Summary

The structure of the ethyl ester, $C_{18}H_{22}O_8$, m.p. 116°, which was obtained from O,O-diacetylusnic acid by the ozonolysis followed by alcoholysis was established by infrared spectral analyses as being ethyl 2-(2-hydroxy-3-acetyl-5-methyl-4,6-diacetoxy-phenyl)-propionate (VI). An alternative possible structure of usnic acid (IV) has therefore been excluded, and the structure of usnic acid (III) has been confirmed.

The behaviors of lactone A, m.p. 132°, an ozonolytic product of O,O-diacetylusnic acid was reëxamined. It was proved by infrared and nuclear magnetic resonance spectra, that reacetylation of deacetyl-lactone A with acetic anhydride and pyridine was affected at the 3-position of 2-coumaranone ring to furnish lactone B, m.p. 132°. Acetylating with acetic anhydride and conc. H_2SO_4, lactone A was regenerated from deacetyl-lactone A. Thus the earlier conclusions concerning with the lactones A and B have been corrected.

(Received March 29, 1961)

UDC 547.979.07

77. **Junzo Shoji**[*1] : Decomposition of Usnic Acid. VII.[*2] Pyrolysis of Dihydrousnic Acid. (3).[*3] Isodihydrousnic Acid.

(*Faculty of Pharmaceutical Sciences, University of Tokyo*[*1])

Shibata, Takahashi and Tanaka[*3] found that on heating above 200°, *in vacuo*, dihydrousnic acid (DHU), m.p. 149°, was converted into an isomeric compound named isodihydrousnic acid (IDHU), m.p. 128°, before it was completely decomposed into 6-hydroxy-7-acetyl-3,5-dimethyl-2-coumaranone and acetylacetone. DHU and IDHU could be distinguished neither by the color reactions nor by their infrared and ultraviolet absorption spectra. The both compounds, however, gave different optical rotations and migration distances on paper electrophoresis using buffer solution at pH 8.8.

$$\begin{array}{ccc} (-)\text{ DHU m.p. } 149^\circ & \longrightarrow & (+)\text{ IDHU m.p. } 128^\circ \\ [\alpha]_D\ -86.8^\circ & & [\alpha]_D\ +57.5^\circ \end{array}$$

In the previous report,[*3] it was suggested that DHU and IDHU would be *cis-trans* isomers at B/C ring fusion. On renewed investigation on this transformation of DHU, it has been found that the earlier suggestion would not be probable to elucidate the relation of DHU and IDHU.

All the attempts to obtain acetate of IDHU were failed, and the product of acetylation of IDHU was identical with the diacetate of DHU. DHU and IDHU were, however, differentiated by the individual Cu-complex salt having different color and optical rotation (DHU Cu-salt : $[\alpha]_D$ $-123\pm10^\circ$; IDHU Cu-salt : $[\alpha]_D$ $0\pm10^\circ$).

Observing the change of optical rotation, it has been shown that DHU and IDHU are interconvertible in pyridine or in aq. alkali solution to form an equilibrium (approx. 50:50)

[*1] Hongo, Tokyo (庄司順三).

[*2] Part VI : S. Shibata, J. Shoji, N. Tokutake, Y. Kaneko, H. Shimizu, H. C. Chiang : This Bulletin, **10**, 477 (1962).

[*3] (2) : S. Shibata, K. Takahashi, Y. Tanaka (nee Hiizumi) : This Bulletin, **4**, 65 (1956).

mixture of both compounds (observed $[\alpha]_D$ on a crude product obtained by the acidification of the reaction mixture : $-19.8°$ ($CHCl_3$): Calcd. $[\alpha]_D$ on 50:50 mixture of (−) DHU and (+) IDHU : $-15°$). DHU and IDHU were separated by recrystallization.

The infrared spectra of DHU and IDHU showed only a slight difference in the finger print region giving no remarkable information for the structural relation, while some evidences for the localization of hydrogen bonding were suggested.

The infrared absorption spectra (in $CHCl_3$) of DHU and IDHU showed weak and broad bands at 2800∼3000 cm^{-1} and 3200 cm^{-1} region, which suggested that all the hydroxyls would be hydrogen bonded with carbonyls. DHU and IDHU gave no definite free carbonyl absorption band at 1630∼1700 cm^{-1} region, while a silght shoulder was observed at 1670 cm^{-1}. The band at 1610∼1630 cm^{-1} would represent a chelated conjugated ketone and phenyl grouping.

The infrared spectrum (in Nujol) of O,O-diacetyl-DHU showed the phenolic acetate bands at 1775 and 1757 cm^{-1}, $\alpha\beta$-unsaturated ketone absorption at 1675 cm^{-1} with a shoulder at 1660 cm^{-1}, which would correspond to the non-hydrogen-bonded carbonyl in the C-ring and aryl acetyl in the A-ring.

O-Monoacetyl-DHU showed in its infrared spectrum (in $CHCl_3$) no free hydroxyl, while it gave a phenolic acetate band at 1759 cm^{-1}, an $\alpha\beta$-unsaturated ketone band at 1670 cm^{-1}, and chelated conjugated carbonyl and phenyl band at 1630∼1603 cm^{-1} (overlapped).

Above observations indicate that the phenolic hydroxyl in the A-ring of DHU is hydrogen-bonded with the carbonyl group in the C-ring, and acetylation of the hydroxyl in the A-ring resulted the appearance of nonhydrogen-bonded carbonyl band in the infrared spectrum.

On the other hand, the N.M.R. spectra of DHU and IDHU showed a noticeable difference. As the references for the assignment of the N.M.R. spectral signals of DHU and IDHU, the N. M. R. spectra of the ozonolytic products of O-diacetylusnic acid (Lac-

Table I. The Assignment of N.M.R. Spectral Bands as the References to those of DHU and IDHU.

	CH_3			$OCOCH_3$	$COCH_3$	$:CH-$	$-CHCH_2-$	$-CH-CH_2-$	$-CH-CH_3$
Lactone A	···	8.59 8.43	8.04	7.69 7.63	7.40	···	···	···	6.49 6.35 6.22 6.07
Lactone B	···	8.36	8.11	7.75 7.71	7.96 7.41	···	···	···	···
Usnic acid	···	8.28	7.92	···	7.37	4.04	···	···	···
Pummerer's ketone	···	8.41	7.69	···	···	···	octet (7.10)	quartet (5.32)	··· ···
Methylphloroglucinol triacetate	···	···	8.01	7.71 7.73	···	···	···	···	···
2-Acetyl-5,5-dimethyl-1,3-cyclohexanedione	8.92	···	···	···	7.41	···	···	···	···
DHU	···	8.33	8.00	···	7.44	···	doublet (6.93)	triplet (5.22)	···
IDHU	···	8.30	8.06 7.98	···	7.46 7.42 7.31	···	doublet (6.90)	quartet (5.20)	···

* The figures are the τ-values measured in $CHCl_3$ solution using Varian Associates 4300-C N.M.R. spectrometer at 56.4 Mc.
The figures in parenthesis are the values measured at the center of the multiplet bands.

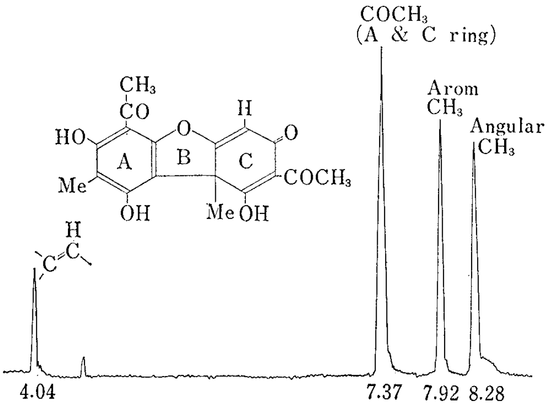


Fig. 1. N.M.R. Spectrum of Usnic Acid

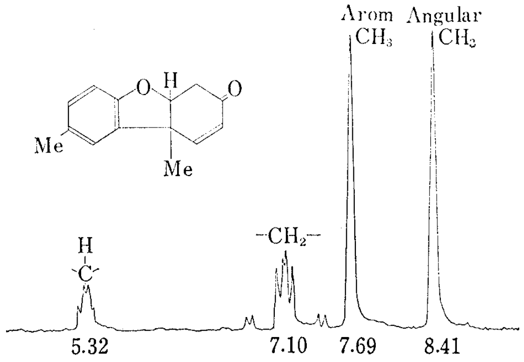


Fig. 2. N.M.R. Spectrum of Pummerer's Ketone

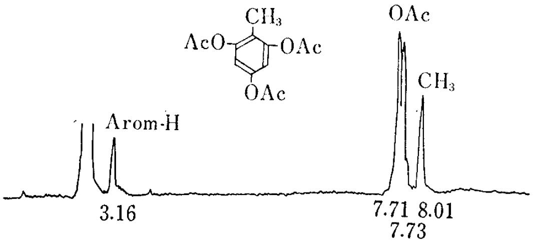
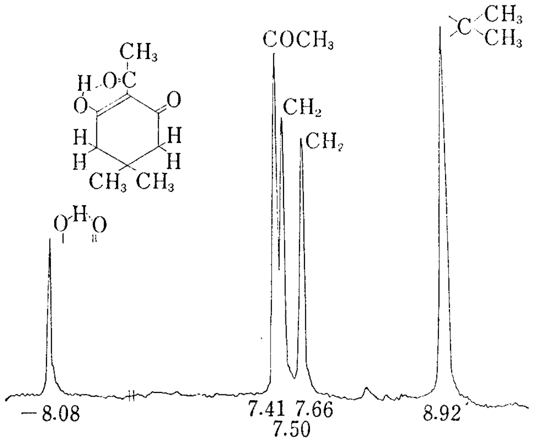


Fig. 3. N.M.R. Spectra of Methylphloroglucinol Triacetate and 2-Acetyl-5,5-dimethyl-1,3-cyclohexanedione



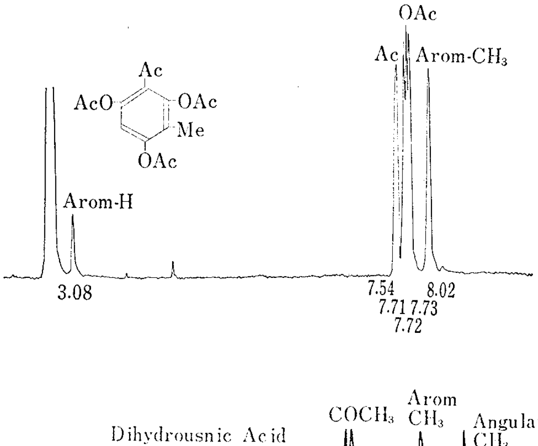


Fig. 4. N.M.R. Spectrum of Methylphloroacetophenone Triacetate.

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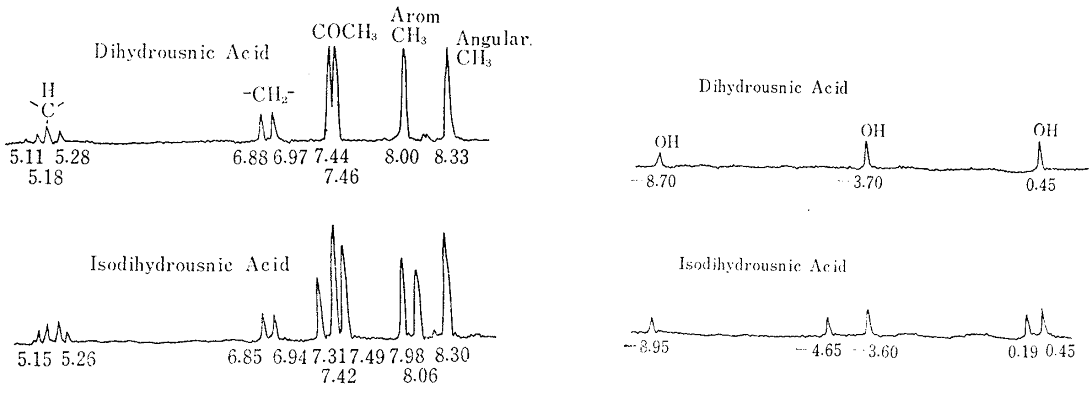

Fig. 5. N.M.R. Spectra of DHU and IDHU.

tones A and B),[1] (+) usnic acid, Pummerer's ketone,[2,3] 2-acetyl-5,5-dimethyl-1,3-cyclohexanedione,[4] and methylphloroglucinol triacetate[5] were measured.

The N.M.R. spectral band at the higher field (8.33 (DHU); 8.30 (IDHU)) would undoubtedly account for angular methyl regarding to those of usnic acid (8.28) and Pummerer's ketone (8.41). The second band which was shown by usnic acid at 7.92, and by DHU at 8.00 would be the signal of aromatic methyl, while that in Pummerer's ketone was shifted to lower field (7.69). The appearance of aromatic methyl band in higher field would be resulted by the effect of adjacent substitutions. Such an effect of substitution was indicated in the aromatic methyl band (8.01) of methylphloroglucinol triacetate and methylphloroacetophenone triacetate (8.02).

The band which would correspond to the aromatic methyl was split into doublet in the N.M.R. spectrum of IDHU (8.06, 7.98).

The third group of bands would correspond to acetyl groupings which were shown at 7.37 by usnic acid, and at 7.40~7.41 by lactones A and B.

The acetyl bands appeared at 7.44 7.46 in the N.M.R. spectrum of DHU and those in IDHU were split into three (7.49 (m), 7.42 (s), 7.31 (w)).

A doublet band centered on 6.93 and a triplet centered on 5.22 in the N.M.R. spectrum of DHU would correspond to $-\underset{|}{\mathrm{C}}\mathrm{H}-\mathrm{CH}_2-$ system in the C-ring. A corresponding doublet band centered on 6.90 appeared also in the N.M.R. spectrum of IDHU, while the bands centered on 5.20 which would correspond to the triplet band of DHU at 5.22, corrupted into a multiplet, which looks like a quartet.

With the purpose to determine whether the splitting of N.M.R. bands of aromatic methyl, acetyl region and the quartet like bands in IDHU is due to spin-spin coupling or chemical shift, the frequencies of oscillator were altered from 56.4 Mc. to 40 Mc.

In the N.M.R. spectrum of IDHU measured by Japanese N.M.R. spectrometer (JNM-III (Japan Electron Optics Laboratory Co.)) at 40 Mc. gave a spacing distance of the split bands at aromatic methyl region 3.2 c.p.s. corresponding to that measured at 56.4 Mc. (4.6 c.p.s.).

It has, therefore, been concluded that the doublet near 8.00 in the N.M.R. spectrum of IDHU is not displayed by spin-spin coupling, but it must be a chemical shift.

The spacing distance of the split acetyl bands (7.31, 7.49) in the N.M.R. spectrum of IDHU measured at 56.4 Mc. is 10.1 c.p.s. which changes into 5 c.p.s. at 40 Mc. Thus the splitting in the acetyl region has also been shown by the chemical shift.

Moreover, a remarkable difference has been observed in the lower field of N.M.R. spectra of DHU and IDHU. Three bands of hydroxyls (corresponding 3 hydroxyls) in the N.M.R. spectrum of DHU which appeared in the very lower field, at 0.45, −3.70, and −8.70 showed that all the hydroxyls, both enolic and phenolic, are strongly hydrogen bonded. The strength of hydrogen bonding was indicated by the sequence of τ-values from lower to higher.

The hydroxyl bands in the N.M.R. spectrum of IDHU were split giving two pairs of bands at +0.45 (s), +0.19 (w), and −3.60 (s), −4.65 (w), and single broad band (−8,95). The magnitude ratio of the paired bands was approximately 3:2.

Referring also the chemical shift of aromatic methyl and acetyl bands with the

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1) S. Shibata, J. Shoji, N. Tokutake, Y. Kaneko, H. Shimizu, H.S. Chiang: This Bulletin, **10**, 477 (1962).

2) R. Pummerer, D. Melamed, H. Puttfarcken: Ber., **55**, 3116 (1922).

3) D.H.R. Barton, A.M. Deflorin, O.E. Edwards: J. Chem. Soc., **1956**, 530; A. Robertson *et al.*, *Ibid.*, **1956**, 2322.

4) W. Dieckmann, R. Stein: Ber., **37**, 3379 (1904); A.W. Crossley, N. Renouf: J. Chem. Soc., **1912**, 1524.

5) H. Weidel: Monatsh., **19**, 227. (1898).

magnitude ratio approximately 3:2 in the N.M.R. spectrum of IDHU, the splitting of hydroxyl bands would suggest that IDHU would be an approximately 60/40 mixture of two forms, which are conveniently called forms A and B. These two forms of IDHU could not be separated each other by the usual methods even by the electrophoresis, and are in interconvertible states forming an equilibrium with a very low energy barrier.

On the basis of the foregoing results, the structural relation of DHU and IDHU including that of two forms of IDHU has now been considered. The *cis-trans* stereochemical isomerism was first pressumed to elucidate the conversion of DHU into IDHU. However, it has become doubtful as the molecular model showed that *trans* B/C ring fusion in DHU is obviously much strained making the *trans* fusion virtually impossible. Robertson *et al.*[4] stated that Pummerer's ketone would have *cis* B/C ring fusion by the same reason.

The N.M.R. spectrum of DHU showed a spin-spin coupling doublet with almost equivalent magnitude centered on 6.93 and a corresponding triplet centered on 5.22.

This suggests a geometrical relation of B/C ring fusion in DHU showing that the methylene in the C-ring is bisected with the adjacent angular proton at the B/C ring junction.[6] The B/C *cis*-ring fusion can only satisfy such a relation.

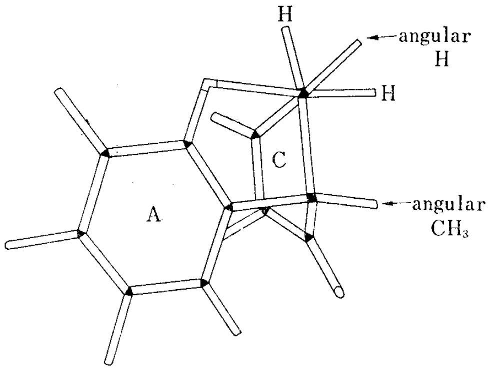


Fig. 6. Conformation of DHU

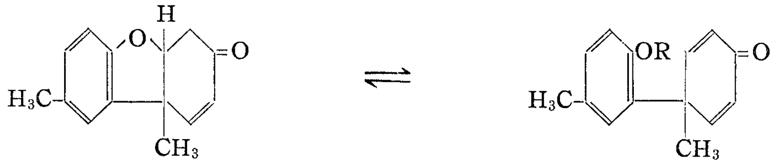
The doublet with an equivalent magnitude centered on 6.90, whose spacing distance (4.9 c.p.s.) at 56.4 Mc. did not change by the alteration of frequencies of oscillator (5.0 c.p.s. at 40 Mc.), is also observed in the N.M.R. spectrum of IDHU. Thus the geometrical relation of B/C ring fusion in the IDHU molecule is also same as that of DHU as being *cis*.

On the basis of the same geometrical relation at the B/C ring fusion, the relation of DHU and IDHU has been considered.

It would be difficult to explain the structural relation of DHU and IDHU by the presence of stabilized keto-enol isomers of cyclic triketone at the C-ring, as DHU and IDHU afforded different Cu-salts which regenerated DHU, and IDHU, respectively.

It would, therefore, be not unreasonable to presume that a rearrangement of A-ring occurs by the cleavage of B-ring in the conversion of DHU into IDHU.

Thus IDHU would be represented by the formula which possesses methyl and acetyl groupings in the A-ring at the alternate positions of DHU.



Pummerer's ketone

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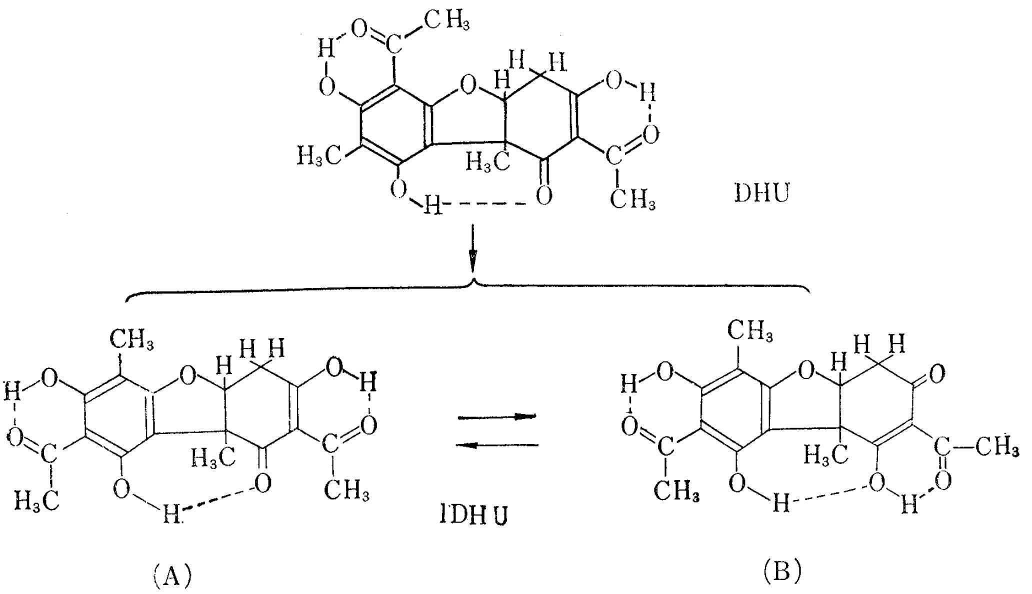
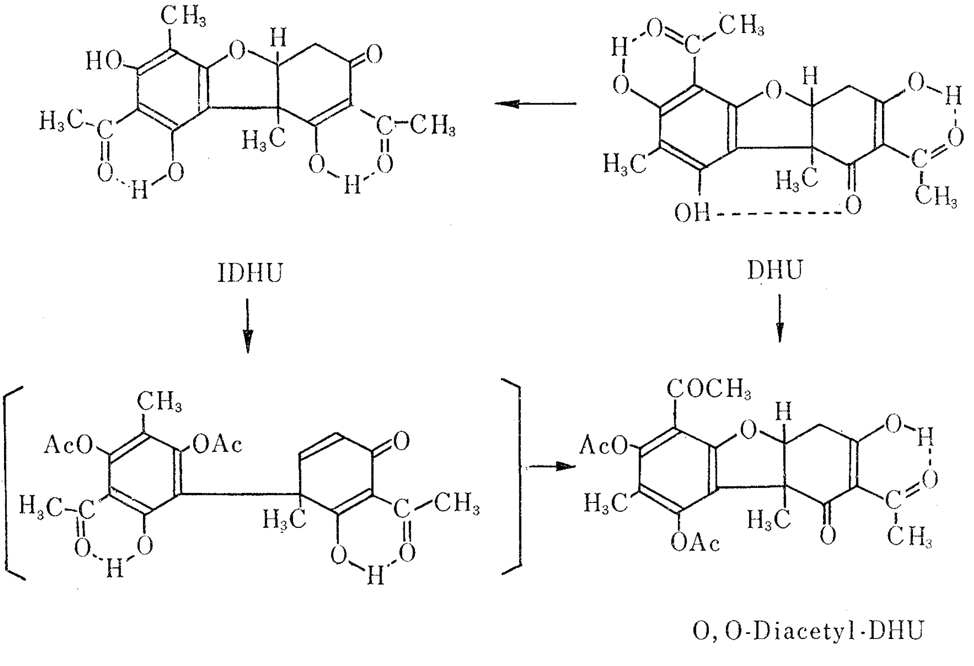
[6] cf. M. Karplus: J. Chem. Phys., **30**, 11 (1955).

As shown by Robertson *et al.*,[4] the B-ring of Pummerer's ketone is cleaved by sodium alcoholate to give a sodium salt of phenolic compound which is readily recyclized on heating in water to regenerate Pummerer's ketone. This would suggest that on heating or base-catalyzed reaction the ring cleavage and rearrangement of DHU is quite possible.

The N.M.R. spectrum of IDHU showed that it is a 60/40 mixture of two different forms A and B, which can be represented by the different situation of hydrogen bonding between hydroxyls and ketones. Such a different situation of hydrogen bonding might give a shift of the bands of aryl methyl, acetyl, and hydroxyls in the N.M.R. spectrum of IDHU.





On acetylation of IDHU, a ring cleavage would occur first at the oxygen bridge of B-ring, and the free hydroxyl attached to the A-ring might be acetylated, while the hydroxyl at the adjacent position of acetyl in the A-ring is protected against acetylation by the strong hydrogen bonding. The recyclization would occur at this free hydroxyl to furnish O,O-diacetyl-DHU.

N.M.R. Spectra——The nuclear magnetic resonance spectra were obtained with a Varian Associates 4300-C spectrometer operating at 56.4 Mc. and a Japan Electron Optics Laboratory Co. Ltd. JNM-III operating at 40 Mc. The positions of resonances are measured by the side band technique and given as values of τ which are obtained in chloroform as an internal reference. The τ-value of chloroform was assumed to be 2.75. The error of the given τ-values is an order of ± 0.03 ppm. and that of spin-spin coupling is ± 0.3 cps. The measurement was carried out at $22 \pm 1°$.

Experimental

Catalytic Hydrogenation of O,O-Diacetylusnic Acid——(+) O,O-Diacetylusnic acid was hydrogenated by the method of Asahina, Yanagita, and Mayeda.7) On recrystallization from MeOH, (+) O,O-diacetyldihydrousnic acid was obtained as colorless needles, m.p. 148°. *Anal.* Calcd. for $C_{22}H_{22}O_9$: C, 61.39; H, 5.15. Found : C, 61.19; H, 5.32. $[\alpha]_D^{17.5}$ +7.4° (c=3.96, $CHCl_3$). UV λ_{max}^{EtOH} mμ (ε) : 220 (22,000), 275 (11,200), 316 (5,400).

(−) **Dihydrousnic Acid** (**DHU**)——Hydrolysis of (+) O,O-diacetyldihydrousnic acid with cold conc. H_2SO_4 gave (−) dihydrousnic acid. Recrystallization from MeOH gave orange yellow plates, m.p. 149°. $[\alpha]_D^{12.3}$ −86.8° (c=1.64, $CHCl_3$) UV λ_{max}^{EtOH} mμ (ε) : 227 (15,700), 283 (24,000), 337 (2,800).

(−) Dihydrousnic acid was obtained directly from (+) usnic acid by the catalytic hydrogenation using Pd-black as a catalyst and tetrahydrofuran as the solvent.*3)

(+) **Isodihydrousnic Acid** (**IDHU**)*3)——Dihydrousnic acid was heated at 220~230° (bath temp.) *in vacuo* for 30 min. in H_2 stream. Distillation afforded yellowish crystalline product, which was recrystallized from MeOH to pale yellow needles, m.p. 128°. *Anal.* Calcd .for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24. Found : C, 62.07, 62.67; H, 5.07, 5.33. $[\alpha]_D^{12.3}$ +57.5° (c=1.61, $CHCl_3$) and $[\alpha]_D^{25}$ +57.5° (c=1.58, $CHCl_3$). UV λ_{max}^{EtOH} mμ (ε) 228 (14,900), 286 (23,500). It gives a brown red coloration with $FeCl_3$ in MeOH.

Molecular Weight Determination of Isodihydrousnic Acid——Molecular weight of isodihydrousnic acid was determined by Rast method and by Barger-Akiya's method (using Me_2CO as the solvent and azobenzene as the standard). Calcd. for $C_{18}H_{18}O_7$: Mol. wt. 346.3. Found : Mol. wt. (Rast) 335.1, 395.5, 358.0, 331, 326; (Barger-Akiya) 348.4.

Change of Optical Rotation of Dihydrousnic Acid and Isodihydrousnic Acid in Pyridine and Alkali

The optical rotations of dihydrousnic acid and isodihydrousnic acid were measured in pyridine and 8% NaOH solution. After 24 hr. (pyridine) or 3 hr. (NaOH) standing at room temperature, the solution was poured into ice-water containing dil. HCl. The precipitates were collected and washed with water. The crude material was used for measurement of optical rotation without further purification.

$[\alpha]_D$ in pyridine :

Comp. Time	15 min.	24 hr.	Recovered mixture (after 24 hr.)
IDHU	−64.5°	−69.3°	−19.8°
DHU	−73.9°	−70.1°	−25.1°

$[\alpha]_D$ in 8% NaOH

Comp. Time	10 min.	3 hr.	Recovered mixture (after 3 hr.)
IDHU	−101.2°	−103.2°	−21.3°
DHU	−86.8°	−103.3°	−42.9°

Paper Electrophoresis——The separation of dihydrousnic acid and isodihydrousnic acid was carried out by paper electrophoresis on Toyo Roshi No. 50 as the filter paper using Borax-buffer solution at pH 8.8. The spots separated on the filter paper were visible, but the following reagents were also employed for detection : i) 0.5% $KMnO_4$ solution, ii) Chloramine-T (CAT) saturated in EtOH, and iii) 5% $FeCl_3$ solution in MeOH.

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7) Y. Asahina, M. Yanagita, S. Mayeda : Ber. **70**, 1500 (1937).

Condition : 300 V. 0.94 mA/cm. at room temperature for 3 hr.
Migration distance : IDHU 5.9 cm., DHU 9 cm.

The material treated with pyridine or 8% NaOH showed two spots on electrophoresis, which were shown to be identical with the spots of IDHU and DHU.

Acetylation of Dihydrousnic Acid——Acetylation of isodihydrousnic acid with Ac_2O and conc. H_2SO_4 was failed to obtain crystalline substance.

A mixture of isodihydrousnic acid (0.1 g.), Ac_2O (1 cc.) and AcONa (0.1 g.) was heated for 3 hr. on a boiling water bath. After cooling, the reaction mixture was poured into ice-water. The faint yellow precipitates were collected and dried. Recrystallization from MeOH gave colorless needles, m.p. 146∼148^c, $[\alpha]_D^{14}$ +5.52°(c=3.46, $CHCl_3$). The acetate was identified with O,O-diacetyldihydrousnic acid by mixed fusion, IR and N.M.R. spectra.

Treatment of Isodihydrousnic Acid and Dihydrousnic Acid with Phenylhydrazine Hydrochloride——A solution of isodihydrousnic acid (0.2 g.) and phenylhydrazine HCl (0.2 g.) in EtOH (5 cc.) was refluxed for 8 hr. After cooling the reaction mixture was poured into ice-water. The precipitates were recrystallized from EtOH to give pale yellow needles, m.p. 210°. *Anal.* Calcd. for $C_{24}H_{22}O_5N_2$: C, 68.89; H, 5.30; N, 6.70. Found : C, 68.96; H, 5.27; N, 6.83. $[\alpha]_D^{11.8}$ +247.6° (c=0.51, $CHCl_3$), UV λ_{max}^{EtOH} mμ (ε) 226 (22,600), 272 (22,600), 337 (3,800). It gives a dark greenish blue coloration with $FeCl_3$ in MeOH. The acetylation of this product with Ac_2O and pyridine at room temperature afforded colorless needles, m.p. 187°. *Anal.* Calcd. for $C_{28}H_{26}O_7N_2$: C, 66,92; H, 5.22; N, 5.58. Found : C, 67.05; H, 5.16; N, 5.81. UV $\lambda_{max}^{CHCl_3}$ mμ (ε) : 257 (17,400), 316 (3,900).

On treatment (−) dihydrousnic acid with phenylhydrazine hydrochloride under the same condition as described above, pale yellow needles were obtained, which were recrystallized from EtOH to give m.p. 211°, $[\alpha]_D^{22}$ +247.0° (c=1.95, $CHCl_3$). It was proved to be identical with the phenylhydrazone anhydride obtained from isodihydrousnic acid by mixed fusion and the comparison of IR spectra. The identity was also established by the acetate, colorless needles, m.p. 188°.

Treatment of Isodihydrousnic Acid and Dihydrousnic Acid with aq. NH_4OH——i) Isodihydrousnic acid (0.1 g.) in EtOH (10 cc.) was refluxed with 28% NH_4OH (1 cc.) for 3 hr. The brownish reaction mixture was evaporated to dryness, and the residue was recrystallized from EtOH to give faint yellow granular crystals, m.p. 197°. *Anal.* Calcd. for $C_{18}H_{19}O_6N$: C, 62.61; H, 5.51; N, 4.06. Found: C, 62.75; H, 5.33; N, 4.00, $[\alpha]_D^{15}$ −218.9°(c=0.49, $CHCl_3$).

ii) The amide of (−) dihydrousnic acid was prepared by the method of Asahina and Yanagita. The product had faint yellow granular crystals, m.p. 201°, $[\alpha]_D^{15}$ −222.6° (c=0.61, $CHCl_3$). *Anal.* Calcd. for $C_{18}H_{19}O_6N$: C, 62.61; H, 5.51; N, 4.06. Found : C, 62.70; H, 5.71; N, 4.35. The product derived from (+) isodihydrousnic acid and (−) dihydrousnic acid by the action of NH_4OH were proved to be identical by a mixed fusion and IR spectra.

Copper Salt of (+) Isodihydrousnic Acid and (−) Dihydrousnic Acid——A solution of (+) isodihydrousnic acid (0.1 g.) in benzene (5 cc.) was shaken with a cold saturated $(AcO)_2Cu$ solution. After standing overnight the bluish grey precipitates (0.1 g.) were collected and washed with benzene and then with water. On recrystallization from benzene bluish grey microneedles were obtained. M.p. 220∼230° (decomp.) (darkens from 200°).

It is soluble in pyridine to form a dark green solution and in tetrahydrofuran to give a dark blue solution. In $CHCl_3$ containing a drop of EtOH it dissolves to give a bluish green solution. *Anal.* Calcd. for $(C_{18}H_{17}O_7)_2Cu$: C, 57.33; H, 4.54. Found : C, 57.88; H, 5.06; Ash : 10.36%. The determination of optical rotation was very difficult due to its deep color and small value of rotation. $[\alpha]_D$ 0±10° (c=0.34, 1% EtOH in $CHCl_3$). UV λ_{max}^{EtOH} mμ (ε) : 227 (37,000), 290 (58,000). On treatment with dil. HCl the Cu salt was decomposed to regenerate (+) isodihydrousnic acid which was proved by mixed fusion and the comparison of optical rotation.

The same procedure was adopted to (−) dihydrousnic acid to form Cu salt. The Cu salt of (−) dihydrousnic acid is less soluble in benzene to give bluish grey micro needles, m.p. 200∼210° (decomp.) $[\alpha]_D$ −123±1° (c=0.33, 1% EtOH in $CHCl_3$). UV λ_{max}^{EtOH} mμ (ε) : 226 (35,000), 288 (54,000).

The IR spectra of Cu salt of dihydrousnic acid and isodihydrousnic acid are very similar with a slight difference in the finger print region as observed in the spectra of dihydrousnic acid and isodihydrousnic acid. *Anal.* Calcd. for $(C_{18}H_{17}O_7)_2Cu$: C, 57.33; H, 4.54. Found : C, 57.42; H, 4.92; Ash, 10.23%. On treatment with dil. HCl, Cu salt of dihydrousnic acid regenerated (−) dihydrousnic acid, which was proved by a mixed fusion and the comparison of optical rotation.

Preparation of the Model Compounds for N.M.R. Spectral Determination

Pummerer's Ketone——This compound was prepared by the oxidative coupling of *p*-cresol by the method of Pummerer. M.p. 126°. *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.47; H, 6.58. Found : C, 78.36; H, 6.67. UVλ_{max}^{EtOH} mμ (ε): 222 (23,000), 302 (3,300).

Methylphloroglucinol Triacetate——M.p. 59°. *Anal.* Calcd. for $C_{13}H_{14}O_6$: C, 58.64; H, 5.30. Found: C, 58.96; H, 5.49.

Methylphloroacetophenone Triacetate——M.p. 110.5°. *Anal.* Calcd. for $C_{15}H_{16}O_7$: C, 58.43; H, 5.23.

Found : C, 59.25; H, 4,92. UV λ_{max}^{EtOH} mμ (ε) : 238 (6,000).

2-Acetyl-5,5-Dimethyl-1,3-cyclohexanedione——It was prepared by the method of Dieckmann and Stein, and Crossley and Renouf.[4] M.p. 36° *Anal.* Calcd. for $C_{10}H_{14}O_3$: C, 66.05; H, 7.77. Found: C, 65.81; H, 7.71. UV λ_{max}^{EtOH} mμ (ε) : 234 (10,200), 274 (11,700).

The author wishes to thank Prof. S. Shibata for his kind guidance throughout the course of this work. He is also indebted to Mr. H. Shimizu of this Faculty, who gave much help in discussing the interpretation of N.M.R spectra, to Dr. I. Yamaguchi and Mr. Hayakawa, Japan Institute for Atomic Energy, and Dr. K. Nukada, Government Chemical Industrial Research Institute, Tokyo, for the measurement of N.M.R. spectra.

He wishes to thank Prof. Y. Tsuzuki and Mr. N. Mori, Tokyo College of Science, for the measurement of optical rotatory dispersion curves.

Thanks are due to Miss. M. Ninomiya and Mrs. E. Tanaka for the measurement of infrared spectra, Miss H. Ônishi for the measurement of ultraviolet spectra, and the members of microanalytical laboratory of this Faculty, and the Institute of Applied Microbiology of this University, for microanalyses.

Summary

The structure of (+) isodihydrousnic acid (IDHU), $C_{18}H_{18}O_7$, m.p. 128°, $[\alpha]_D$ +57.5°, which was obtained from (−) dihydrousnic acid (DHU), $C_{18}H_{18}O_7$, m.p. 149°, $[\alpha]_D$ −86.8°, by heating above 200° was studied.

IDHU was separated from DHU by recrystallization from MeOH or by paper electrophoresis. DHU and IDHU were distinguished by their Cu-complex salts which gave markedly different optical rotation. DHU and IDHU are interconvertible to form an equilibrium mixture in pyridine or in aq. alkaline solution, which showed an equilibrium value of optical rotation. The former suggestion that DHU and IDHU would be *cis-trans* isomers at B/C ring fusion has now been revised. The N.M.R. spectra showed a *cis*-ring fusion in both DHU and IDHU. The chemical and N.M.R. spectral studies of DHU, IDHU and their model compounds resulted that a rearrangement of A-ring occurs by the cleavage of B-ring in the course of interconversion of DHU and IDHU. The N.M.R. spectra of IDHU showed that it exists in an equilibrium state of different situation of hydrogen bonding, which is represented as in the formulas (A) and (B).

(Received March 29, 1961)