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33. Shinsaku Natori,*1 Hidejiro Nishikawa,*2 and Hideko Ogawa*1 : Structure of Helicobasidin, a Novel Benzoquinone from *Helicobasidium mompa* TANAKA.

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Helicobasidium mompa TANAKA (Tremellales, Basidiomycetes) is a noxious pathogenic fungus for plants originally found in Japan and infects subterranean organs of many plants, causing the "violet root rot." Although its acid metabolites, such as oxalic acid[1] and itaconic acid,[2] had been known, isolation of other metabolites, especially coloring matters which might be characteristic of the mold, had not been reported till quite recently. In 1962, one of the authors (H. N.)[3] reported the isolation of two coloring matters, helicobasidin, m.p. 194°, $C_{16}H_{22}O_4$, and mompain, m.p. >300°, $C_{10}H_6O_6$, and of three colorless substances, helmonic acid, m.p. 224°, licobasin, m.p. 136°, and D-arabitol, from mycelium of the mold grown in a malt medium. At about the same time Takai[4] also reported the isolation of an orange-yellow pigment from the steam-distillate of the whole culture and its identification with helicobasidin, though he put forward a molecular formula of $C_{15}H_{20}O_4$. In these papers some properties of helicobasidin were described, but its structural elucidation was not mentioned.

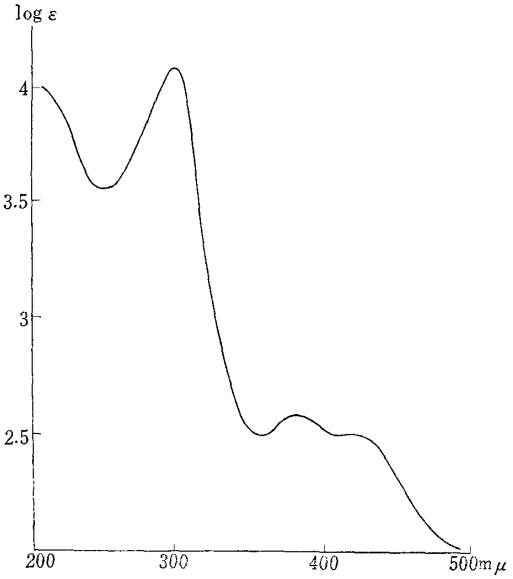

Fig. 1. Ultraviolet Spectrum of Helicobasidin (EtOH solution)

In the present work, the structure of helicobasidin was proved to be (*S*)-3-methyl-2,5-dihydroxy-6-(1,2,2-trimethylcyclopentyl)-benzoquinone.

Helicobasidin, the major coloring matter in the mycelium, comes as orange-red needles of m.p. 190~192°, $[\alpha]_D^{25}$ −123° ($CHCl_3$). It easily sublimes under reduced pressure and dissolves in sodium carbonate in violet-red solution. The alkaline solution of helicobasidin is decolorized by the addition of sodium dithionite, showing quinonic property. The ultraviolet spectrum of helicobasidin (Fig. 1) showed a characteristic absorption (λ_{max}^{EtOH} 297 mμ) of benzoquinone[5,6] and they are well elucidated as a dihydroxybenzoquinone derivative as shown in Table I. Its infrared spectrum (in chloroform solution) revealed the presence of hydroxyl group(s) (3327, 1353 cm^{-1}), medium sized aliphatic side chain(s)

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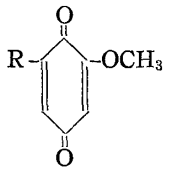
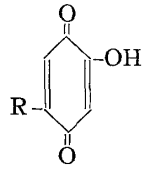
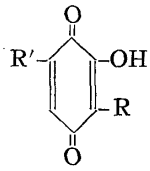
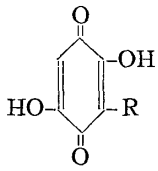
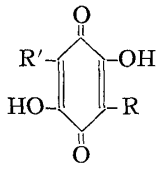
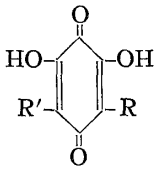
1) N. Tanaka : J. Coll. Sci., Imp. Univ., Japan, **4**, 193 (1891); K. Ito : Bull. Gov. Forest. Exptl. Station, **43**, 126 (1946).
2) N. Suzuki, *et al.* : Bull. Natl. Inst. Agr. Sci., Ser. C, No. 8 (1957).
3) H. Nishikawa : Agr. Biol. Chem. (Tokyo), **26**, 696 (1962).
4) S. Takai : Phytopathol. Z., **43**, 175 (1961-1962).
5) W. Flaig, J. C. Salfeld, E. Baume : Ann., **618**, 117 (1958).
6) B. W. Bycroft, J. C. Roberts : J. Org. Chem., **28**, 1429 (1963).

Table I. Ultraviolet and Infrared Spectra of Benzoquinones

R	R′	UV λ_{max}^{EtOH} mμ (log ε)			IR (cm^{-1}) ν_{O-H}		$\nu_{C=O}$ ($\nu_{C=C}$)	
					solid[a]	soln.[b]	solid[a]	soln.[b]
	(2-Methoxy-6-alkylbenzoquinones)							
CH_3		<200	265 (3.94)	363 (2.82)	—	—	1678 1649 1605	1680 1649 1606
$C_{11}H_{23}$		<200	268 (4.09)	364 (2.90)	—	—	1685 1651 1606	1680 1647 1605
$C_{12}H_{25}$		<200	268 (4.03)	363 (2.91)	—	—	1679 1646 1624 1599	1681 1650 1607
	(2-Hydroxy-5-alkylbenzoquinone)							
$C_{16}H_{33}$		209 (4.04)	268 (4.12)	383 (2.85)	3372	3452	1649 1633 1613	1656
	(2-Hydroxy-3,6-dialkylbenzoquinones)							
CH_3	C_8H_{17}	<200	270 (4.10)	406 (2.99)	3272	3472	1666 1637 1613	1657 1636 1613
CH_3	$-CH(CH_3)-(CH_2)_3-CH(CH_3)_2$	<200	270 (4.08)	406 (2.99)	3267	3463	1663 1634 1608	1658 1640 1617
CH_3	$-CH(CH_3)_2$[d]	—	267 (4.16)	404 (3.01)	3252[c]	3431	1668[c] 1643	1662 1645
	(3-Alkyl-2,5-dihydroxybenzoquinones)							
$C_{11}H_{23}$		202 (4.16)	291 (4.25)	427 (2.45)	3318	3356	1637(sh) 1613	1636
$C_{13}H_{27}$		203 (4.18)	291 (4.26)	425 (2.46)	3324	3324	1635(sh) 1612	1639
$C_{18}H_{37}$		201	290	428	3330	3322	1614	1638 1613
	(2,5-Dihydroxy-3,6-dialkylbenzoquinones)							

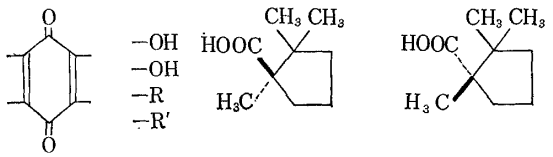
CH_3	$-C=CH$ [d] $H_3C\ CH_3$	—	287 (4.24)	436 (2.40)	3310[c]	3365	1617[c]	1642
CH_3	$-CH(CH_3)_2$ [d]	—	293 (4.31)	435 (2.36)	3319[c]	3327	1616[c]	1640
CH_3	$C_{19}H_{37}$	209 (4.24)	294 (4.36)	440 (2.47)	3320	3360	1615	1635
CH_3	$C_{19}H_{39}$	—	292 (4.37)	—	3320 (3315)[c]	3360	1615 (1609)[c]	1633
$C_{10}H_{21}$	$C_{10}H_{21}$	209 (4.14)	295 (4.29)	429 (2.30)	3325	3374	1614	1630
 (2,6-Dihydroxy-3,5-dialkylbenzoquinone)								
CH_3	CH_3 [d]	—	297 (4.26)	426 (2.26)	3417[c]	3476	1660[c] 1641	1653 1645
Helicobasidin		210 (4.13)	297 (4.15)	377, 430 (2.61, 2.47)	3319 (3300)[c]	3327	1613 (1609)[c]	1638

a) Determined as Nujol mull unless otherwise specified.
b) Determined in $CHCl_3$ solution.
c) Detemined as KBr disc.
d) By Bycroft, Roberts[6]

(2953, 2872, 1462, 1382 cm^{-1}), and conjugated carbonyls and C=C bonds characteristic of benzoquinones[6~9] (1684 (w), 1638 (br., s) cm^{-1}). The molecular formula of helicobasidin was established as $C_{15}H_{20}O_4$ by elemental analyses and molecular weight determination of helicobasidin and its derivatives.

Helicobasidin absorbs one mole of hydrogen in the presence of platinum catalyst and the colorless solution thus formed regains the original color by exposure to air, recovering the starting material. These facts indicate the absence of unsaturation in the side chain(s) and again quinonic property.

Helicobasidin formed a diacetate of pale yellow needles, m.p. 70~71°, $[\alpha]_D^{25}$ −12.4° ($CHCl_3$), and a dimethyl ether, yellow oil, b.p_3 ca. 120~130°, by the usual method. Reductive acetylation gave a leucotetraacetate, $C_{23}H_{30}O_8$, colorless prisms of m.p. 152~154°, $[\alpha]_D^{25}$ −9.5°($CHCl_3$), which showed an ultraviolet absorption of a benzene derivative at 268 mμ. Formation of these derivatives showed the presence of two hydroxyl groups in helicobasidin. Infrared spectra of the diacetate and dimethyl ether showed the quinonic carbonyls at 1679 and 1660 cm^{-1}. suggesting that the carbonyl group(s) is originally bonded to hydroxyl group(s). The acetyl carbonyl absorption of the acetate and leucoacetate appears at 1777 and 1774, 1762 cm^{-1} respectively and shows that the hydroxyl groups in helicobasidin are phenolic or enolic. These facts indicated that helicobasidin should be expressed by the formula (I), in which R+R′ is C_9H_{18}.



I II III

Nuclear magnetic resonance spectrum of helicobasidin (Fig. 2) showed the absence of olefinic proton, and the presence of one methyl group attached to an olefinic carbon atom (τ 8.07) and three methyl groups attached to quaternary carbon atoms (τ 9.15, 8.90, 8.65).

7) P. Yates, M. I. Ardao, L. F. Fieser : J. Am. Chem. Soc., **78**, 650 (1956).
8) J. F. Bagli : *Ibid.*, **84**, 177 (1962).
9) W. Flaig, J. C. Salfeld : Ann., **626**, 215 (1959).

The side-chains were confirmed by alkaline hydrogen peroxide oxidation of helicobasidin. From the reaction mixture, colorless crystals were separated by acidification, which, after purification through repeated sublimation, showed m.p. 187~189°, $[\alpha]_D^{25}$ −18° ($CHCl_3$). It was proved to be a saturated monocarboxylic acid of the molecular formula, $C_9H_{16}O_2$, and the presence of three methyl groups attached to quaternary carbon atoms was suggested by its nuclear magnetic resonance spectrum. These properties were consistent with those of (+)-camphonanic acid (II), m.p. 191~192°, $[\alpha]_D^{25}$ +21° ($CHCl_3$),[10,11] except for its opposite sign of the rotation. Thus (+)-camphonanic acid (II) was prepared from (+)-camphor by the known method,[11] as shown in Chart 1.

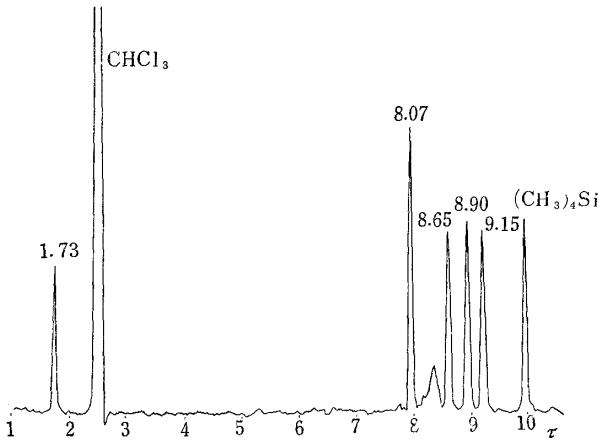


Fig. 2. Nuclear Magnetic Resonance Spectrum of Helicobasidin in $CHCl_3$ (60 Mc.)

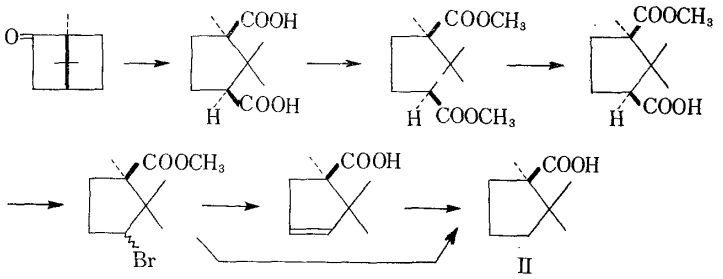
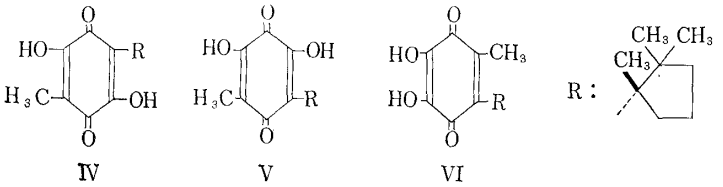


Chart 1.

Comparison of the (+)-acid (II) with the oxidation product (III) by a mixed fusion,*3 infrared spectra, and optical rotation showed that they are enantiomers. Therefore, the presence of (*S*)-1,2,2-trimethylcyclopentyl group in helicobasidin was established.

The mother liquor of the oxidation was steam-distilled and the presence of acetic acid, propionic acid, and camphonanic acid was suggested by paper chromatography. The main constituent, acetic acid, was separated as its *p*-bromophenacyl ester and identified by a mixed fusion.

These facts revealed that the structure of helicobasidin should be expressed by one of the following three formulae (IV~VI).



In the structural studies of ubiquinones, it has been pointed out that 2,3-dimethoxy compound is distinguishable from the other two types of compound by their ultraviolet

*3 Melting point of (±)-camphonanic acid is reported as 194~194.5°.[12]

10) H. Appel: Z. physiol. Chem., **218**, 202 (1933).
11) C. Enzel, H. Erdtman: Tetrahedron, **4**, 361 (1958).
12) K. Hancock, H. L. Lochte: J. Am. Chem. Soc., **61**, 2448 (1939).

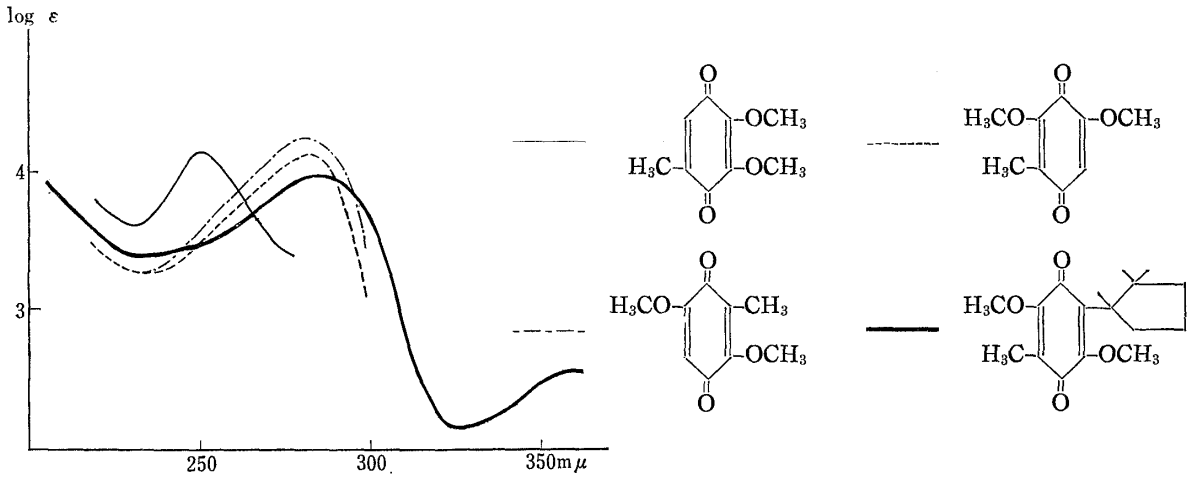


Fig. 3. Ultraviolet Spectra of Dimethoxytoluquinones (EtOH solution)

spectra.[13] Since helicobasidin dimethyl ether shows absorption maximum at 284 mμ (Fig. 3), the formula (Ⅵ) is excluded. Zinc dust fusion of helicobasidin, after purification through chromatography, gave a neutral aromatic hydrocarbon fraction. Although further purification and isolation were impossible due to scarcity of the sample, gas chromatography of the fraction showed a peak, having the same retention time with cuparene (Ⅷ), a sesquiterpene hydrocarbon from Cupressaceae plants.[11,14,15] The ultraviolet absorption maximum of helicobasidin agrees well with those of 2,5-dihydroxy-3,6-dialkylbenzoquinones (cf. Table I), yet the fact does not exclude 2,6-dihydroxy-3,5-dialkylbenzoquinone structure (Ⅴ), as was pointed out by Bycroft and Roberts.[6] In the infrared spectrum of benzoquinones, carbonyl stretching vibration is rather complicated.[7~9] The carbonyl absorption is influenced by hydrogen bond formation with hydroxyl group at α-position and also by resonance effect of β-substituents, and sometimes overlaps with C=C stretching. Thus, an accurate assignment of infrared spectra of helicobasidin for the distinction for the substitution pattern is not very reliable, but the hydroxy and carbonyl absorption of helicobasidin both in solid and solution states fall into the range of 2,5-dihydroxy-3,6-dialkylbenzoquinones (Table I).

Biogenetic origin of the trimethylcyclopentyl side-chain of helicobasidin is apparently mevalonic acid. In the case of structure (Ⅴ), the origin of the remaining seven carbon atoms is rather unexplainable. On the contrary, structure (Ⅳ) may be assumed to be derived from three mevalonic acid units through the sesquiterpene hydrocarbons, cuprenene (Ⅶ)[14] and cuparene (Ⅷ),[11,14,15] biogenesis of which have been well elucidated.[11,15,16] Perezone (Ⅸ : R=H),[17] m.p. 102~103°, $[\alpha]_D^{20}$ −17° (ether), isolated from a Mexican compositae plant, *Perezia adnata* A. Gray, is known as a sesquiterpene containing benzoquinone chromophore and the structure (Ⅳ) corresponds to the cyclic isomer of oxyperezone (Ⅹ : R=OH), m.p. 129°, the hydroxyl derivative of perezone (Chart 2).

These facts provide preference for the structure (Ⅳ) than Ⅴ.

Synthetic confirmation of the structure (Ⅳ) by the condensation of camphonanoyl peroxide with 3-methyl-2,5-dihydroxybenzoquinone[18,19] by Fieser's method[20] has been

13) R. A. Morton, *et al.* : Helv. Chim. Acta, **41**, 2343 (1958).
14) T. Nozoe, H. Takeshita : Tetrahedron Letters, No. 23, 14 (1960).
15) W. Parker, R. Ramage, R. A. Raphael : J. Chem. Soc., **1962**, 1558.
16) J. B. Hendrickson : Tetrahedron, **7**, 82 (1959).
17) F. Kögl, A. G. Böer : Rec. trav. chim., **54**, 779 (1935).
18) T. Zincke : Ber., **16**, 1558 (1883).
19) W. A. Anslow, J. N. Ashley, H. Raistrick : J. Chem. Soc., **1938**, 439.
20) L. F. Fieser, E. M. Chamberlin : J. Am. Chem. Soc., **70**, 71 (1948).

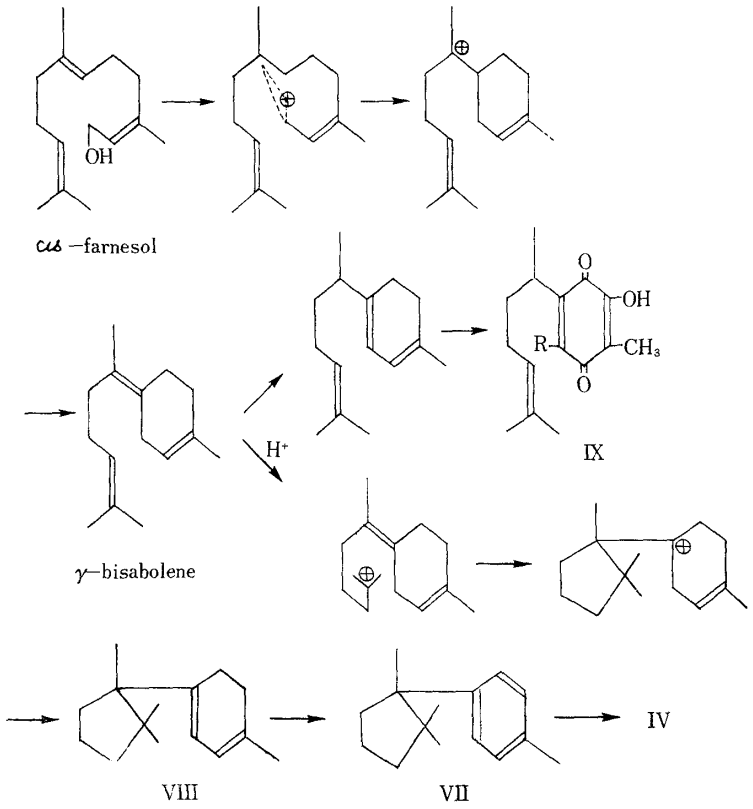


Chart 2.

unsuccessful due to a very poor yield of the peroxide by the conventional method. Another synthetic approach and the biosynthesis of helicobasidin are now under investigation.

There have been known many mold quinones, many of which are of acetate-malonate origin and the remainder are shikimic acid origin. If helicobasidin actually belongs to isoprenoids, this is a first example in fungal quinones.

Experimental*4

Helicobasidin*5,3)——Recrystallization from MeOH or petr. benzin gave orange-red needles of m.p. 190~192°, $[\alpha]_D^{25}$ −123.1° (c=1.00, $CHCl_3$) (cf. Fig. 4). It is insoluble in $NaHCO_3$ and soluble in Na_2CO_3. It gave a purple $Mg(OAc)_2$ reaction and a violet-brown $FeCl_3$ reaction. The yellow AcOH solution shows a green fluorescence under an UV light. The violet alkaline solutions was decolorized by the addition of $Na_2S_2O_4$. UV (cf. Fig. 1) λ_{max}^{EtOH} mμ (log ε): ca. 210 (inf.), 297 (4.15), 377 (2.61), 430 (2.47). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3327 (m), 2953, 2872 (m), 1684 (w), 1638 (br., s), 1462 (w), 1382 (w), 1353 (s), 1154, 1133, 1067. NMR (cf. Fig 2). *Anal.* Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63; mol. wt., 264. Found: C, 67.86; H, 7.71; mol. wt., 259 (Rast, camphor).

Helicobasidin Diacetate——Helicobasidin was treated with Ac_2O and a drop of H_2SO_4 by the usual method. Recrystallization from MeOH-H_2O gave pale yellow needles of m.p. 70~71°, $[\alpha]_D^{25}$ −12.4°

*4 All melting points were determined in a sulfuric acid bath and are uncorrected. IR spectra were measured as Nujol mull or in $CHCl_3$ solution using a Koken Model 301 Infrared Spectrophotometer. UV spectra were measured in EtOH soln. in a Cary Model 11 Recording Spectrophotometer. NMR spectra were measured in $CHCl_3$ or $CDCl_3$ soln. by a Varian A60 Spectrometer at 60 Mc., using Me_4Si as an internal standard. Optical rotations were measured in $CHCl_3$ soln. by a Rudolf photoelectric polarimeter.

*5 Thin layer chromatography of crude sample of helicobasidin[3] revealed the contamination with minute amounts of two substances, presumably homologous benzoquinones with less lipophilic character.

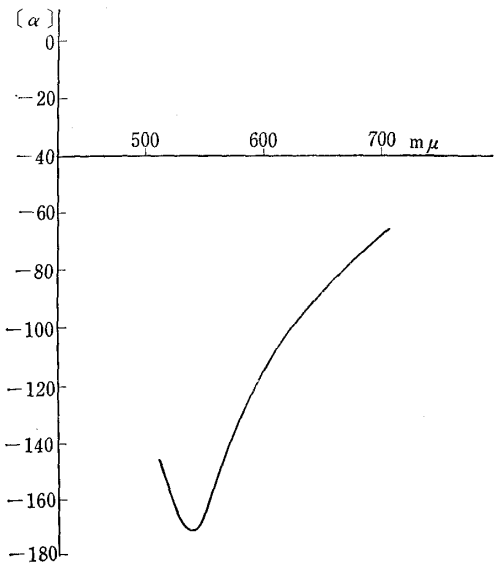


Fig. 4. Optical Rotatory Dispersion Curve of Helicobasidin ($CHCl_3$ solution, c=1.00)

(c=0.512, $CHCl_3$). UV λ_{max}^{EtOH} mμ (log ε): 267 (4.23), 337 (2.53). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2955, 2876, 1777 (s), 1679 (s), 1603 (w), 1462. 1428, 1376, 1290, 1177 (s), 1125, 1013 (s), 923, 876, 858. *Anal.* Calcd. for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94; $2CH_3CO$, 24.80. Found: C, 65.23; H, 6.95; CH_3-CO, 27.14, 29.00 (*p*-toluenesulfonic acid).

Helicobasidin Dimethyl Ether——Helicobasidin (250 mg.), K_2CO_3 (3.0 g.), and $(CH_3)_2SO_4$ (5.6 g.) in Me_2CO (70 ml.) were refluxed for 2 hr. After filtration while hot, the reaction mixture was evaporated and the Et_2O solution of the residue was washed with KOH soln. to remove the starting material. The neutral portion was passed through a column of alumina (Wöhlm, neutral) as hexane solution and a pale yellow fraction was purified by distillation under reduced pressure to pale yellow oil of $b.p_3$ 120~130°. UV λ_{max}^{EtOH} mμ (log ε): 284 (3.99), 381 (2.61). IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 2955, 2890, 1660, 1580, 1464, 1451, 1376, 1302, 1271, 1213, 1151, 1087, 1016, 940, 919, 804, 758. *Anal.* Cacd. for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 70.73: H, 8.35.

Helicobasidin Leucotetraacetate——A mixture of helicobasidin (200 mg.), Zn powder (2.0 g.), and Ac_2O (20 ml.) was refluxed for 2 hr. The hot filtrate of the reaction mixture was poured into H_2O and, after neutralization with Na_2CO_3, extracted with Et_2O. The ethereal residue was recrystallized from AcOEt-petr. ether to colorless prisms, m.p. 152.5~154°, $[\alpha]_D^{25}$ −9.5° (c=0.42, $CHCl_3$). UV λ_{max}^{EtOH} mμ (log ε): 268 (2.62) IR ν_{max}^{Nujol} cm^{-1}: 1774, 1762, 1192, 1175, 1055, 1005, 928, 894, 876, 839.*6 *Anal.* Calcd. for $C_{23}H_{30}O_8$: C, 63.58; H, 6.96; $4CH_3CO$, 39.62. Found: C, 63.91, 63.96; H, 7.01, 6.95; CH_3CO, 40.5, 40.1 (*p*-toluenesulfonic acid).

Hydrogenation of Helicobasidin——Helicobasidin (50 mg.) in EtOH (100 ml.) was hydrogenated in the presence of Pt catalyst (10 mg.). After absorption of ca. 1 mole of H_2, the solution became colorless and absorption ceased. By exposure to the atmosphere, the solution returned to the original orange-red color and helicobasidin was recovered by evaporation of the solvent.

Hydrogen Peroxide Oxidation of Helicobasidin——To the solution of helicobasidin (500 mg.) in 0.1*N* KOH (100 ml.), H_2O_2 (80%, 60 ml.) was added at a room temperature and, after several hour when the violet-red color of the solution turned colorless, the solution was acidified with H_2SO_4. The separated colorless crystals were recrystallized from H_2O-EtOH and repeatedly sublimed under reduced pressure (2 mm.Hg; bath temperature, ca. 80°) to colorless prisms of m.p. 187~189° (in a sealed tube), $[\alpha]_D^{25}$ −18.0° (c=0.592, $CHCl_3$). It has an odor like camphor and does not decolorize Br_2-H_2O or $KMnO_4$ soln. UV: end absorption. IR ν_{max}^{KBr} cm^{-1}: 3080, 2962, 2872, 2680 (br.), 1688, 1460, 1406, 1392, 1372, 1313, 1292, 1251, 1223, 1162, 1145, 1102, 935. NMR: τ ($CDCl_3$): 9.06 (s, 3H), 8.95 (s, 3H), 8.82 (s, 3H), 8.2~8.5 (m, 4~6H). *Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32; COOH, 28.84. Found: C, 69.52; H, 10.48; COOH, 28.54. IR spectra in KBr disk and CS_2 solution were identical with those of (+)-camphonanic acid. A mixed fusion with (+)-camphonanic acid, m.p. 189~192°, melted at the same melting point.

The mother liquor of the oxidation was examined by paper chromatography[21] (solvent: BuOH satd. with 1.5*N* NH_4OH) for the presence of acidic substances. The presence of camphonanic acid (Rf 0.83), propionic acid (Rf 0.42), and AcOH (Rf 0.19) was detected. The mother liquor was then steam-distilled and the distillate was filtered, neutralized with NaOH, and concentrated to ca. 5 ml. Treatment with *p*-bromophenacyl bromide (200 mg.) by the usual method gave a deposit, which was dissolved in benzene and chromatographed through a column of silica gel. The eluate was recrystallized from EtOH-H_2O to colorless crystals of m.p. 82~84°, which showed no depression of the melting point with an authentic specimen of *p*-bromophenacyl ester of AcOH.

Synthesis of (+)-Camphonanic Acid——The acid was synthesized from (+)-camphoric acid essentially by the same method as that of Enzell and Erdtman.[11] Overall yield from (+)-camphoric acid to (+)-camphonanic acid, m.p. 189~192°, was 2%. Since crude camphonanic acid prepared from methyl 3-bromo-1,2,2-trimethylcyclopentanecarboxylate by the treatment with EtONa followed by hydrolysis was proved to be contaminated with an unsaturated compound, probably 1,2,2-trimethylcyclopent-3-enylcarboxylic acid, from its IR spectrum, the crude product was catalytically hydrogenated in the presence of Pd-C; the process facilitating the following purification procedure.

*6 No absorption was observed around 1600~1500 cm^{-1} region.

21) R. L. Reid, M. Lederer: Biochem. J., **50**, 60 (1951).

p-Toluidide of the acid melted at 108~112°.

Zinc Dust Fusion of Helicobasidin——A mixture of helicobasidin (100 mg.), $ZnCl_2$ (500 mg.), Zn powder (100 mg.), and NaCl (100 mg.) was placed at the bottom of a long glass tube and heated at 260° for 15 min. The reaction mixture was extracted with Et_2O, the extract was washed thoroughly with NaOH soln., and evaporated. The residue was dissolved in hexane and chromatographed through a column of alumina (Wöhlm, neutral, grade 3). The eluate was collected in 5 ml. fractions and examined by UV absorption. Fraction No. 5, which showed UV absorption at 250~280 mμ, was rechromatographed and 2 ml. fractions were collected. The third fraction, which showed characteristic benzenoid absorption at 256~283 mμ, was examined by gas chromatography (Shimadzu GC 1B type; column, 1.5% SE-30 on Chromosorb W, 80~100 mesh, 150 cm. × 4 mm.; column temp., 150°). It gave a peak at the retention time (4.3 min.), which was identical with that of cuparene, prepared from a mixture of cuprenene and cuparene by a known method[14] and showed the correct physical constants.[11]

Attempted Synthesis of (±)-Helicobasidin——2-Methyl-3,6-dihydroxybenzoquinone, m.p. 177°, was prepared by the known method.[18,19] Several attempts to prepare camphonanoyl peroxide by the action of Na_2O_2 on (+)-camphonanyl chloride, prepared from (+)-camphonanic acid with $SOCl_2$, according to the direction of the literature[20] or by the several modifications failed and titration revealed that the formation of the peroxide was less than 1% in each cases. Under a similar reaction condition, lauric, myristic, and arachidic acids showed satisfactory results in the formation of the correrponding peroxide.

Nitration of cuparene was also unsuccessful in obtaining a crystalline product.[11]

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Summary

The structure of helicobasidin, a major pigment of *Helicobasidium mompa* TANAKA, was proved to be (*S*)-3-methyl-2,5-dihydroxy-6-(1,2,2-trimethylcyclopentyl)benzoquinone (Ⅳ).

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