d-1-Methyl-4-acetylcyclohexanone-2 Dioxime: The crude dioxime, m.p. 194~178°, prepared from 0.14 g. of (XX), 2 cc. EtOH, 0.15 g. $NH_2OH \cdot HCl$, and 0.1 g. Na_2CO_3 is recrystallized from dil. EtOH to colorless needles, m.p. 200~202°, $[\alpha]_D^{20.5}$: +40.0°(4% solution in 10% NaOH solution). *Anal.* Calcd. for $C_9H_{16}O_2N_2$: C, 58.65; H, 8.69; N, 15.21. Found: C, 58.86; H, 8.78; N, 15.41.

d-1-Methyl-4-acetylcyclohexanone-2 Disemicarbazone: The crude disemicarbazone, m.p. 210~212°, prepared from 0.15 g. of (XX), 0.15 g. semicarbazide hydrochloride, 0.8 g. AcOK, 2 cc. MeOH, and 0.5 cc. of water is recrystallized from dil. EtOH to coloress needles, m.p. 220~222°. *Anal.* Calcd. for $C_{11}H_{10}O_2N_6$: C, 49.22; H, 7.52. Found: C, 49.49; H, 7.35.

v) ***rac*-1-Methyl-4-acetylcyclohexanone-2 (XVI-B)**—A solution of 1.5 g. of (XX) in 15 cc. of 12% NaOH solution is heated for 2 hrs., the reaction mixture is extracted with ether, and the ethereal residue is distilled under vacuum, b.p_{12} 119°, $[\alpha]_D^{14.9}$: 0°(3% solution in EtOH). Yield, 1.2 g. Admixture of the dioxime, m.p. 190~194°, (Tiemann,[7] m.p. 197~198°; Wallach,[8] m.p. 195°) with the dioxime, m.p. 191~195°, prepared from (XVI) shows no depression. The melting point 220°(decomp). (Wallach[8], m.p. 203~204°) of the disemicarbazone also agrees well with that (222°(decomp.)) of the disemicarbazone of (XVI).

Summary

It has previously been shown that in view of its ability to form peracid and its behaviour to alkali, *trans*-π-oxocamphor resembles an α,β-unsaturated aldehyde compound and that the bridged bond of camphor acts like a double bond. In the present study, *d*-isoketopinic acid (I) was subjected to Hofmann reaction, and the resulting *d*-methoxycarbonylamino-α-santenone (VI) was hydrolyzed on the assumption that if the bridged bond of camphor acts like a double bond, the resulting 7-hydroxysantenone (III) should be converted into the methyl ketone compound (XVI) by ring cleavage, and this assumption was confirmed. At the same time, the racemization in this reaction was clarified.

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42. **Masahisa Yoshida**: Ring Cleavage of 7-Hydroxysantenone. II.*

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Previously Ishidate and Tani[1] reported that *d*-7-amino-α-santenone (III) was not diazotized by the conventional method and that if the same reaction is conducted in a sealed tube, it was converted into a colored substance probably by the introduction of a nitroso group into the carbon atom adjacent to the carbonyl group, whereas when the compound was warmed a little with caustic alkali, it was readily changed into *rac*-7-hydroxy-α-santenone, evolving ammonia quantitatively.

The author[2] thereafter confirmed by synthetic method that the compound which had been considered as *rac*-7-hydroxy-α-santenone was nothing but *rac*-1-methyl-4-acetylcyclohexanone-2 (IX) produced by the ring cleavage of the 7-hydroxy compound.

However, the fact that (III) is stable to hydrochloric acid and is hardly diazotized and that it is readily hydrolyzed by caustic alkali to (IX) aroused the doubt that (III) might already be an imino compound produced by the ring cleavage. The author, therefore, investigated this point in the present study and found that it is an amino compound possessing a bridged bond. That is, the fact that (III) is positive to both dimethylaminobenzaldehyde and nitroprusside-acetaldehyde color reactions shows that

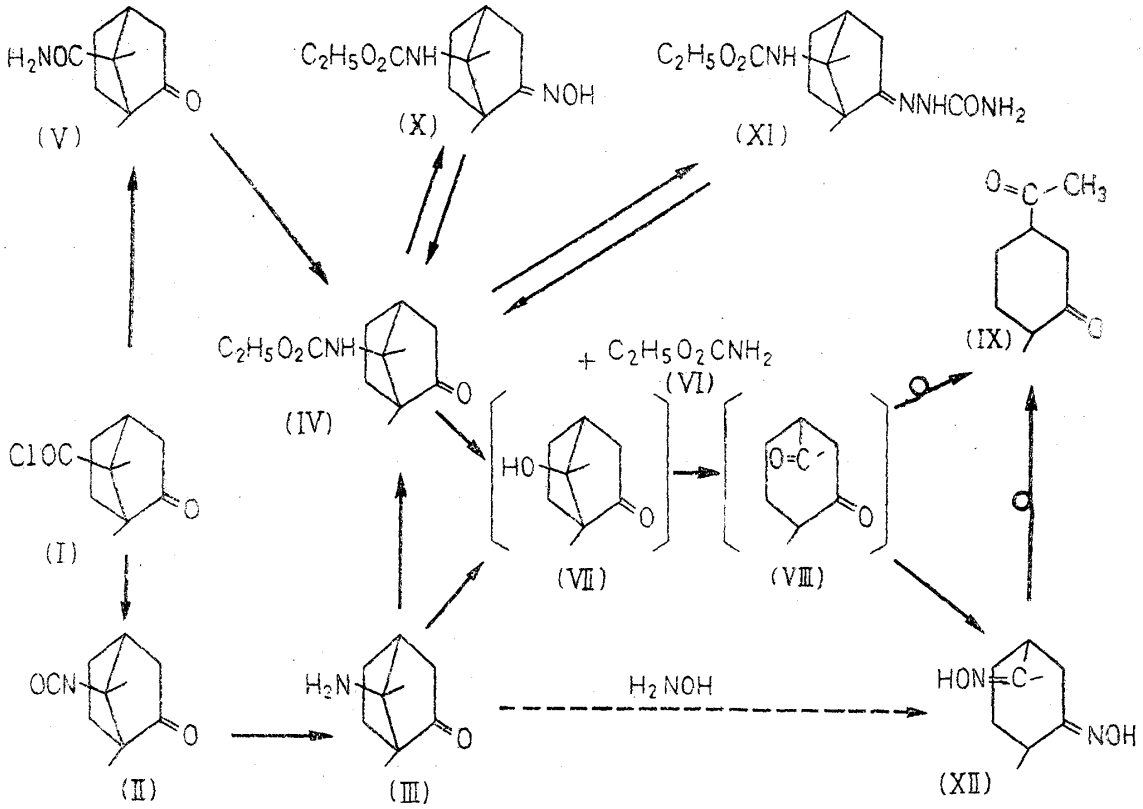
* This work is a part of series entitled "Studies on the Cleavage of Camphor Ring" by M. Ishidate.

** Hongo, Tokyo (吉田正久).

1) M. Ishidate, T. Tani: J. Pharm. Soc. Japan, **62**, 12(1932).

2) M. Yoshida: This Bulletin, **3**, 215(1955).

(III) is an aliphatic primary amine. Furthermore, from the fact that (III), though very showly, is diazotized and gives the corresponding hydroxy compound after prolonged heating, that *d*-ethoxycarbonylamino-α-santenone (IV) prepared from (III) by the action of ethyl chlorocarbonate is in complete agreement in melting point and optical rotation with (IV), synthesized from isoketopinic acid by the Hofmann reaction, and that there is no such drastic reaction in the course of the prerapation of (IV) that may cause ring cleavage, it is certain that (III) is an amino compound having a bridged bond.



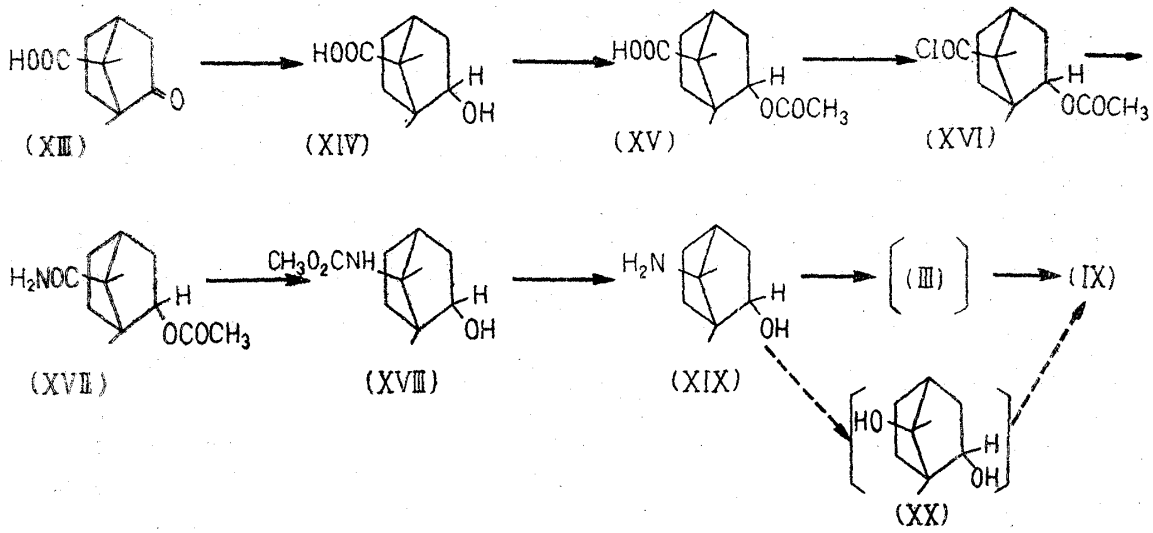
When (III) was reacted with hydroxylamine in an alkaline medium, it afforded optically active dioxime (XII). At a glance, (XII) seems to have been produced by the initial combination of the carbonyl at C_2 with hydroxylamine, then the hydrolysis of the amino group to hydroxyl, and finally the formation of a dioxime by the cleavage of the bridged bond. Thus, prevention of the enolation of the carbonyl group at C_2 appears to have produced the optically active product (XII).

On the other hand, the oxime (X) and the semicarbazone (XI) of (IV) are stable to alkali and they give (IX) only when boild with concentrated hydrochloric acid for a long time. Since no amine color reaction is observed during the reaction, (X) and (XI) in this case seem first to retrogress to (IV) and then hydrolyzed to (IX). This fact shows that the above-mentioned dioxime (XII) was produced by the hydrolysis of (III) by the alkaline medium to (VII), then converted to (VIII) by ring cleavage, and finally combined with hydroxylamine before undergoing racemization attributable to the enolation of the hydrogen at C_4.

This presumption is further supported by the fact that the same optically active dioxime was prepared[2] under the same conditions from (VIII), synthesized from *l*-carvone, and that in general the carbonyl at C_2 hardly combines with hydroxylamine.

Next, the possibility of ring cleavage of 7-hydroxysantenol-type compounds, which are the derivatives of borneol, was studied. First of all, *d-trans*-7-chlorocarbonyl-π-

apobornyl acetate (XVI) was prepared by the method of Asahina, Ishidate[3] and Sano,[4] and then it was converted into the amino compound (XVII), and further led to *d*-7-methoxycarbonylamino-α-santenol (XVIII) by the Hofmann reaction. Unlike (IV), (XVIII) is stable to alkali and when heated with concentrated hydrochloric acid for a long time it gives positive amino reaction and negative Legal reaction, and gives *d*-7-amino-α-santenol (XIX). Differing from (III), (XIX) is stable to alkali and is not hydrolyzed by it even on warming. In this, (XVIII) differs from the α,β-unsaturated urethan-type compounds. This seems to mean that the change of the keto bond angle of 120° at C_2 into hydroxyl bond angle of 109° decrease the intramolecular tension, which in turn decreased the double bond-like property of the bridged bond ascribable to the tension.



Like amino-santenone (III), aminosantenol (XIX) is hardly diazotized by nitrous acid, and when heated with excess nitrous acid for a long time, it gives, not the hydroxysantenol (XX), but a diketo compound (IX). This seems to mean that aminosantenol (XIX) is first oxidized to aminosantenone (III) and then converted to the diketo compound (IX).

The author is grateful to Mr. Daijiro Ohata and Mr. Eisaku Kimura for the elementary analyses.

Experimental*

Curtius Reaction of Isoketopinic Acid :

d-trans-π**-Apocamphor-7-isocyanate (II)**[1]—To a solution of 72 g. of isoketopinyl chloride (I) in 200 cc. of dry benzene is added 36 g. of sodium azide, and the mixture is heated at 90° for 8 hrs. The benzene layer is separated, evaporated, and the residue is recrystallized from benzene to colorless prisms, m.p. 94~96°, $[\alpha]_D^{11.0}$: +30.1°(2% solution in EtOH).

d-**7-Amino-***trans*-π**-apocamphor (***d*-**7-Amino-**α**-santenone) (III)**[1]—To a solution of 36 g. of (II) in 100 cc. of benzene is added 100 cc. of 20% HCl and the mixture is heated at 70° for 2 hrs. with stirring. The acid layer is separated, neutralized with Na_2CO_3, made alkaline with an excess of NaOH, and extracted with ether. The ether solution is evaporated and the residue is recrystallized from petr. ether to hygroscopic colorless needles, m.p. 158~159°, $[\alpha]_D^{11.0}$: +10.1°(10% solution in EtOH). *Anal.* Calcd. for $C_9H_{15}ON$: C, 70.54; H, 9.87; N, 9.15. Found : C, 70.50; H, 9.94; N, 9.42.

Detection of the Amino Group of *d*-**7-Amino-**α**-santenone (III)**—i) The product is negative to the color reaction with sodium pentacyanoferriate (reagent for aromatic primary amines).

ii) The product gives bluish purple color with nitroprusside-acetaldehyde (reagent for aliphatic secondary amines).

iii) Color reaction of the product with potassium 1,2-naphthoquinone-4-sulfonate. Immediately

* All melting points are not corrected.

3) Y. Asahina, M. Ishidate : J. Pharm. Soc. Japan, **55**, 670(1935).
4) Y. Asahina, M. Ishidate, T. Sano : *Ibid.*, **56**, 381(1936).

after the reaction the resulting color is the same with that of the control, but gradually turns brown and finally reddish brown. Orange color in an acetic acidic medium.

iv) The product is positive (yellow) to the color reaction with dimethylbenzaldehyde.

From these results, the amino group of (III) is qualitatively proved.

Diazotization of *d*-7-Amino-α-santenone (III) with HNO_2—To a solution of 6.1 g. of (III) in 150 cc. of 30% H_2SO_4 is added dropwise an aq. solution of 3 g. $NaNO_2$ with cooling and stirring, and the mixture is left standing overnight. The reaction mixture is heated at 50° until it becomes negative to ZnI_2-starch paper and after standing overnight, heated further at 90°, when it becomes positive to the Legal reaction. The reaction mixture, after the addition of anhyd. Na_2SO_4, is extracted with ether and the residue (2.2 g.) of the dry ether solution is subjected to fractional distillation. The main product distills at 130°/14 mm., 1 g. $[\alpha]_D^{18}$: 0°(5% solution in EtOH). Semicarbazone, m.p. 220~222°, shows no depression on admixture with *rac*-1-methyl-4-acetylcyclohexanone semicarbazone.

***d*-7-Ethoxycarbonylamino-α-santenone (IV) from *d*-7-Amino-α-santenone (III)**—To a solution of 5 g. of (III) in ether is added 5 g. of ClCOOEt. The reaction mixture is neutralized with $NaHCO_3$, the ether is distilled off, and the residue is recrystallized from EtOH in colorless prisms, m.p. 101~102°, $[\alpha]_D^{21.4}$: −10.4°(3% solution in EtOH). *Anal.* Calcd. for $C_{12}H_{19}O_3N$: C, 64.04; H, 8.50; N, 6.22. Found: C, 64.02; H, 8.78; N, 6.28. Admixture of the product with that prepared by the Hofmann reaction (I→V→IV) shows no depression.

***d*-7-Ethoxycarbonylamino-α-santenone (IV)**—Twenty grams of (V) is dissolved in EtONa solution prepared from 5 g. of Na and 200 cc. EtONa, and 5.5 cc. Br_2 is gradually dropped therein with cooling. The mixture is heated at 50° for 4 hrs., left standing overnight, and extracted with ether. The ethereal solution is dried, evaporated, and the residue is recrystallized from EtOH in colorless needles, m.p. 101~102°, $[\alpha]_D^{21.4}$: −10.0°(3% solution in EtOH). Yield, 10.5 g. *Anal.* Calcd. for $C_{12}H_{19}O_3N$: C, 64.04; H, 8.50; N, 6.22. Found: C, 64.00; H, 8.59; N, 6.33.

Hydrolysis of *d*-7-Ethoxycarbonylamino-α-santenone (IV)—Like (III), (IV) is readily hydrolyzed by alkali; decomposed with 10% NaOH solution at a room temperature to give (IX). Although it is stable to acid it is hydrolyzed when heated with conc. HCl for a long time, becoming negative to the amine reaction and positive to the Legal reaction. Twenty grams of (IV) is heated with 150 cc. of 30% HCl for 6 hrs. The reaction mixture is neutralized with K_2CO_3, and after removing the resulting resinous substance, further K_2CO_3 is added. The separated oil is extracted with ether, the ether solution is dried and the ether residue is subjected to fractional distillation. The colorless crystals, m.p. 50°, $[\alpha]_D^{23.0}$: 0°(5% solution in EtOH), separated from the forerun, $b.p_{13}$ 120~130°, show no depression of m.p. on admixture with ethylurethan. *Anal.* Calcd. for $C_3H_7O_2N$: N, 15.73. Found: N, 16.08.

The main distillate, $b.p_{13}$ 130°, $[\alpha]_D^{23.0}$: 0°(5% solution in EtOH), agrees with *rac*-1-methyl-4-acetylcyclohexanone-2 (IX).

Hydrolysis of *d*-7-Ethoxycarbonylamino-α-santenone Oxime (X)—To a solution of 2.25 g. of (IV) in 20 cc. EtOH is added 1.5 g. $NH_2OH \cdot HCl$, followed by 1.0 g. Na_2CO_3, and the resulting crystals are recrystallized from EtOH, m.p. 129~131°. *Anal.* Calcd. for $C_{12}H_{20}O_3N_2$: C, 59.96; H, 8.39; N, 11.66. Found: C, 59.92; H, 8.32; N, 11.63.

When 1 g. of the product (X) is heated with 20 cc. of 20% NaOH solution for a long time, the mixture remains negative to the amine and Legal reactions, and only the starting material is recovered from the mixture. When heated with 20% HCl, (X) remains negative to the amine reaction but becomes positive to the Legal reaction, and is converted into (IX).

Hydrolysis of *d*-7-Ethoxycarbonylamino-α-santenone Semicarbazone (XI)—The semicarbazone is prepared from (IV) by the usual method and purified by recrystallization from EtOH to colorless needles, m.p. 232~235°. *Anal.* Calcd. for $C_{13}H_{22}O_3N_4$: C, 55.28; H, 7.86; N, 19.86. Found: C, 55.13; H, 7.90; N, 20.19.

When 1 g. of the semicarbazone (XI) is heated with 10% or 20% NaOH solution for a long time, the mixture remains negative to the amine and the Legal reactions, and only the starting material is recovered from the mixture. When heated with 20% HCl, (XI) remains negative to the amine reaction but becomes positive to the Legal reaction, and is converted into (IX).

***d*-1-Methyl-4-acetylcyclohexanone-2 Dioxime (XII) from *d*-7-Amino-α-santenone (III)**—The dioxime is prepared from 10 g. of (III), 5 g. of $NH_2OH \cdot HCl$, 3.6 g. of Na_2CO_3, 10 cc. EtOH, and 15 cc. of water. After standing overnight in an ice-box, the product, m.p. 195~203°, is filtered and recrystallized from dil. EtOH to colorless needles, m.p. 202°, $[\alpha]_D^{19.5}$: +40.6°(4% solution in 10% NaOH solution). *Anal.* Calcd. for $C_9H_{16}O_2N_2$: C, 58.65; H, 8.76; N, 15.21. Found: C, 58.69; H, 8.72; N, 15.39. The product agrees in m.p. and optical rotation with the dioxime synthesized from *l*-carvone.

***rac*-1-Methyl-4-acetylcyclohexanone-2 (IX) from *d*-1-Methyl-4-acetylcyclohexanone-2 Dioxime (XII)**—One gram of (XII) is heated with 10 cc. of 20% H_2SO_4 for 1 hr. and the mixture, after cooling, is neutralized with K_2CO_3 and extracted with ether. The ether solution is evaporated and the residue (0.5 g.) is distilled; $b.p_{10}$ 129~130°, $[\alpha]_D^{23.0}$: 0°(3% solution in EtOH). Semicarbazone, m.p. 220~222°.

(XII) is racemized by the hydrolysis and therefore, it is impossible to obtain optically active (IX).

Ring Cleavage of 7-Hydroxy-α-santenol : i) ***d-trans*-7-Carboxy-π-apoborneol (XIV)**[3]—To a solution of 100 g. of isoketopinic acid (XIII) in 1500 cc. of abs. EtOH is added 200 g. Na in several portions. The reaction mixture is diluted with water, EtOH is removed by steam distillation, and the aq. solution, after being acidified with H_2SO_4, is extracted with ether. The ethereal solution is dried and the ether residue is recrystallized from AcOEt to colorless prisms, m.p. 275°, $[\alpha]_D^{13.5}$: +5.6° (8% solution in MeOH) (Reported, m.p. 278°; m.p. 273°, $[\alpha]_D^{20}$: +2.2°(EtOH)). Yield, 84 g.

ii) ***d-trans*-7-Carboxy-π-apoborneol Acetate (XV)**[4]—To a solution of 80 g. of (XIV) in 400 cc. pyridine is added dropwise 45 g. AcCl with cooling and stirring, and the mixture is allowed to stand overnight. The mixture is diluted with water, acidified with HCl, and extracted with ether. The ethereal solution is dried, evaporated, and the residue is recrystallized from petroleum ether in prisms, m.p. 106~107°, $[\alpha]_D^{13.5}$: +25.0°(4% solution in MeOH). Yield, 80 g.

iii) ***d-trans*-7-Chlorocarboxy-π-apoborneol Acetate (XVI)**[4]—To 65 g. of (XV) is added 130 cc. of $SOCl_2$ and the mixture is heated for 30 mins. The excess $SOCl_2$ is distilled off and the residue is distilled under a reduced pressure, $b.p_{10}$ 136°(reported, $b.p_6$ 124°). Yield, 50 g.

iv) ***d-trans*-7-Aminocarbonyl-π-apoborneol Acetate (XVII)**—To a solution of 100 g. of (XVI) in ether is added conc. NH_4OH, and the separated crystals are recrystallized from dil. EtOH in colorless plates, m.p. 190~192°, $[\alpha]_D^{13.5}$: +31.5°(4.5% solution in MeOH). *Anal.* Calcd. for $C_{12}H_{18}O_3N$: C, 64.24; H, 8.09; N, 6.25. Found : C, 64.45; H, 8.79; N, 6.45.

v) ***d-trans*-7-Methoxycarbonylamino-π-apoborneol (*d*-7-Methoxycarbonylamino-α-santenol) (XVIII)**—To a solution of 45 g. of (XVII) in MeONa solution prepared from 20 g. Na and 400 cc. MeOH is added dropwise 17 cc. of Br_2 and the mixture is heated at 50~55° for 6 hrs. After standing overnight, the reaction mixture is diluted with water, extracted with ether, and the residue of the dried ether solution is recrystallized from MeOH to colorless plates, m.p. 123~124°, $[\alpha]_D^{13.5}$: −17.0°(5% solution in MeOH). Yield, 35 g. *Anal.* Calcd. for $C_{11}H_{19}O_3N$: C, 61.92 ; H, 8.98 ; N, 6.57. Found: C, 61.65; H, 8.57; N, 6.10.

vi) ***d-trans*-7-Amino-π-apoborneol (*d*-7-Amino-α-santenol) (XIX)**—Thirty grams of (XIX) is heated with 60 cc. of 36% HCl on a water bath, further 40 cc. of the same HCl is added, and the heating is continued for additional 6 hrs., and when the mixture becomes negative to amino reaction, the mixture is made alkaline with NaOH solution, extracted with ether, and the residue of the dried ethereal solution is recrystallized from dil. EtOH to colorless plates, m.p. 217~219°, $[\alpha]_D^{13.5}$: +12.3° (4.5% solution in MeOH). *Anal.* Calcd. for $C_{11}H_{17}ON$: C, 69.62; H, 11.04; N, 9.05. Found : C, 69.86; H, 10.98; N, 9.24.

vii) **Diazotization of *d*-7-Amino-α-santenol (XIX) by HNO_2**—To a solution of 6.2 g. of (XIX) in 30% H_2SO_4 is added dropwise a solution of 3 g. $NaNO_2$ in a little water, with cooling and stirring, and after standing overnight, the mixture is heated at 70~80° for 5 hours, when it becomes positive to the Legal reaction. The reaction mixture is extracted with ether, and the residue of the dried ethereal solution is distilled under a reduced pressure, $b.p_{16}$ 130°, $[\alpha]_D^{13.5}$: 0°(5% solution in MeOH). Yield, 2 g. after redistillation. *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found : C, 68.66; H, 9.61.

Dioxime, m.p. 195°; Semicarbazone, m.p. 221~222°. *Anal.* Calcd. for $C_{11}H_{20}O_2N_6$: N, 31.34. Found: N, 31.36.

The product was identified as (IX) by admixture of its dioxime and disemicarbazone. When the impure (XIX) recovered from the reaction mixture is hydrolyzed with alkali, it becomes positive to the Legal reaction. On the other hand, from the fact that when (XIX) is warmed with dil. HNO_2 and then hydrolyzed with alkali, it also becomes positive to Legal reaction, it seems that (XIX) is first oxidized to (III) by the catalytic action of HNO_2 and then converted into (IX) by diazotization. When this reaction is conducted with excess HNO_2, the yield of (IX) is good, while the yield is very poor when the reaction is carrid out in CO_2 atmosphere.

Summary

It was confirmed qualitatively that *d*-7-amino-α-santenone (III) is an amino compound possessing a bridged bond. It was also ascertained that 7-hydroxysantenone (VII) obtained by the action of nitrous acid on (III) undergoes cleavage of the bridged bond.

d-7-Methoxycarbonylamino-α-santenol (XVIII), which is a derivative of borneol, differs from the α,β-unsaturated urethane compound in that it is hydrolyzed by hydrochloric acid to *d*-7-amino-α-santenol (XIX). This seems to mean that the change from the keto bond angle of 120° at C_2 to the hydroxyl bond angle of 109° caused decrease

in intramolecular tension, which in turn decreased the double bond-like property of the bridged bond ascribable to the tension.

(Received March 26, 1955)

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43. Morizo Ishidate,* Minoru Sekiya,** Yoshiro Osaki,*** Ichiro Kurita,*** and Yukichi Harada**: Studies on Xanthine and Related Compounds. II[1]. A New Synthesis of Xanthine from 4-Amino-5-phenylazouracil.

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A new process for the synthesis of xanthine (I), using 4-amino-5-phenylazouracil as an intermediate material, was devised and is reported in the present paper. This process was found to be valuable for an industrial preparation of xanthine.

Although 5-phenylazobarbituric acid was first prepared in 1891,[2] 4-amino-5-phenylazouracil has not been found in literature. Todd *et al.*[3] synthesized purine nucleosides starting from 5-phenylazopyrimidine, but no report has been found on the preparation of xanthine from 4-amino-5-phenylazouracil.

The new compound, 4-amino-5-phenylazouracil (II), was prepared by the following two methods: (i) 4-Aminouracil (III) coupled with phenyldiazonium chloride, and (ii) cyanoacetylurea (IV) coupled with phenyldiazonium chloride yielding phenylazocyanoacetylurea (V), which was cyclized by alkali hydroxide solution.

Phenylazocyanoacetylurea thus obtained formed yellow plates decomposing at 206~209°. If this coupling reaction was carried out in strongly alkaline medium, formazyl cyanide ($\begin{pmatrix} C_6H_5-N=\!=\!=N \\ C_6H_5-NH-N \end{pmatrix}$>C—CN) was produced as a by-product.

By coupling 4-aminouracil with phenyldiazonium chloride 4-amino-5-phenylazouracil was obtained as orange yellow needles. This was reduced giving 4,5-diaminouracil (VI) in a good yield, either by zinc (or iron) powder with dilute sulfuric acid or by hydrogenolysis in acetic acid with palladium-carbon catalyst.

4-Amino-5-phenylazouracil was partially converted into xanthine by heating with formamide.[4] In this reaction, xanthine obtained was very impure and difficult to purify, so that its yield was very poor, but by carrying out the hydrogenolysis in the presence of formamide at high pressure and temperature with Raney nickel catalyst, the yield of xanthine could be increased to about 90%. In this catalytic procedure, instead of formamide, ammonium formate was also used. For the industrial preparation of xanthine derivative, such as caffeine, the process using 4-amino-5-phenylazouracil as an intermediate is regarded as the most valuable method in the present work on this series. As reported,[1] the catalytic procedure had already been tried on 4-

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1) Part I: J. Pharm. Soc. Japan, **74**, 420 (1954).
2) Kühlung: Ber., **24**, 4141 (1891); *ibid.*, **31**, 1973 (1898).
3) Lythgoe, Todd, Topham: J. Chem. Soc., **1944**, 315; Baddiley, Lythgoe, Todd: *Ibid.*, **1944**, 318; Kenner, Lythgoe, Todd: *Ibid.*, **1944**, 652.
4) A similar reaction to 4-iminovioluric acid has already been reported (cf. Footnote 1).