

Notes

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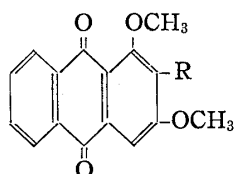
Yoshio Hirose, Haruko Ueno, Motoko Iwashita, and Eiko Kawagishi*¹ :Studies on the Synthesis of Munjistin. II.¹⁾

Synthesis of 3-O-Methyldamnacanthal.

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In the previous paper,^{1,2)} it was reported that demnacanthal(1-methoxy-3-hydroxy-2-anthraquinonecarboxaldehyde) (I) was synthesized from damnacanthol(1-methoxy-2-hydroxymethyl-3-hydroxyanthraquinone) (II), and that nor-damnacanthal(1,3-dihydroxy-2-anthraquinonecarboxaldehyde) (III) and munjistin(1,3-dihydroxy-2-anthraquinonecarboxylic acid) (IV) were synthesized directly from lucidin(2-hydroxymethyl-1,3-dihydroxyanthraquinone) (V). 3-O-Methyldamnacanthal (VI), m.p. 185~186° was obtained as a pre-step product en route to 1,3-O-dimethylmunjistin (VII),*² though the melting point of VI was reported to be 125° VIII,³⁾ prepared from I by the methylation with dimethyl sulfate and potassium carbonate in acetone. It is therefore the purpose of this paper to ascertain the melting point of VI which was shown at 185~186°.

When lucidin (V)^{4,5)} was repeatedly dissolved in 90% ethanol and either concentrated or refluxed for 6 hours, the substance of m.p. 180°(decomp.) was obtained. Since the substance of m.p. 180°(decomp.) could be synthesized to 2- ω -O-ethyl-1,3-O-dimethyl lucidin (IX),⁵⁾ m.p. 141~142°, which was derived from 2- ω -O-ethyl-3-O-methyl lucidin,⁵⁾ the structure of substance, m.p. 180°(decomp.), should be indicated to be 2- ω -O-ethyl lucidin (X). V was refluxed in acetic acid solution to afford its alcoholic acetate, 2- ω -O-acetyl lucidin (XI), m.p. >300°(decomp.), which was confirmed by methylation to 2- ω -O-acetyl-1,3-O-dimethyl lucidin (XII), m.p. 173~174° as reported in the literature.⁵⁾



VI : R = -CHO

XVI : R = -CH₂OH

On selective acetylation by means of boro-triacetate and acetic anhydride, V gave 2- ω ,3-O-diacetyl lucidin (XIII), m.p. 152~153°, which was also confirmed by methylation to 1-O-methyl-2- ω ,3-O-diacetyl lucidin (XIV), m.p. 156~157°, as reported in the literature.²⁾ On the other hand, V gave XIII directly by the treatment with acetic anhydride. V was methylated directly to lucidin trimethyl ether (XV), m.p. 162°, which was confirmed to be identical with 2-methoxymethyl-1,3-dimethoxyanthraquinone, prepared from II.²⁾ It was reported that XIII gave 1,3-O-dimethyl lucidin (XVI), m.p. 175°,^{4,5)} on hydrolysis with 3% methanolic sulfuric acid. On oxidation with active manganese dioxide,²⁾ XVI gave 3-O-methyldamnacanthal (VI), m.p. 185~186°. Treatment of I by the method described in the literature³⁾ also afforded VI as a sole product. Infrared spectrum of VI in Nujol

*¹ Oe-Machi, Kumamoto (広瀬良男, 上野治子, 岩下素子, 河岸栄子).*² Unpublished work.

1) Part. I. Y. Hirose : This Bulletin, 10, 985 (1962).

2) Y. Hirose : *Ibid.*, 8, 417 (1960).3) S. Nonomura : *Ibid.*, 5, 366 (1957).

4) L.H. Briggs, G.A. Nicholls : J. Chem. Soc., 1949, 1241, 1246.

5) B.S. Joshi, N. Parkash, K. Venkataraman : J. Sci. Ind. Research (India), 14B, 87 (1955).

mull showed the presence of aldehyde absorption at 1704 cm^{-1} , and the corresponding absorption to the literature³⁾ was not observed at $1700\sim 1710\text{ cm}^{-1}$ region assigned to C=O stretchings in free aldehyde.

Experimental

2- ω -O-Ethyllucidin (X)—V (0.2 g.) was refluxed in 90% EtOH (100 ml.) for 6 hr. The solution was concentrated to separate crystalline solid which was repeatedly recrystallized from EtOH to pale yellow needles of m.p. 180° (decomp.). Its paper chromatogram using filter paper, Toyo Roshi No. 50, and BuOH saturated with 28% NH_4OH as a developing solvent showed Rf. 0.84. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_5$: C, 68.45; H, 4.73. Found: C, 68.88; H, 4.32.

2- ω -O-Ethyl-1,3-O-dimethylucidin (IX)—It was prepared from X by usual way, m.p. $141\sim 142^\circ$. The identity of IX with that described in the literature⁵⁾ was established m.p. determination by admixture. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_5$: C, 69.92; H, 5.56. Found: C, 70.04; H, 5.62.

2- ω -O-Acetyllucidin (XI)—V (0.6 g.) was refluxed in AcOH (60 ml.) for 1 hr. The solution was concentrated to separate crystalline solid which was repeatedly recrystallized from AcOH together with charcoal to yellow needles of m.p. $>300^\circ$ (decomp.). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_6$: C, 65.38; H, 3.87. Found: C, 65.45; H, 3.81. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 3370 (OH), 1730 (alcoholic acetate), 1663 (non-chelated C=O), 1638 (chelated C=O), 1600 and 1588 (phenyl).

2- ω -O-Acetyl-1,3-O-dimethylucidin (XII)—A mixture of XI (1.2 g.), Ag_2O (6 g.), CH_3I (5 ml.) and Me_2CO (80 ml.) was refluxed for 10 hr. Recrystallization from EtOH in the presence of charcoal, afforded pale yellow needles of m.p. $173\sim 174^\circ$, which was identified by mixed melting point, IR spectrum with that prepared by the method of Venkataraman⁵⁾ from 2-bromorubiadin dimethyl ether. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_6$: C, 67.05; H, 4.75. Found: C, 67.29; H, 4.45. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 1728 (alcoholic acetate), 1674 (non-chelated C=O), 1583 (phenyl).

2- ω ,3-O-Diacetyllucidin (XIII)—i) A mixture of V (1 g.), boroacetic anhydride (2.5 g.) and Ac_2O (10 ml.) was refluxed for 10 min. The crystalline precipitate separated after cooling was digested in H_2O . The resulted precipitate was recrystallized from dil. AcOH to yellow needles of m.p. $151\sim 153^\circ$. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_7$: C, 64.40; H, 3.98. Found: C, 64.05; H, 4.24.

ii) A mixture of V (0.3 g.) and Ac_2O (30 ml.) was refluxed for 1 hr., and poured into H_2O . The precipitate separated was recrystallized from dil. AcOH together with charcoal to yellow needles of m.p. $151\sim 153^\circ$, which showed no depression by mixed melting point with that described above. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_7$: C, 64.40; H, 3.98. Found: C, 64.80; H, 4.01.

1-O-Methyl-2- ω ,3-O-diacetyllucidin (XIV)—A mixture of XIII (0.5 g.), Ag_2O (2.5 g.), CH_3I (3 ml.) and Me_2CO (60 ml.) was refluxed for 10 hr. Recrystallization from MeOH added with charcoal afforded pale yellow needles of m.p. $156\sim 157^\circ$, which was established by mixed m.p. determination with an authentic sample.²⁾

Lucidin Trimethyl Ether (XV)—A mixture of V (0.5 g.), Me_2SO_4 (2.5 g.), K_2CO_3 (10 g.) and Me_2CO (100 ml.) was refluxed for 20 hr. Recrystallization from MeOH afforded pale yellow needles of m.p. 162° , which was established by mixed m.p. determination with an authentic sample.²⁾

3-O-Methyldamnacanthal (VI)—i) A mixture of XVI (0.5 g.), active MnO_2 (2.5 g.) and AcOEt (150 ml.) was refluxed for 0.5 hr. Recrystallization from Me_2CO with charcoal afforded pale yellow needles of m.p. $185\sim 186^\circ$. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_5$: C, 68.91; H, 4.08. Found: C, 69.14; H, 4.40. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 1704 (Aryl-CHO), 1676 and 1663 (non-chelated C=O), 1580 (phenyl).

ii) I was methylated with either Me_2SO_4 , K_2CO_3 and Me_2CO or Ag_2O , MeI and Me_2CO . The product was recrystallized from Me_2CO to yellow needles of m.p. $185\sim 186^\circ$, the identity of which with that described above was established by a mixed m.p. determination and IR spectra in Nujol. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_5$: C, 68.91; H, 4.08. Found: C, 69.04; H, 3.99.

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Summary

Synthesis of 3-O-methyldamnacanthal (VI), m.p. $185\sim 186^\circ$, was described.

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