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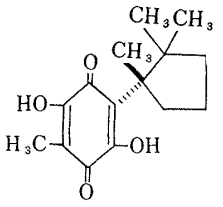
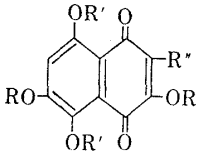
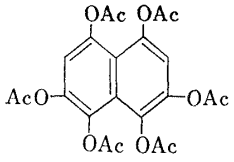
The Structure of Mompain, a Naphthoquinone from *Helicobasidium mompa* TANAKA, and its Relation to Spinochrome A (M)

Mompain[1] is a tetrahydroxynaphthoquinone,[2] isolated from *Helicobasidium mompa* TANAKA (Tremellales, Basidiomycetes) along with helicobasidin (I).[3] The structure of mompain (IIa) is now proved to be 2,5,7,8-tetrahydroxy-1,4-naphthoquinone by the correlation with spinochrome A (M),[4] the structure of which has been revised to IIb by Scheuer, *et al.*[5,6]



I





III

	R	R′	R″
IIa :	H	H	H
IIb :	H	H	CH_3CO
IIc :	CH_3CO	CH_3CO	H
IId :	CH_3	H	H
IIe :	CH_3	CH_3	H
IIf :	CH_3	CH_3CO	H

Mompain (IIa), deep red leaflet of m.p. >300° (decomp.), $C_{10}H_6O_6$, mol. wt. 222 (mass spectrum), shows quinonic properties with coloration reactions and by reduction. IIa forms tetraacetate (IIc), m.p. 176~179°, and leucohexaacetate (III), m.p. 229~232°. Methylation of IIa gave dimethyl ether (IId), m.p. 260~262°, and tetramethyl ether (IIe), m.p. 169~171°, according to the reaction conditions.

The ultraviolet absorptions of IIc, λ_{max}^{EtOH} mμ (log ε) : 248, 266 (shoulder), 352 (4.18, 4.02, 3.53), and III, λ_{max}^{EtOH} mμ (log ε) : 231, 295, 328 (shoulder) (4.83, 3.92, 3.23), clearly indicated that IIa is a 1,4-naphthoquinone derivative. Formation of the derivatives, the molecular formula, and infrared and nuclear magnetic resonance spectra showed the presence of four hydroxyl groups and absence of other substituents on 1,4-naphthoquinone nucleus.

There are eight isomers in tetrahydroxy-1,4-naphthoquinones; namely 2,3,5,6-(A), 2,3,5,7-(B), 2,3,5,8-(=5,6,7,8-)-(C), 2,3,6,7-(D), 2,5,6,7-(E), 2,5,6,8-(F), 2,5,7,8-(G), and 2,6,7,8-tetrahydroxy-1,4-naphthoquinone (H). The Hawaiian workers[5] treated spinochrome M (=A)[6] with methanolic hydrogen chloride in obtaining the dimethyl ether of a tetrahydroxy-1,4-naphthoquinone, m.p. 235~236°. The spectroscopic properties suggested that the dimethyl ether must be either that of F or G, in which the former was ruled out by the comparison with the synthetic specimen, m.p. 295~296°, thus establishing the structure of spinochrome A (M) as IIb. Although the properties of IId are identical with those of the dimethyl ether derived from spinochrome A (M), discrepancy of the melting points urged us the examination of the location of the hydroxyl groups in IIa.

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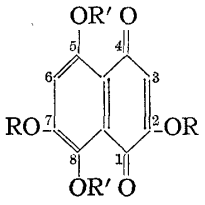
Among these isomers, B (spinochrome B[7] = spinochrome N[8]) and C (spinazarin[9]) are known compounds and their properties are differenet from IIa. Synthetic specimens[10] of tetramethyl ethers of E and H were not identical with IIe. Formation of dimethyl

Table I. Nuclear Magnetic Resonance Spectra of Mompain and the Derivatives
(δ values in p.p.m. from the internal standard (TMS). All signals are singlets.)



	Solvent	C_3- and C_6-H	C_2- and C_7-OCH_3	C_5- and C_8-OH, OCH_3 or $OCOCH_3$
Mompain (IIa)	DMSO	6.31 (2H)	—	ca. 13.1
Dimethyl ether (IId)	$CDCl_3$	6.40 (2H)	3.97 (6H)	12.73 (1H), 13.16 (1H)
Tetramethyl ether (IIe)	〃	5.96 (1H), 6.78 (1H)	3.82 (3H), 3.87 (3H)	3.94 (6H)
Dimethyl ether diacetate (IIf)	〃	5.98 (1H), 6.92 (1H)	3.87 (3H), 3.95 (3H)	2.45 (6H)

ether (IId) and ultraviolet absorptions of IIa, λ_{max}^{EtOH} mμ (log ε) : 228, 272, 318, 486, 517, 554 (4.48, 4.06, 3.93, 3.78, 3.84, 3.65), and IId, λ_{max}^{EtOH} mμ (log ε) : 227, 277, 308, 475, 507, 544 (4.46, 3.82, 3.83, 3.73, 3.79, 3.61) suggested a naphthazarin structure, having two hydroxyl groups at peri-positions. In nuclear magnetic resonance spectra (Table I), two ring protons in IIa and IId and two methoxyls in IId showed equivalent chemical shifts, while the same ring protons and the methoxyls in IIe and IIf showed non-equivalency and the newly formed methoxyls and acetyls in IIe and IIf respectively were equivalent. All these findings are only compatible with the structures (F) and (G). Between the two structures, the latter is more likely from the biogenetical point of view and non-equivalent chemical shifts of the two hydrogen-bonded hydroxyl protons in IId, as was pointed out by Scheuer, *et al.*[5] Thus IId must be identical with the dimethyl ether of desacetylspinochrome A (M).[5]

Treatment of spinochrome M (IIb), kindly supplied by Dr. M. Okajima,*1 Ochanomizu Women's University, with conc. sulfuric acid afforded the desacetyl compound, the crude product of which showed the identity with IIa by thin-layer chromatography. Methylation of the product with diazomethane, followed by purification through a column of secondary calcium phosphate, afforded the dimethyl ether, m.p. 260~262°, which showed the complete identity with IId by a mixed fusion, infrared spectra, and thin-layer chromatography. Thus the structure of mompain was established as 2,5,7,8-tetrahydroxy-1,4-naphthoquinone (G=IIa), corresponding to the desacetyl compound of spinochrome A (M)[5,6] and the 8-hydroxyl compound of flaviolin.[12]

*1 Kuroda and Okajima have now accepted the revision of the structure of spinochrome M.[11]

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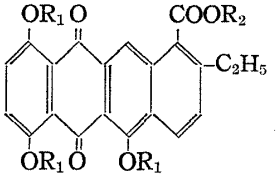
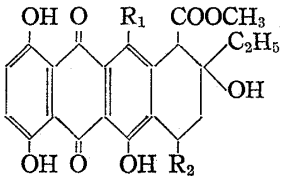
Conversion of Methyl 2-Ethyl-6,11-dihydro-6,11-dioxo-5,7,10-trimethoxy-1-naphthacenecarboxylate into η-Pyrromycinone

In the preceding communication[1] were reported the synthesis of methyl 2-ethyl-6,11-dihydro-6,11-dioxo-5,7,10-trimethoxy-1-naphthacenecarboxylate (I) and the demethylation of I to η-pyrromycinonic acid (II). Later, we re-examined this demethylation and found that it gave η-pyrromycinone (III) as well. The present paper describes the identification of synthetic I, II, and III with natural η-pyrromycinone trimethyl ether, η-pyrromycinonic acid and η-pyrromycinone, respectively.



I : $R_1=R_2=CH_3$
II : $R_1=R_2=H$
III : $R_1=H$, $R_2=CH_3$



IV : $R_1=H$, $R_2=OH$
V : $R_1=R_2=H$
VI : $R_1=R_2=OH$
VII : $R_1=OH$, $R_2=H$

Natural I (bright yellow needles from methanol, m.p. 235~237°) was prepared by refluxing natural II with methyl iodide in dry acetone in the presence of anhydrous potassium carbonate, and was identified with synthetic I, by comparison of their infrared spectra (KBr) and mixed melting point determination.

Demethylation of synthetic I was carried out by the method reported previously,[1] that is, with a large excess of boron tribromide in dry methylene chloride at room temperature, giving bright red needles of III, m.p. 238~239° (IR ν_{max}^{KBr} cm^{-1} : 1724, 1644), as a neutral fraction and dark red needles of II, m.p. 260~262° (decomp.) (IR ν_{max}^{KBr} cm^{-1}: 1704, 1648, 1600, 1587), as an acidic fraction. The former was identified with natural III[2,3] and the latter with natural II[2] by comparison of their infrared spectra (KBr).

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