fied with HCl, which caused orange precipitate to form. The precipitate was collected and recrystallized from water. Yield 0.7 g., m.p. 238°(decomp.). *Anal.* Calcd. for $C_{18}H_{20}O_6N_2Br_2S$: N, 5.07; Br, 28.90. Found : N, 4.82; Br, 29.05.

Summary

A total of 20 azo compounds related to 6-(2′-hydroxy-3′,5′-dibromophenylazo)-4-hexylresocinol were prepared. The effect of these newly synthesized azo compounds upon Yoshida sarcoma and Ehrlich ascites sarcoma is described briefly.

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Shoji Shibata, Kôtaro Takahashi, and Yôko Tanaka (nèe Hiizumi) :

Decomposition of Usnic Acid. V.[*] Pyrolysis of Dihydrousnic Acid. (2). Some Observations on Dihydrousnic Acid.

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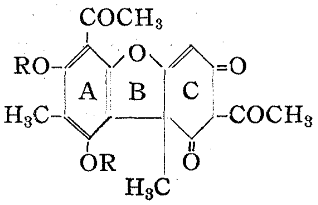
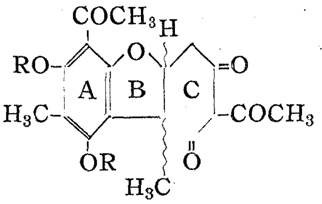
The structural formula of usnic acid, which was previously advanced by Robertson[1] and Schöpf,[2] has recently been established by Barton and his co-workers[3] by their elegant synthesis of (±)usnic acid which was accomplished by the oxidative condensation of methylphloroacetophenone.



(I) R=H Usnic acid
(II) R=$COCH_3$ Diacetylusnic acid



(III) R=H Dihydrousnic acid
(IV) R=$COCH_3$ Diacetyldihydrousnic acid

It should be noted, however, that dihydrousnic acid (III) showed some peculiar behavior on pyrolysis, on which we elucidated previously.[4]

The earlier workers[5] described that usnic acid resists direct catalytic hydrogenation and dihydrousnic acid could only be prepared through diacetylusnic acid which is hydrogenated catalytically to give diacetyldihydrousnic acid.

In this reaction process a conversion of optical rotation occurs in giving (−)dihydrousnic acid from (+)usnic acid, and (+)dihydrousnic acid from (−)usnic acid.

The present communication concerns direct hydrogenation of usnic acid and an isomerization of dihydrousnic acid.

Using tetrahydrofuran as a solvent and palladium-black as a catalyst, dihydrousnic acid was obtained directly from usnic acid in a sufficient yield. The optical conversion was also observed in this case as in the indirect hydrogenation.

On the other hand, during the course of examination on the pyrolysis of dihydro-

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[*] Part IV. K. Takahashi : This Bulletin, **1**, 36 (1953).

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1) F. H. Curd, A. Robertson : J. Chem. Soc., **1937**, 894.

2) C. Schöpf, F. Ross : Ann., **546**, 1(1941).

3) D. H. R. Barton, A. M. Delforin, O. E. Edwards : Chemistry & Industry, **1955**, 1039.

4) S. Shibata, K. Arakawa, K. Takahashi : J. Pharm. Soc. Japan, **72**, 255(1952). The earlier literatures are cited in this article.

5) a) C. Schöpf, K. Heuck : Ann., **459**, 233(1927). b) Y. Asahina, M. Yanagita, S. Mayeda : Ber., **70**, 2462(1937).

usnic acid, we found that an isomerization of dihydrousnic acid occurs. By heating under a definite experimental conditions, the detail of which we describe in the experimental part of this paper, (−)dihydrousnic acid (m.p. 147°; $[\alpha]_D$: −85°) gave a (+)-rotatory compound of the same molecular formula, $C_{18}H_{18}O_7$ (m.p. 128°; $[\alpha]_D$: +47.5°), while (+)dihydrousnic acid (m.p. 147°; $[\alpha]_D$: +85°) afforded a corresponding (−)-rotatory compound (m.p. 128°; $[\alpha]_D$: −48.4°) and (±)dihydrousnic acid converted into an optically inactive compound (m.p. 158°).

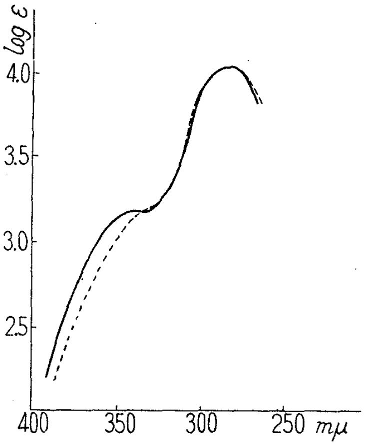

Fig. 1.

—— (−)Dihydrousnic acid

------ (+)Isodihydrousnic acid

$M/10000$ in C_2H_5OH

The color reactions, the ultraviolet (Fig. 1) and infrared spectra, as well as its behavior in pyrolysis with anhydrous calcium chloride giving acetylacetone and 3,5-dimethyl-7-acetyl-6-hydroxycoumaran-2-one suggested that the product would be a stereoisomer of dihydrousnic acid, which has, therefore, been named isodihydrousnic acid.

The optical inversions involved in the above-mentioned reactions are summarized as follows:

$$(+)\text{Usnic acid} \longrightarrow (-)\text{Dihydrousnic acid} \longrightarrow (+)\text{Isodihydrousnic acid}$$
$$(-)\text{Usnic acid} \longrightarrow (+)\text{Dihydrousnic acid} \longrightarrow (-)\text{Isodihydrousnic acid}$$

Four stereoisomers (2 pairs of enantiomorphs) of dihydrogenated usnic acid could be effected by the *cis*- and *trans*-fusion of the B- and C-rings of the molecule. It would be quite possible that the conversion of the configuration at one of the conjunction points of the two rings in dihydrousnic acid would be caused by heating and give isodihydrousnic acid, though the precise evidence for the configurations of the two compounds has not been obtained as yet.

We thank Mr. Tanaka, in the Department of Applied Chemistry of this University, for infrared absorption spectral analyses. The microanalyses were carried out by the members of the analytical laboratory of this Institute to whom our thanks are due. We are indebted to the Ministry of Education for the Science Research Fund in aid of the present research work.

Experimental

Catalytic Reduction of Usnic Acid—(+)Usnic acid (2.0 g.) dissolved in tetrahydrofuran (50 cc.) was catalytically hydrogenated with Pd-black (0.4 g.). After 1 hr.'s shaking when 180 cc. of H_2 was absorbed the solvent was removed *in vacuo* and the syrupy residue was recrystallized from MeOH to faint yellow needles, m.p. 147°; $[\alpha]_D^{24}$: −85° (c=2.66 in $CHCl_3$). Yield: 1.4 g.

It gave no melting point depression on admixture with authentic sample of (−)dihydrousnic acid prepared by the indirect method of Asahina, Yanagita, and Mayeda.5b) By the same method (−)usnic acid was directly hydrogenated to (+)dihydrousnic acid, m.p. 147°; $[\alpha]_D^{24}$: +85°.

(+)Isodihydrousnic Acid—On distillation at 230° (bath temp.) *in vacuo* (0.005 mm. Hg), (−)-dihydrousnic acid was recovered unchanged, whereas on heating at 220~230° *in vacuo* (0.005 mm. Hg) for 30 mins. in H_2 stream followed by distillation (bath temp. 230°), (−)dihydrousnic acid yielded a yellowish crystalline substance. The product was recrystallized from MeOH to faint yellow needles, m.p. 128°; $[\alpha]^{21}_{D}$: +47.5°(c=1.38 in $CHCl_3$). Yield : 0.1 g.

(−)Isodihydrousic acid, faint yellow needles (from MeOH), m.p. 128°; $[\alpha]^{20}_{D}$: −48.4°(c=1.59 in $CHCl_3$), and (±)isodihydrousnic acid, faint yellow plates (from MeOH), m.p. 158°; $[\alpha]_D$ 0, were obtained from (+) and (±)dihydrousnic acids, respectively, under the same procedure used for the preparation of (−)isodihydrousnic acid. *Anal.* Calcd. for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24. Found ((+)Isodihydrousnic acid) : C, 62.60; H, 5.46. ((−)Isodihydrousnic acid) : C, 62.43; H, 5.36. ((±)Isodihydrousnic acid) : C, 62.54; H, 5.30.

On heating isodihydrousnic acid with anhyd. $CaCl_2$ under ordinary pressure, a small amount of acetylacetone distilled out and then yellowish needles, m.p. 127°, were obtained on sublimation *in vacuo*, which were identified with 3,5-dimethyl-6-hydroxy-7-acetylcoumaran-2-one by a mixed fusion (mixed m.p. 127°).

Summary

(−) and (+)Dihydrousnic acid were directly prepared from (+) and (−)usnic acid by catalytic hydrogenation using palladium black as a catalyst and tetrahydrofuran as a solvent. On heating *in vacuo*, (−) and (+)dihydrousnic acid were converted into isomeric (+) and (−)isodihydrousnic acid, respectively.

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Tatsuhiko Nakano : Studies on the Alkaloids of Magnoliaceous Plants. XVI[1]. Alkaloids of *Magnolia denudata* Desr. (2).[2]*

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An earlier paper[2] of this series showed the presence of three quaternary bases, salicifoline, magnocurarine, and a new alkaloid of undetermined structure (picrate, m.p. 222~223°) in the bark of *Magnolia denudata* Desr. (Japanese name "Haku-mokuren"). The new supply of the root of the plant material being now available, further investigation was continued, and this paper presents the isolation of another quaternary base from this root.

The treatment with a procedure so far described in this series yielded a quaternary base as the styphnate forming yellow aggregate crystals, m.p. 230~231°(decomp.)[3], in a small quantity. The analyses were in accord with the composition, $C_{20}H_{24}O_4N \cdot C_6H_2O_8N_3$, in which two methoxyls and one $N(CH_3)_2$ group were confirmed. The picrate, crystallized as slightly brownish yellow microscopic pillars, m.p. 202~203° (decomp.). The iodide came in colorless pillars, m.p. 248~249°(decomp.). The methylation of the iodide with methyl iodide and alkali furnished the O,O-dimethyl ether iodide, as colorless needles, m.p. 243°(decomp.). On ethylation with ethyl iodide and alkali, the O,O-diethyl ether iodide was obtained as colorless needles, m.p. 235°.

The molecular formula and general properties of this alkaloid suggested a similarity to the aporphine bases, and this relationship became evident when these

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* This constitutes a part of a series entitled "Studies on the Alkaloids of Magnoliaceous Plants" by Masao Tomita.

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[1] Part XV. T. Nakano : This Bulletin, **3**, 234 (1955).

[2] Part (1). M. Tomita, T. Nakano : J. Pharm. Soc. Japan, **72**, 1260 (1952).

[3] This decomposition point somewhat dependeds upon the rate of heating.