214-5(VI).



(I)



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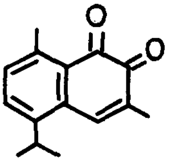

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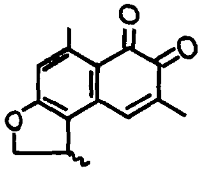

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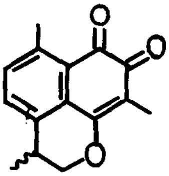

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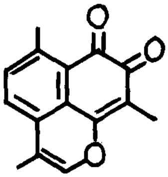

(VI)

We have also investigated acetone extractives of the heartwood of Mansonia altissima and observed more than ten spots on P.P.C. and T.L.C. By means of column chromatography on silica gel, six pigments (Table I), β-sitosterol and β-sitosteryl palmitate were isolated from the extractives. *

TABLE I

Compound	Color	Formula	m.p.
A (VIII)	red	$C_{15}H_{20}O_2$	118-9
B (III)	orange	$C_{15}H_{16}O_2$	134-5
C (VII)	orange	$C_{15}H_{14}O_3$	144-6
D (VI)	violet	$C_{15}H_{12}O_3$	214-6
E (XI)	orange	$C_{15}H_{16}O_3$	210-3
F (X)	red	$C_{15}H_{14}O_4$	$>$320

Amongst the pigments mentioned above, compounds A, B, C and D were identical with Mansonone A, C, E and F, respectively, in their molecular formulae, melting points, u.v. and n.m.r. spectra. Compounds E and F are considered new sesquiterpenoid quinones, and so we propose to term them Mansonone G and Mansonone H. The evidences of our investigation (i.r., u.v. and n.m.r.) supported the structures for Mansonone C, E and F proposed by Marini Bettòlo and coworkers.

Mansonone E (Compound C (VII))

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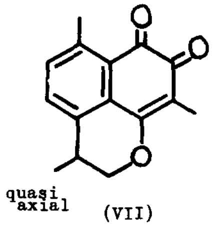
* The isolation and partial structures of these pigments were reported in the previous paper. 3)

Compound C is, however, optically active ($[\alpha]_D^{21}$ +82°) and its n.m.r. spectrum (in $CDCl_3$ with TMS as internal standard, Varian A 100 instrument) indicates that the methyl group attached to the asymmetric carbon atom is in a quasi axial position (VII), because the signal of methylene group in the heterocyclic ring appears as AB quartet centered at $\tau 5.68$ in which each of the peaks is split into doublets (δ_{AB}=21.0 cps, J_{AB}= 11.7 cps, J_{AX}=3.8 cps, J_{BX}=5.0 cps). These coupling constants reveal that the dihedral angles are about 60°.[4)]



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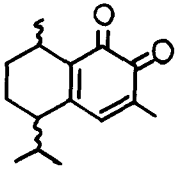


(VIII)

Mansonone A (Compound A (VIII))

For the structure of Mansonone A, Marini Bettòlo and coworkers have proposed the formula (I) but the absorption spectrum of compound A shows λ_{max}^{MeOH} at 432 mμ which is the characteristic absorption of o-quinone structure, and the leucoacetate has λ_{max}^{MeOH} at 270 mμ indicating the presence of benzenoid ring. Furthermore, the dehydrogenation of compound A with chloranil under the mild condition gave compound B (Mansonone C). On these bases we propose the formula (VIII) for Mansonone A.

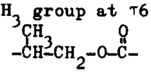
Mansonone H (X)

The i.r. spectrum of Mansonone H reveals the presence of OH group (3160 cm^{-1}) and this compound gave a monoacetate ($C_{17}H_{16}O_5$ m.p. 202–4°, $[\alpha]_D^{21}$ +424°) and a monomethyl ether (with dimethyl sulfate and K_2CO_3 in acetone, $C_{16}H_{16}O_4$ m.p.208-9°, $[\alpha]_D^{21}$ +526°), and their i.r. spectra do not show any OH band. Its color disappeared with $Na_2S_2O_4$, and was regenerated by aeration. The reductive acetylation of Mansonone H gave a leucoacetate ($C_{21}H_{22}O_7$ m.p.163-5°) which had the characteristic u.v. absorption band of naphthalene structure (λ_{max}^{MeOH} 238, 265, 293, 320 and 334mμ). When the methyl ether was treated with o-phenylenediamine, it gave a quinoxaline derivative ($C_{22}H_{20}O_2N_2$ m.p.175-8°).

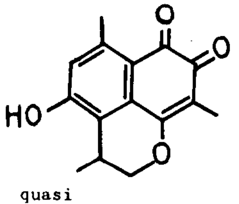
After the methyl ether absorbed one mol. of hydrogen on catalytic reduction with Adams' Pt, its color disappeared, and the reduction product returned to the original methyl ether by air oxidation.

From the above results it has been recognized that Mansonone H is an o-naphthoquinone possessing one OH and a heterocyclic ring. The n.m.r. spectrum of the monoacetate shows the presence of a CH_3 group on a peri position[5] (τ7.36 singlet, 3H), a CH_3 group on a quinonoid ring[6] (τ8.05, singlet, 3H), an acetyl group (τ7.36, singlet, 3H) and one aromatic proton (τ2.92, singlet, 1H). Besides them the signals of a doublet at τ8.66 (J=9cps , 3H), a multiplet at τ6.95 (1H) and a quartet centered at τ5.67, which is split into two peaks (δ_{AB} =14.2cps, J_{AB} =11cps, J_{AX} =1.0cps, J_{BX} =2.6cps, 2H) are observed. These signals can be assigned to a system ($-\overset{CH_3}{\overset{|}{C}H}-CH_2-O-$) which has been supported by the decoupling test, and from these coupling constants it is indicated that the methyl group on the heterocyclic ring is in a quasi axial position.

The methyl ether yielded one mol. of acetic acid identified as a p-bromophenacyl ester (m.p.78-9°) and a phthalic acid derivative ($C_{13}H_{16}O_6$ m.p.223°) on oxidation with H_2O_2 . The i.r. spectrum of the acid shows the presence of OH group (3480 cm^{-1}) and one mol. of

H_2O was eliminated and a δ-lactone ($C_{13}H_{14}O_5$ m.p. 220°, 1725 cm^{-1} δ-lactone carbonyl, 1700 cm^{-1} COOH) was formed when the acid was heated at 100°C. The n.m.r. spectrum of the lactone shows the signals of an aromatic CH_3 group at τ7.64, an OCH_3 group at τ6.07, one aromatic proton at τ2.78 and a lactone ring  $-\overset{CH_3}{\overset{|}{C}}H-CH_2-O-\overset{O}{\overset{\|}{C}}-$ (τ8.73, doublet J=8.2 cps, 3H, τ6.63, multiplet 1H, quartet centered at τ5.79, δ_{AB}=19.8cps, J_{AB}=11cps, J_{AX}=3cps, J_{BX}=1cps, 2H). The above fact reveals that the positions of two methyl groups are 3 and 8, and the cyclisation can be done between positions 4 and 5 of naphthoquinone nucleus.

Since Mansonone H and G (described below) gave similarly a green color with nickel acetate (the coloration may be due to the formation of chelate complex with the enol form (IX)), it can be considered that the positions of their OH groups are on the same positions in both molecules. Methylation of Mansonone G with diazomethane was difficult, and this behaviour seemed to be due to the steric hindrance by the isopropyl group. Furthermore, although clear signals do not appear, the presence of a long range coupling between the aromatic proton and the methyl group on peri position is observed. This indicates that the position of hydroxyl group is 6. Therefore, we propose the structure (X) for Mansonone H.



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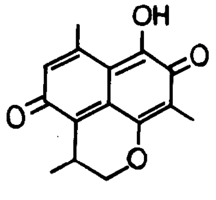


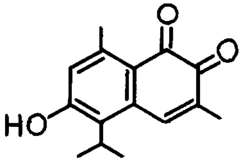
(IX)

Mansonone G (XI)

Mansonone G is an orange pigment and decolorised with $Na_2S_2O_4$, and regenerated by aeration. It shows the presence of OH group (3300 cm^{-1}) and gave a monoacetate (oil) and a monomethyl ether (with dimethyl sulfate and K_2CO_3 in acetone, oil). The reductive acetylation of Mansonone G yielded a leucoacetate ($C_{21}H_{24}O_6$ m.p.188-9°). The u.v. spectrum of the leucoacetate shows the characteristic absorption of naphthalene nucleus (λ_{max}^{MeOH} 233, 288 and 328mμ).

The treatment of the monomethyl ether with o-phenylenediamine gave a quinoxaline derivative ($C_{22}H_{18}ON_2$ m.p.152-3°). These results indicate that Mansonone G is an o-naphthoquinone possessing one OH group.

In the n.m.r. spectrum of the leucoacetate three acetyl groups and an aromatic CH_3 group appear as two peaks at τ7.65 (singlet, 6H) and at τ7.67 (singlet, 6H), and an aromatic CH_3 group (τ7.32, singlet, 3H), two aromatic H (τ3.14, singlet, 1H and τ2.02, singlet, 1H) and an isopropyl group (τ8.59, doublet, J=8cps, 6H, τ6.25, multiplet, J=8cps, 1H) are also observed. The skeleton of Mansonone G is considered to be an o-naphthoquinone of cadalene type because of the fact that all quinones in the heartwood of Mansonia are the cadalene type. Moreover, from the facts of the presences of hydroxyl group at position 6 and of two aromatic protons which do not couple with each other, the structure of Mansonone G is presumed as formula (XI).



(XI)

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