von 5 g. Diese wurde mit 320 ml Florisil (60～100 mesh) chromatographiert und ergab Triacanthin (I). Ausbeute: 15 mg (0.0001%).

iii) **Aus den luftgetrockneten Früchten**——10 kg luftgetrocknete Früchte (die auf dem Markt als Drogen verkauft werden) wurden zerschnitten und dreimal mit 40 L MeOH je 6 Std. unter Rückfluß extrahiert. Der MeOH-Extrakt wurde im Vakuum eingedampft. Ein hierbei erhaltener Rückstand von 1.34 kg wurde in 7.5 L MeOH gelöst. Dazu wurden 9 L Et_2O gegeben. Es schied sich ein rotbrauner Niederschlag aus. Dieser wurde möglichst schnell abgesaugt und getrocknet. Er enthielt eine große Menge Saponin (1.07 kg, 10.7%). Das Filtrat wurde im Vakuum eingedampft und ergab einen Rückstand von 310 g. Der letztere wurde in 1.4 L 3% HCl und 700 ml Essigester aufgenommen. Nach dem Alkalisieren mit Na_2CO_3 wurde die HCl-Phase mit 700 ml $CHCl_3$ extrahiert. Die $CHCl_3$-Lösung ergab nach dem Trocknen über Na_2SO_4 und dem Eindampfen im Vakuum eine Rohalkaloidmenge von 1.13 g. Diese Rohalkaloide wurden mit 300 ml Florisil (60～100 mesh) chromatographiert. Die mit Benzol-EtOH (8:2) eluierten Fraktionen ergaben Triacanthin (I). Ausbeute: 50 mg (0.0005%).

Triacanthin Pikrat——Gelbe Nadeln (aus MeOH), Zers. Pkt. 245～248°, $C_{16}H_{16}O_7N_8$—Ber.: C, 44.45; H, 3.73; N, 25.92. Gef.: C, 44.49; H, 3.78; N, 25.83.

Triacanthin Hydrochlorid——Farblose Nadeln (aus EtOH), Zers. Pkt. 234°.

Triacanthin Nitrat——Farblose Nadeln (aus EtOH), Zers. Pkt. 162°.

Die Autoren möchten Herrn Prof. Dr. Leonard (Department of Chemistry and Chemical Engineering, University of Illinois) für seine freundliche Schenkung einer authentischen Probe von Triacanthin ihren Dank aussprechen. Ferner sind die Autoren Herrn M. Togashi in diesem Institut für das Sammeln der Ausgangsmaterialien, Herrn N. Matsumoto in diesem Laboratorium für seine Mithilfe und den Damen und Herren, die die Elementaranalysen und die Messung der physikalischen Konstanten durchgeführt haben, sehr dankbar.

Zusammenfassung

In *Gleditschia horrida* MAKINO (皂莢) wurde ein Alkaloid, das Triacanthin (I), gefunden. Die Ausbeute betrug, bezogen auf die getrockneten Ausgangsmaterialien: 0.01% aus Blättern, 0.0001% aus der Rinde und 0.0005% aus luftgetrockneten Früchten (der auf dem Markt verkauften Drogen).

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Tetsuji Kametani and Keiichiro Fukumoto: Cularine and Related Compounds. IV.[*2] The Oximation and Reduction of 2,3,6-Trimethoxydibenzo[*b*,*f*]oxepin-10(11*H*)-one.[*3]

(*Pharmaceutical Institute, School of Medicine, Tohoku University*[*1])

10-Amino-2,3,6-trimethoxy-10,11-dihydrodibenzo[*b*,*f*]oxepine (I) was synthesized by the Leuckart reaction[1] but its yield was not so good that the oximation as well as the reaction of the ketone (II) was investigated.

An alternate method for the preparation of the amine (I) was elaborated through reduction of oxime of the ketone (II).[2] The latter reacted with hydroxylamine

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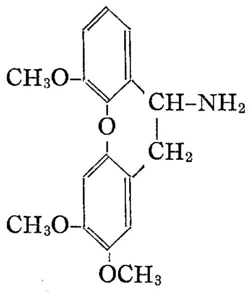
[*1] No. 85, Kita-4-bancho, Sendai (亀谷哲治, 福本圭一郎).

[*2] Part III. T. Kametani, K. Fukumoto: Chem. & Ind. (London), **1963**, 291.

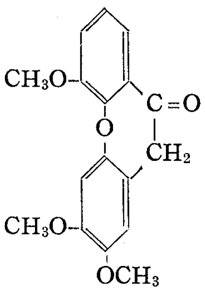
[*3] This forms Part (LXXXIII) of "Studies on the Syntheses of Heterocyclic Compounds" by Tetsuji Kametani.

1) T. Kametani, K. Fukumoto: J. Chem. Soc., to be published.

2) T. Kametani, K. Fukumoto, T. Nakano: Yakugaku Zasshi, **82**, 1307 (1962).

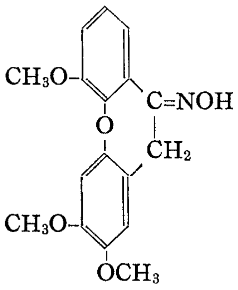


I

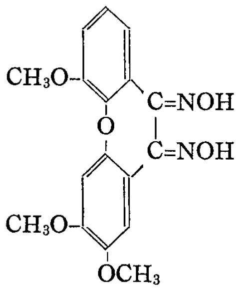


II

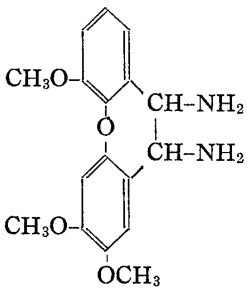
hydrochloride only in the presence of pyridine, but the product was proved to be a mixture of at least three compounds. Through chromatography they were separated and it was revealed that the aimed monooxime (III) was formed only in such a minute amount that its further reduction was impossible.*[4] Two other compounds were designated as IV and V, the latter of which was proved to be the dioxime, because on reduction it yielded the diamine (VI), and both V and VI gave satisfactory analytical data. The structure of II still remains obsecure.



III



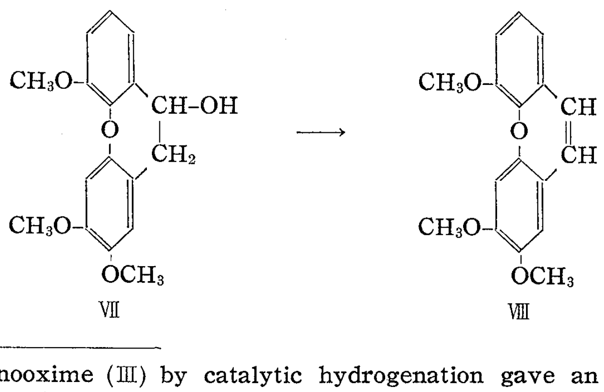
V



VI

Catalytic hydrogenation of the ketone (II) in the presence of Adams catalyst in acetic acid gave the carbinol (VII), m.p. 167°, accompanied by a small amount of the starting material.

When the carbinol (VII) was heated with *p*-toluenesulfonic acid at 120~140° for 10 minutes, VII was dehydrated and yielded yellow needles (VIII), m.p. 115~116.5°, which showed the presence of a double bond by the potassium permanganate test. Infrared spectrum of the latter showed absorption bands of CH stretching at 3012 cm^{-1}, phenyl conjugated C=C stretching vibration at 1620 cm^{-1}, and CH out-of-plane deformation at 720 cm^{-1} which is attributed to the *cis*-CH=CH, and absorption at 3530 cm^{-1} (OH) originally



VII VIII

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*[4] Reduction of the monooxime (III) by catalytic hydrogenation gave an yellowish, amorphous compound, m.p. 147~159°, which had an IR absorption band of NH group at 3333 cm^{-1}, but its purification was so difficult that the preparation of I from III was given up.

present in VII disappeared. It has been shown[3] that the reduction of dibenzo[*b,f*]oxepin-10(11*H*)-one to the corresponding carbinol was readily achieved by heating it with aluminum isopropoxide in isopropyl alcohol, and quantitatively dehydrated to oxepine ring when warmed with *p*-toluenesulfonic acid.

Experimental[*5]

The Reaction of the Ketone (II) with Hydroxylamine——4.5 g. of $NH_2OH\cdot HCl$ was added to a solution of 4.5 g. of the ketone (II) in 22.5 ml. of pyridine and the mixture was refluxed in an oil bath for 5 hr. The solution became reddish-brown. The reaction mixture was poured into a large amount of H_2O and the reddish-pink oil that separated was extracted with $CHCl_3$. The $CHCl_3$ extract was washed successively with H_2O, 10% HCl, and H_2O, dried (Na_2SO_4), and the solvent was evaporated. Chromatography of the residue with $CHCl_3$ gave three fractions. The first fraction gave the monooxime (III) as pale yellow crystals (1.6 g.), which were recrystallized from EtOH to pale yellow cubes, m.p. 147° (sublimes at 150°). *Anal.* Calcd. for $C_{17}H_{17}O_5N$: N, 4.44. Found : N, 4.27.

The second fraction gave 0.7 g. of a pale orange powder (IV), which formed colorless needles, m.p. 218° (decomp.) (Found : C, 62.76; H, 4.45; N, 6.65), whose structure has not been elucidated.

The last fraction gave 0.1 g. of a brown, amorphous substance, m.p. 100°, which was assumed to be the dioxime (V). IR : ν_{max}^{KBr} 1622 cm^{-1} (C=N).

Since purification of this compound was accompanied with great difficulty it was reduced without purification. This substance was also separated from the other compounds by treatment of the mixture with dioxane, in which only this was soluble.

Catalytic Hydrogenation——The above compound (V) (0.9 g.) in 25 ml. of dioxane was hydrogenated with H_2 over Adams Pt (231.3 mg.), 45 ml. of H_2 being absorbed. To complete the hydrogenation a mixture of 200 mg. of $PdCl_2$, 2 ml. of conc. HCl, and 15 ml. of dioxane was added and additional 132 ml. of H_2 was taken up. Concentration of the filtrate from the catalyst gave a dark brown, viscous oily residue, which was extracted with $CHCl_3$. The $CHCl_3$ extract was again extracted with 10% HCl, the acid solution was basified with 10% NH_4OH, and extracted with benzene. The benzene extract was washed with H_2O and dried (Na_2SO_4). Removal of the solvent gave 0.2 g. of a dark green, resinous substance, m.p. 98~102° (decomp.). Recrystallization from benzene-petr. ether afforded the diamine (VI) as a dark green powder, m.p. 117°. *Anal.* Calcd. for $C_{19}H_{20}O_4N_2\cdot\frac{1}{2}H_2O$: C, 62.85; H, 6.51. Found: C, 62.75; H, 6.31.

Lithium Aluminum Hydride Reduction——A solution of 1 g. of V dissolved in 40 ml. of dioxane was added to a stirred suspension of 0.4 g. of $LiAlH_4$ in 20 ml. of dioxane at 18° during 35 min. and the mixture was stirred at room temperature for additional 3 hr. After being allowed to stand overnight, it was decomposed with moist Et_2O and then H_2O. An insoluble substance was filtered off, the orange brown filtrate was evaporated to dryness in a reduced pressure, and ca. 1 g. of the residue was extracted with 10% HCl. The acid solution was basified with 10% NaOH, extracted with benzene, and the extract was washed with H_2O and dried (K_2CO_3). Removal of the solvent gave a viscous oil, which solidified on triturating with petr. ether, forming 0.1 g. of powder, m.p. 96~104° (decomp.). Recrystallization from benzene-petr. ether gave the same diamine (VI) mentioned above as a dark green powder.

2,3,6-Trimethoxy-10,11-dihydrodibenzo[*b,f*]oxepin-10-ol (VII) (Catalytic Hydrogenation of the Ketone (II))——A Solution of 1.5 g. of the ketone (II) in 40 ml. of AcOH was catalytically reduced over 117.9 mg. of Adams Pt and 120 ml. of H_2 was absorbed in 5 hr., during which time the red solution became yellow. The catalyst was filtered off and the solvent was evaporated. Recrystallization of the residue from EtOH gave colorless needles (VII), m.p. 167°. *Anal.* Calcd. for $C_{17}H_{18}O_6$: C, 67.54; H, 6.00. Found: C, 66.91; H, 5.91.

2,3,6-Trimethoxydibenzo[*b,f*]oxepine (VIII)——A mixture of 2.8 g. of the carbinol (VII) and 3.8 g. of *p*-toluenesulfonic acid was heated at 115° for a while, to give a reddish pink substance. This was then heated at 140° for 10 min. and decomposed with 100 ml. of H_2O after being cooled. The resultant solution was extracted with $CHCl_3$, the extract was washed with 10% Na_2CO_3 solution and H_2O, dried (Na_2SO_4), and the solvent was removed. The residue was purified by chromatography (benzene used as a solvent) to give yellow needles, m.p. 109°. Recrystallization from MeOH afforded the oxepin derivative (VIII) as pale yellow needles, m.p. 115~116.5°. *Anal.* Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found : C, 71.74; H. 6.43.

[*5] All melting points are uncorrected. Infrared spectra were measured with a Model EPI-2 Hitachi Infrared Spectrophotometer.

3) R. H. F. Manske, A. E. Ledingham : J. Am. Chem. Soc., **72**, 4797 (1950).

Thanks are due to Miss H. Miyaji for microanalyses and to Miss S. Oizumi for Infrared spectral measurement.

Summary

Oximination of 2,3,6-trimethoxydibenzo[*b,f*]oxepin-10(11*H*)-one (II) yielded three compounds, among which mono- and di-oximes were elucidated. Catalytic hydrogenation of the ketone (II) in the presence of Adams catalyst in acetic acid gave the carbinol (VII), m.p. 167°, accompanied by a small amount of the starting material. When the carbinol (VII) was heated with *p*-toluenesulfonic acid at 120~140° for 10 minutes, VII was dehydrated and yielded yellow needles (VIII), m.p. 115~116.5°.

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