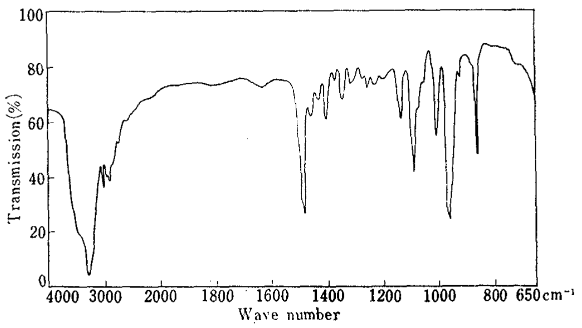

Fig. 1. Infrared Absorption Spectrum of the Chloride of the Quaternary Ammonium Base from Panax Ginseng (in KBr wafer)

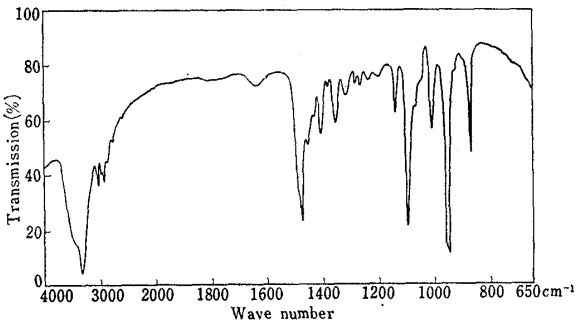

Fig. 2. Infrared Absorption Spectrum of Choline Chloride (in KBr wafer)

Also, from this chloride and choline chloride the same picrate (m.p. 240~241°) and chloroaurate (m.p. 250~252°) were obtained. Then, this chloride was identified as choline chloride. Choline contents of this crude durg was 0.1~0.2% weight of the roots.

This facts finely coincide with the reports of many authors that *Panax ginseng* has parasympathomimetic action, and the Petkov's report that ginseng extract was suppressed by atropine.

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Gifu College of Pharmacy,
Kokonoe-cho, 3,
Gifu.

Kichitaro Takatori (高取吉太郎)
Terushige Kato (加藤暉成)
Shingo Asano (浅野進吾)

Department of Pharmacology,
School of Medicine,
Nagoya City University,
Mizuho-dori, Mizuho-ku, Nagoya.

Masawaka Ozaki (尾崎正若)
Toshio Nakashima (中島敏夫)

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Structure of Helicobasidin, a Novel Benzoquinone from *Helicobasidium mompa* TANAKA

Helicobasidium mompa TANAKA, a noxious plant pathogenic fungus causing the "violet root rot," produces two coloring matters, helicobasidin, m.p. 190~192°, and mompain, m.p. >300° (decomp.), on which one of us (H.N.)[1] and Takai[2] reported previously.

The structure, 3-methyl-6-((1S)-1,2,2-trimethylcyclopentyl)-2,5-dihydroxybenzoquinone, is now proposed for helicobasidin (I).

Helicobasidin (I), orange-red needles of m.p. 190~192°, $[\alpha]^{25}_{D}$ −123° (c=1.00, CHCl$_3$), is sublimable, soluble in sodium carbonate, and its violet alkaline solution is decolorized

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[1] H. Nishikawa: Agr. Biol. Chem., (Tokyo), **26**, 696 (1962).

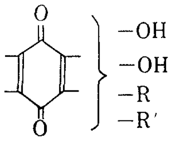
[2] S. Takai: Phytopathol. Z., **43**, 175 (1961~1962).

with sodium dithionite. Spectral data are as follows : UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε) : ca. 210 (inf.), 297 (4.15), 377 (2.61), 430 (2.47); IR ($CHCl_3$ soln.) cm^{-1} : 3327, 1353 (OH), 2953, 2872, 1462, 1382 (aliphatic side chain), 1684 (w), 1638 (br., s) (conj. C=O, C=C).

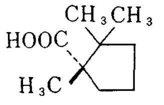
Molecular formula of I was established as $C_{15}H_{20}O_4$ by elemental analyses and molecular weight determination of I and its derivatives.

Helicobasidin (I) absorbs one mole of hydrogen in the presence of platinum catalyst and the resulting colorless solution regains the original color by exposure to air to recover the starting material. These properties, especially the molecular formula and ultraviolet absorption, showed that I is a benzoquinone derivative.

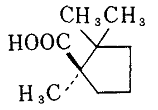
Helicobasidin gave following derivatives : Diacetate (II), pale yellow needles of m.p. 70~71°, $[\alpha]_D^{25}$ −12.4° ($CHCl_3$), IR ($CHCl_3$ soln.) $\nu_{C=O}$ cm^{-1} : 1777, 1679; dimethyl ether (III), yellow oil, b.p$_3$ ca. 120~130°, IR ($CHCl_3$ soln.): $\nu_{C=O}$ 1660 cm^{-1}; and leucotetraacetate (IV), colorless prisms of m.p. 152~154°, $[\alpha]_D^{25}$ −9.5° ($CHCl_3$), IR (Nujol) $\nu_{C=O}$ cm^{-1}: 1774, 1762. Formation of the derivatives, along with their infrared spectra, suggested the presence of two phenolic or enolic hydroxyls in I. Thus the structure of I is expressed by the formula (V) in which R+R′ is C_9H_{18}. Nuclear magnetic resonance spectrum of I suggested the absence of olefinic proton and the presence of one methyl group attached to the olefinic carbon atom (τ 8.07) and three methyl groups attached to quarternary carbon atoms (τ 9.15, 8.90, 8.65).



V



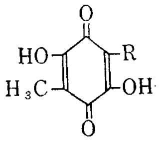
VI



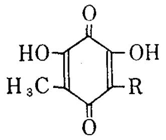
VII

The side chains were confirmed by alkaline hydrogen peroxide oxidation of I. From the reaction mixture, colorless prisms (VI) of m.p. 190~192°, $[\alpha]_D^{25}$ −18° ($CHCl_3$), was separated. It was proved to be a saturated monocarboxylic acid of the molecular formula, $C_9H_{16}O_2$, and the properties were consistent with those of (+)-camphonanic acid[3] (VII) except for its oposite sign of the rotation. Comparison by a mixed fusion, infrared spectra, and optical rotation of VI with those of the (+)-isomer (VII), prepared from (+)-camphor by the known method,[3] showed that they are enantiomers. Therefore, the presence of (1S)-1,2,2-trimethylcyclopentyl group in I was established. The mother liquor of the oxidation was steam-distilled and the presence of acetic acid in the distilate was proved by paper chromatography and isolation of its *p*-bromophenacyl ester.

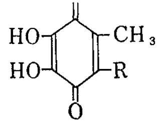
Thus the structure of I should be expressed by one of the following three formulae (VIII)~(X).



VIII

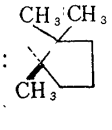


IX



X

R :



2,3-Dihydroxy compound (X) is distinguishable from the other two types of compound by their ultraviolet spectra of the dimethyl ethers.[4] Since III shows absorption

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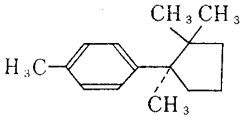
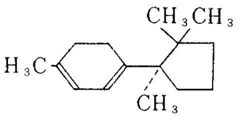
[3] C. Enzel, H. Erdtman : Tetrahedron, **4**, 361 (1958).
[4] R. A. Morton, *et al.* : Helv. Chim. Acta, **41**, 2343 (1958).

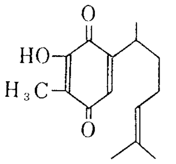
maximum at 284 mμ, the formula (X) is excluded. Zinc dust fusion of I, after purification through chromatography, gave a neutral aromatic hydrocarbon fraction, gas chromatography of which showed a peak, having the same retention time with cuparene (XI), a sesquiterpene from Cupressaceae plants.[3] The absorption maximum of I, 297 mμ, agrees well with those of maesaquinone (VIII, $R=C_{19}H_{37}$) and 2,5-dihydroxy-3,6-didecylbenzoquinone. Biogenesis of I was assumed to be derived from mevalonic acid through the sesquiterpene hydrocarbons, cuprenene[5] (XII) and cuparene (XI).[3,5] Perezone (XIII),[6] isolated from *Perezia adnata* A. GRAY (Compositae), has been known as a sesquiterpene containing benzoquinone chromophore, and the structure (VIII) corresponds to a cyclic isomer of oxyperezone (XIV),[6] the hydroxyl derivative of perezone. These facts provide preference for the structure (VIII) than (IX).



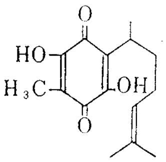
XI



XII



XIII



XIV

Synthetic confirmation of the structure (VIII) by the condensation of camphonanoyl peroxide with 3-methyl-2,5-dihydroxybenzoquinone[7] by Fieser's method[8] was unsuccessful due to a very poor yield of the peroxide. Another synthetic approach and biosynthesis of I are now in progress.

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National Institute of Hygienic Sciences,
Tamagawayoga-machi,
Setagaya-ku, Tokyo.

Shinsaku Natori (名取信策)
Hideko Ogawa (小川秀子)
Kazutaka Yamaguchi (山口一孝)

College of Agriculture and Veterinary Medicine,
Nihon University,
Shimouma-3-chome,
Setagaya-ku, Tokyo.

Hidejiro Nishikawa (西川英次郎)

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5) T. Nozoe, H. Takeshita: Tetrahedron Letters, No. 23, 14 (1960).
6) F. Kögl, A.G. Böer: Rec. trav. chim., **54**, 779 (1935).
7) T. Zincke: Ber., **16**, 1558 (1883); W.A. Anslow, *et al.*: J. Chem. Soc., **1938**, 439.
8) L.F. Fieser, *et al.*: J. Am. Chem. Soc., **70**, 71 (1948).