Notes

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Studies on the Synthesis of Munjistin. II.[1)]
Synthesis of 3-O-Methyldamnacanthal.

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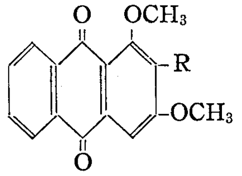
In the previous paper,[1,2)] it was reported that demnacanthal(1-methoxy-3-hydroxy-2-anthraquinonecarboxaldehyde) (I) was synthesized from damnacanthol (1-methoxy-2-hydroxymethyl-3-hydroxyanthraquinone) (II), and that nor-damnacanthal(1,3-dihydroxy-2-anthraquinonecarboxaldehyde) (III) and munjistin (1,3-dihydroxy-2-anthraquinonecarboxylic 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 substane of m.p. 180° (decomp.) could be synthesized to 2-ω-O-ethyl-1,3-O-dimethyllucidin (IX),[5)] m.p. 141∼142°, which was derived from 2-ω-O-ethyl-3-O-methyllucidin,[5)] the structure of substance, m.p. 180° (decomp.), should be indicated to be 2-ω-O-ethyllucidin (X). V was refluxed in acetic acid solution to afford its alcoholic acetate, 2-ω-O-acetyllucidin (XI), m.p. >300° (decomp.), which was confirmed by methylation to 2-ω-O-acetyl-1,3-O-dimethyllucidin (XII), m.p. 173∼174° as reported in the literature.[5)]



VI : R= -CHO
XVI : R= $-CH_2OH$

On selective acetylation by means of boro-triacetate and acetic anhydride, V gave 2-ω,3-O-diacetyllucidin (XIII), m.p. 152∼153°, which was also confirmed by methylation to 1-O-methyl-2-ω,3-O-diacetyllucidin (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, perpared from II.[2)] It was reported that XII gave 1,3-O-dimethyllucidin (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 literature[3)] also afforded VI as a sole product. Infrared spectrum of VI in Nujol

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[*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 literature[3] was not observed at 1700~1710 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 $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.88; H, 4.32.

2-ω-O-Ethyl-1,3-O-dimethyllucidin (IX)——It was prepared from X by usual way, m.p. 141~142°. The identity of IX with that described in the literature[5] was established m.p. determination by admixture. *Anal.* Calcd. for $C_{19}H_{18}O_5$: 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° (decomp.). *Anal.* Calcd. for $C_{17}H_{12}O_6$: C, 65.38; H, 3.87. Found: C, 65.45; H, 3.81. IR $\nu_{\max}^{\text{Nujol}}$ 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-dimethyllucidin (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. 173~174°, which was identified by mixed melting point, IR spectrum with that prepared by the method of Venkataraman[5] from 2-bromorubiadin dimethyl ether. *Anal.* Calcd. for $C_{19}H_{16}O_6$: C, 67.05; H, 4.75. Found: C, 67.29; H, 4.45. IR $\nu_{\max}^{\text{Nujol}}$ 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. 151~153°. *Anal.* Calcd. for $C_{19}H_{14}O_7$: 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 seperated was recrystallized from dil. AcOH together with charcoal to yellow needles of m.p. 151~153°, which showed no depression by mixed melting point with that described above. *Anal.* Calcd. for $C_{19}H_{14}O_7$: 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 yellowneedles of m.p. 156~157°, 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. 185~186°. *Anal.* Calcd. for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08. Found: C, 69.14; H, 4.40. IR $\nu_{\max}^{\text{Nujol}}$ 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. 185~186°, the identity of which with that described above was established by a mixed m.p. determination and IR spectra in Nujol. *Anal.* Calcd. for $C_{17}H_{12}O_5$: 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. 185~186°, was described.

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