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THE STRUCTURE OF AMITENONE

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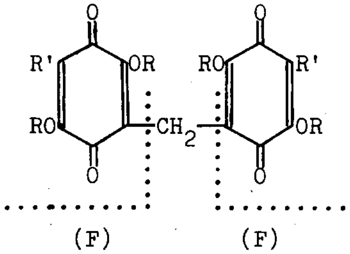
Three pigments A, B and C were isolated from acetone extract of a kind of edible mushroom, Amitake(Suillus bovinus (Fr.) Kuntze), in yield, 0.09% of oven-dried fruit-body.$^{1)}$In the present paper, the chemical structure of the pigment A, named amitenone(1), is elucidated as methylenebis(2,5-dihydroxy-4-all-trans-geranylgeranyl-3,6-benzoquinone) by evidences described below.

Its analytical figures corresponded to $C_{53}H_{72}O_8$; calcd. C 76.04% H 8.67%, found C 75.84% H 8.44% OCH_3 0%. M.W.; calcd. 837.16, found 850(vapor pressure equilibrium method). Yellow orange crystal. m.p. 187-8°. IR, cm^{-1}:(in KBr), 3290 (OH), 1615(quinone), 1300, 1050, 840, 770, 690;(in $CHCl_3$), 3358(OH), 1646(quinone) ;deuterium-substituted(in $CHCl_3$), 2490(OD). UV, $m\mu(\log\varepsilon)$: 288(4.45)(in ethanol), 410(shoulder, 2.67)(in $CHCl_3$), 323(in 0.1N-NaOH+ethanol, 1:1 v/v). NMR, τ(in $CDCl_3$) (Q:quinone): 2.42(4H, s; exchangeable by D_2O— method; $Q-O\underline{H}$), 4.85-5.05(8H; $-CH_2-C\underline{H}=\overset{|}{C}-$), 6.48(2H, s; $Q-C\underline{H}_2-Q$), 6.93(4H, d; $Q-C\underline{H}_2-CH=$), 7.85-8.15(24H; $=C-C\underline{H}_2-C\underline{H}_2-CH=$) 8.30(6H, s; $Q-CH_2-\underset{H}{C}=\underset{R}{C}-C\underline{H}_3$), 8.35(6H, s; $-\underset{H}{C}=C\genfrac{}{}{0pt}{}{CH_3}{C\underline{H}_3}$), 8.43(18H, s; $H-\overset{R}{C}=\underset{R}{C}-C\underline{H}_3$). Mass, m/e; 426.279($F+CH_2+1$), 412.258(F+1), 343(F+1-69), 275(F+1-69-68), 207(F+1-69-68-68) 193, 81, 69(base), 55, 41, 28.

Derivative of amitenone methylated with diazomethane(2). b.p. 210°(decomp.). Yellowish brown oil. $C_{53}H_{68}O_4(OCH_3)_4$; calcd. C 76.64% H 9.03%, found C 76.32% H 9.01%. IR, cm^{-1}(liquid); 1655(C=0), 1610(C=C). UV, $m\mu(\log\varepsilon)$(in ethanol); 286(4.28) 410(shoulder, 2.91). NMR, τ(in $CDCl_3$): 4.85-5.05(8H; $-CH_2-C\underline{H}=\overset{|}{C}-$), 6.05(6H, s; $Q-OC\underline{H}_3$), 6.10(6H, s; $Q-OC\underline{H}_3$), 6.50(2H, s; $Q-C\underline{H}_2-Q$), 6.93(4H, d; $Q-C\underline{H}_2-CH=$), 7.85-8.1 (24H; $=C-C\underline{H}_2-C\underline{H}_2-CH=$), 8.28(6H, s; $Q-CH_2-\underset{H}{C}=\underset{R}{C}-C\underline{H}_3$), 8.33(6H, s; $-\underset{H}{C}=C\genfrac{}{}{0pt}{}{CH_3}{C\underline{H}_3}$), 8.41(18H s; H-$\overset{R}{C}$=$\underset{R}{C}$-C$\underline{H}_3$).

Derivative of amitenone hydrogenated with palladium-carbon catalyst and oxidized with air, named amitanone(3). m.p. 192-4°. Yellow orange crystal. $C_{53}H_{88}O_8$; calcd. C 74.60% H 10.40%, found C 74.50% H 10.71%. M.W.; calcd. 853.29, found 880 (vapor pressure equilibrium method). IR, cm^{-1}(in KBr); 3280(OH), 1610(quinone), 1290, 1120, 1030, 770, 685. UV, mμ(logε)(in ethanol); 292(4.61), 410-430(shoulder). NMR, τ(in $CDCl_3$): 2.35(4H, s; exchangeable by D_2O-method; Q-O$\underline{H}$), 6.43(2H, s; Q-C$\underline{H}_2$-Q), 7.57(4H, t; Q-C$\underline{H}_2$-CH_2-), 8.2-9.0(48H; -C$\underline{H}_2$-, -$\overset{|}{C}\underline{H}$-), 9.07, 9.10, 9.14(sum. 30H -C$\underline{H}_3$). Mass, m/e; 420(F+8H+1), 434(F+CH_2+8H+1), 154, 69, 57, 28(base).



(1) R=H R'=$-(CH_2-\underset{H}{C}=\overset{CH_3}{C}-CH_2)_4$H (all trans)

(2) R=CH_3 R'=(1)

(3) R=H R'=$-(CH_2-CH_2-\overset{CH_3}{CH}-CH_2)_4$H

(4) R=H R'=n-$C_{11}H_{23}$

Ethanolic solution of (1) was decolorized by acidic reduction---zinc hydrochloric acid or sulfur dioxide---and gave purple precipitate with formaldehyde by Feigl method.[2] These facts indicate that (1) belongs to quinone. IR spectra of (1) and its derivatives, having the absorptions near 1610 and 1655 cm^{-1}, support this indication. In its mass spectrum as the description by Aplin and Pike[3] that p-benzoquinone has comparatively large peak of M+2 in comparison with that of M, the peak height of F+1+2, corresponding to M+2, is about 50% of that of F+1 corresponding to M, while the peak height of F+1+2 owing to natural isotopes of C, H and O were to be 4.81% of that of F+1. This fact also supports the quinone structure of (1).

Although the product of catalytic hydrogenation of (1) was decolorized, it readily recovered the color by disclosure to air and reached to stable yellow orange color by aeration. (1) gave brownish purple color with $FeCl_3$ and light purple with magnecium acetate. These suggest that (1) has hydroxyquinone structure. Moreover, the existence of hydroxyl groups were confirmed by following facts: IR spectra of (1) had hydroxyl group absorption at 3290 cm^{-1} in KBr and 3358 cm^{-1} in

$CHCl_3$ and that of (3) at 3280 cm^{-1} in KBr. These absorptions disappeared by easy methylation with diazomethane and by reductive acetylation. In NMR spectrum of (3) the signal, τ2.42(4H, broad), was quenched by addition of D_2O, methylation and reductive acetylation. As for the number of hydroxyl group, it was inferred as four by the number of proton corresponding to CH_3O in the NMR spectrum of (2) and this means that quinone nuclei have two hydroxyl group each, considering the existence of two quinone moieties. Then the position of hydroxyl group is induced on the finding of Bycroft et al.[4)] that 2,5-dihydroxy-p-benzoquinone has a sole absorption at 1617 cm^{-1} in KBr, and 1642 cm^{-1} in $CHCl_3$, and 2,6-dihydroxy-p-benzoquinone two absorptions at 1641 and 1660 cm^{-1} in KBr and at 1645 and 1653 cm^{-1} in $CHCl_3$ in IR spectrum. In the present case, (1) has a sole absorption at 1615 cm^{-1} in KBr and 1646 cm^{-1} in $CHCl_3$, and (3) at 1610 cm^{-1}. Therefore, (1) should be a derivative of 2,5-dihydroxy-p-benzoquinone.

As to the side chain of (1), the oxidation of (1) with hydrogen peroxide furnished a C_{21} aliphatic acid of which methyl ester revealed a parent peak of 332 in its mass spectrum. The ester showed the color reaction of unsaturated group with tetranitromethane and gave a NMR spectrum resembling to that of (1). (1) adsorbed 10 mole hydrogen on catalytic reduction with palladium-carbon catalyst and it means the existence of eight double bonds as two mole hydrogen for reduction of quinone groups should be subtracted from ten mole hydrogen. The oxidation of (3) with hydrogen peroxide furnished a saturated aliphatic acid of which the methyl ester revealed a parent peak of 340 in its mass spectrum. Besides, the mass spectrum of (1) gave 69 as base peak and peaks corresponding to ions removed successively isoprene unit from one to three from P+1 ion while the cleavage of the directly bonded isoprene unit could not be observed because of destruction of quinone nucleus as reported by Muraca et al.[5)] Thus four isoprene units are expectable as a side chain. The signal, τ6.93(4H, d; J=7cps), is assigned to the methylene neighboring to the quinone nucleus owing to the chemical shift position and manifested to be coupled with the methyne($Q-CH_2-\underline{C}\underline{H}=\overset{|}{C}-$), by decoupling method in pyridine. These also support that the isoprene unit attaches to the quinone nucleus.

The signals, τ6.48(2H, s) for (1), τ6.50(2H, s) for (2) and τ6.43(2H, s) for (3), are assigned to the bridge methylene between two quinone nuclei because of their singlet form and chemical shift. Concerning the configuration of the double bonds off the side chain, all trans forms were concluded: according to Bates et al.[6),7)] the NMR signal of the methyl group at the trans position to the olefine hydrogen lies at τ8.41, a little higher than 8.34 of that at the cis position. In the case of the structure Q-CH_2-CH=C(CH_3)-, conversely, the signal of the methyl group at the trans position to the olefine hydrogen lies at τ8.27, rather lower than 8.32 of that at the cis position by the remote anisotropic effect of the carbonyl group of quinone. Since, in addition, the ratio of the strength of methyl signals, τ8.30, 8.35, 8.43 of (1), τ8.28, 8.33, 8.41 of (2) is 1:1:3, all double bonds of the side chain have trans configuration.

Thus, the chemical structure of (1) is concluded as one of methylenebis(dihydroxy-p-benzoquinone) with two tetraprenyl side chains. A natural compound of such a chemical structure is so rare that only one compound, methylenebis-embelinyl, has been isolated from the ripe berries of *Embelia ribes*.[8)]

The detail description of experiments and the total synthesis of (1) will be published in near future.

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