

maximum for $\Delta^{4,6}$ -3-ketone. The C-7 hydroxyl of IXa was not oxidized under the above-mentioned condition. These results suggested that another new hydroxyl introduced may be located at 11 or 12-position. Partial hydrogenation of X with paradium-charcoal resulted in selective saturation of 6,7-double bond giving a Δ^4 -3-ketone (XII), $C_{23}H_{30}O_6$, m.p. 263~269°, UV: λ_{\max}^{EtOH} 226 $m\mu^{*1}$ ($\log \epsilon$ 4.32). XII was shown to be identical with the Δ^4 -3-ketone derived from digoxigenin (XIII) by comparison of their melting points, infrared spectra and mobilities in TLC. In this way the new hydroxyl introduced into ring C was clarified to be at 12 β -position. The configuration of the hydroxyl at 7-position of IXa was confirmed to be β by preparing a cyclocarbonate (XIV), $C_{24}H_{26}O_7$, m.p. 294~300° (decomp.), $[\alpha]_D^{25} +69.1^\circ$ (pyridine) from XI.

Furthermore, we isolated a small amount of 7 β -hydroxy derivative (XV) in the microbiological transformation of V. The structure investigations on other by-products are now being made.

Research Laboratory,
Shionogi & Co., Ltd.,
Fukushima-ku, Osaka.

Tamotsu Okumura (奥村 保)
Yoshio Nozaki (野崎 義雄)
Daisuke Satoh (佐藤 大助)

Received July 29, 1963

[Chem. Pharm. Bull]
11 (10) 1342 ~ 1343

UDC 615.711.76 : 582.892

Choline in *Panax ginseng* C. A. MEYER

Roots of *Panax ginseng* C. A. MEYER has been used as a valuable Chinese drug from ancient times, but pharmacologically effective components of this drug have been yet actually unknown.

Taking a great interest in Petkov's report¹⁾ that alcoholic extract of ginseng roots has a marked hypotonic action on blood pressure which is completely suppressed by atropine, the authors attempted to separate this effective components in parallel with the hypotonic tests on rabbits.

Effective hypotonic substances were extracted with methanol or ethanol. This extracts, obtained with yield of 20~23% weight from the crude drug, were dissolved in water and passed through the column of IRC-50 (H-type). On treatment of this column it can be presumed that this effective substances are chemically basic. On treatment of this column with diluted hydrochloric acid, the hypotonic fraction was collected into early eluted fraction. This fraction was neutralized and concentrated. The saturated solution of Reinecke salt was added, and the Reineckate of the effective quaternary ammonium base was obtained at 0.4~0.5% weight of the crude drug. This Reineckate was purified with alumina-celite 535 (1:1) chromatography and a pure Reineckate (I), m.p. 262~265° (decomp.), was obtained. Following the usual procedure, I was decomposed with silver sulfate and treated with bariumchloride, colorless and hygroscopic crystals of this chloride were obtained. The infrared spectra of this chloride and choline chloride were indicated in Figs. 1 and 2, respectively. This chloride and choline chloride have a same Rf value on paper chromatogram [for example, Rf=0.27; solvent: *sec*-butanol-pyridine-water (10:3:4); location reagent: Dragendorff reagent].

1) Arzneimittel Forschung, 9, 305 (1959).

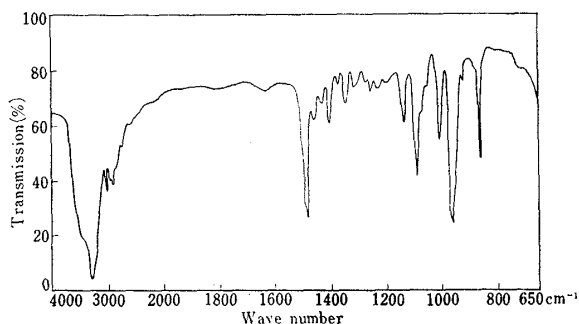


Fig. 1. Infrared Absorption Spectrum of the Chloride of the Quaternary Ammonium Base from Panax Ginseng (in KBr wafer)

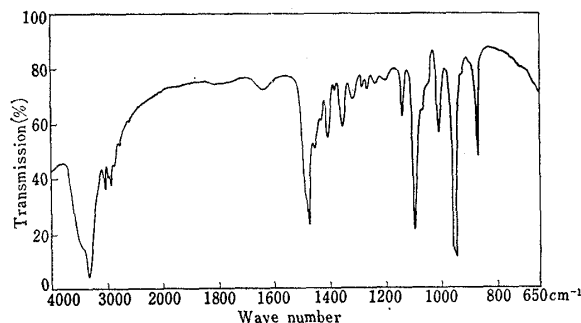


Fig. 2. Infrared Absorption Spectrum of Choline Chloride (in KBr wafer)

Also, from this chloride and choline chloride the same picrate (m.p. 240~241°) and chloraurate (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.

The authors are deeply grateful to Mr. K. Ueno of Kowa Kagaku Co., Ltd. for his kind measurement of IR spectra.

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

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

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

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

Received May 29, 1963
Revised July 25, 1963

[Chem. Pharm. Bull.]
11 (10) 1343 ~ 1345

UDC 547.567 : 582.288

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 Takai²⁾ 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°, $[\alpha]_D^{25} -123^\circ$ (c=1.00, CHCl₃), is sublimable, soluble in sodium carbonate, and its violet alkaline solution is decolorized

1) H. Nishikawa: Agr. Biol. Chem., (Tokyo), 26, 696 (1962).
2) S. Takai: Phytopathol. Z., 43, 175 (1961~1962).