Notes

UDC 581.13:582.288

Yoshio Hirose: Studies on the Syntheses of Munjistin. I.[1]

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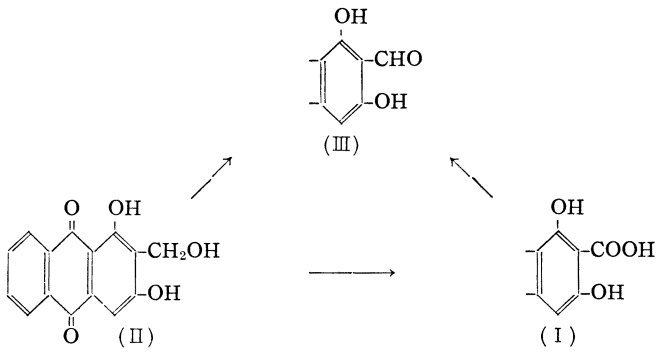
In the previous communication synthesis of munjistin (I)[2] had been reported. Thereafter, Venkataraman *et al.*[3] reported that by oxidation with silver oxide (1 mole) and 6.8% aqueous sodium hydroxide (10 moles) at 75° for 1 hour lucidin (II)[4] (1 mole) yielded munjistin in a yield of 35~40%. In order to confirm by mixed fusion with munjistin[2] (I) obtained from pseudopurpurin, synthesis of munjistin (I) according to the method reported by Venkataraman was attempted. However, contrary to expectation, it was found that lucidin (II) did not always undergo oxidation to form munjistin (I) but nor-damnacanthal[2] (III) principally.

The present paper deals with the investigation on the reaction products of lucidin (II). As the results it was clarified that i) by oxidation under the same condition with the method of Venkataraman[3] lucidin (II) yielded nor-damnacanthal (III) in a yield of 37%; ii) employing 2 moles of silver oxide lucidin (II) yielded munjistin (I) in a yield of 35%; iii) by the same procedure of i) nor-damnacanthal (III) yielded munjistin (I) in a yield of 44%. Munjistin (I) m.p. 232~233°, obtained by two methods described as above and specimen derived from natural damnacanthal[2] were identified each other.



Experimental

Nor-damnacanthal (1,3-Dihydroxy-2-formylanthraquinone) (III)——A solution of lucidin (II) (0.27 g.) (0.001 mole) with Ag_2O freshly prepared from $AgNO_3$ (0.34 g.) (0.002 mole), NaOH (0.4 g.) (0.01 mole) and water (6 cc.) was stirred at 75° for 1 hr. The reaction mixture was filtered and washed with water. The filtrate was acidified with 3% HCl. The depositing precipitate was filtered, washed with water and then the moistened residue was dissolved in benzene, shaken with 1% $NaHCO_3$ (10 cc.), whereby munjistin was obtained in a small amount in the contaminated state, washed with water and the solvent was distilled off. The residue was recrystallized from dil. Me_2CO to yellow needles, constant melting point 221~222° (m.p. 218°,[5] m.p. 220°[3] recorded in the literature), whereby lucidin (II) dis solved in the solvent. Yield was 0.1 g. (37%) as the analytical sample. IR ν_{max}^{Nujol} cm^{-1}: 1678

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1) Y. Hirose: This Bulletin, 8, 417 (1960).
2) S. Nonomura, Y. Hirose: Yakugaku Zasshi, **75**, 1305 (1955).
3) N.R. Ayyanger, K. Venkataraman: J. Sci. Ind. Research (India), **15B**, 359 (1956).
4) L.H. Briggs, G.A. Nicholls: J. Chem. Soc., **1949**, 1241, 1246.
5) S. Nonomura: Yakugaku Zasshi, **75**, 221 (1955).

(non chelated quinone >C=O), 1648 (-CHO chelated to 3-OH), 1634 (chelated quinone >C=O), 1600 and 1582 (phenyl). [lucidin, IR ν_{max}^{Nujol} cm^{-1}: 3475 (-OH), 1667 (non-chelated >C=O), 1618 (chelated >C=O), 1595(phenyl); lit.[6] 3448 and 3367 (broad) (-OH), 1667 (non-chelated >C=O), 1618 (chelated >C=O)] *Anal.* Calcd. for $C_{15}H_8O_5$: C, 67.17; H, 3.01. Found: C, 66.96; H, 3.15.

Munjistin(1,3-Dihydroxy-2-anthraquinonecarboxylic Acid) (I)——i) A solution of lucidin (II) (0.27 g.) (0.001 mole) with Ag_2O freshly prepared from $AgNO_3$ (0.68 g.) (0.004 mole), NaOH (0.4 g.) (0.01 mole) and water (6 cc.) was stirred at 75° for 1 hr. After treating with the usual way recorded by Venkataraman,[3] (I) was recrystallized from aq. Me_2CO to form bright brownish yellow needles, constant m.p. 232~233°. (m.p. 232°, sint. 228°, reported in the literature[3]). Yield was 0.1 g. as the analytical sample, 35%. IR ν_{max}^{Nujol} cm^{-1}: 3250 and 3080 (-OH), 1704 (-COO), 1680 (non-chelated >C=O), 1631 (chelated >C=O), 1597 and 1582 (phenyl). *Anal.* Calcd. for $C_{15}H_8O_6$: C, 63.39; H, 2.84. Found: C, 63.57; H, 2.99.

ii) A solution of nor-damnacanthal (III) (0.27 g.) (0.001 mole) with Ag_2O freshly prepared from $AgNO_3$ (0.34 g.) (0.001 mole), NaOH (0.4 g.) (0.01 mole) and water (6 cc.) was worked up as the above manner. This product, m.p. 232~233°, was identified with foregoing product by mixed melting point and IR spectra. Yield was 0.12 g., 44%. *Anal.* Calcd. for $C_{15}H_8O_6$: C, 63.39; H, 2.84. Found: C, 63.64; H, 3.06.

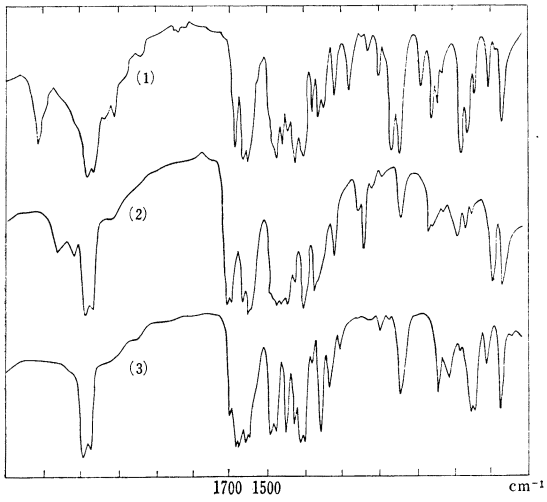

Fig. 1.
Infrared Absorption Spectra (Nujol)

(1) Lucidin
(2) Munjistin
(3) Nor-damnacanthal

(Received June 13, 1961)

6) L.H. Briggs: J. Chem. Soc., **1953**, 3068.