

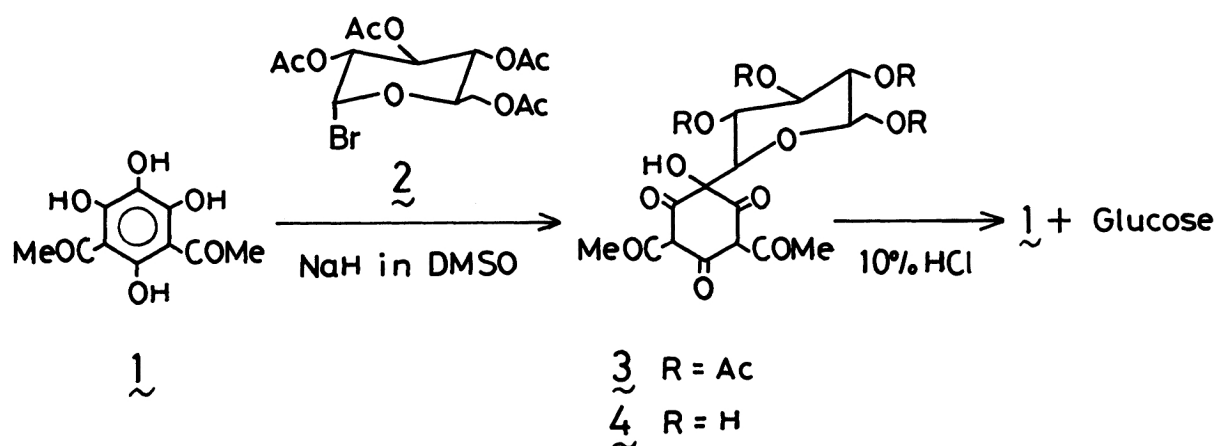
SYNTHESIS OF 2,6-DIACETYL-4-C-(β -D-GLUCOPYRANOSYL)-4-HYDROXYCYCLOHEXANE-1,3,5-TRIONE AND ITS ACID HYDROLYSIS

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2,6-Diacetyl-4-C-(β -D-glucopyranosyl)-4-hydroxycyclohexane-1,3,5-trione was obtained by the deacetylation of 2,6-diacetyl-4-C-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyl)-4-hydroxycyclohexane-1,3,5-trione which prepared by the C-glucosylation of 2,6-diacetyl-1,3,4,5-benzenetetrol with 2,3,4,6-tetra-O-acetyl- α -D-glucopyranosyl bromide. The acid hydrolysis of this new C-glucoside was investigated.

Carthamin, the red coloring matter of the flowers of Safflower (*Carthamus tinctorius* L.), is hydrolyzed with dilute mineral acid to give two flavanones, carthamidin and isocarthamidin, and glucose in spite of a C-glucoside structure.¹⁾ We have previously reported that the elimination of glucose from carthamin is due to its specific pseudoquinol C-glucoside structure.²⁾ In this communication, we wish to report the synthesis of 2,6-diacetyl-4-C-(β -D-glucopyranosyl)-4-hydroxycyclohexane-1,3,5-trione (4)³⁾ as a model compound of the partial structure of carthamin, and acid hydrolysis of this novel C-glucoside.



To a solution of 2,6-diacetyl-1,3,4,5-benzenetetrol (1)⁴⁾ (4.52 g) and sodium hydride (1.68 g) in dimethyl sulfoxide (80 ml) was added 2,3,4,6-tetra-O-acetyl- α -D-glucopyranosyl bromide (2) (8.8 g) under cooling with cold water. After 3 h, the reaction mixture was poured into cold dilute acetic acid and extracted with ethyl acetate. The reaction product was chromatographed on silica gel (Wkogel C-200) using carbon tetrachloride-ethyl acetate-acetic acid (6:3:1) as an eluent to give 2,6-diacetyl-4-C-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyl)-4-hydroxycyclo-

hexane-1,3,5-trione (3) (1.4 g, 12.5%), mp 184-185 °C, UV max (EtOH) 231, 263, and 308 nm (ϵ = 12600, 12700, and 14400), IR (KBr) 3450, 1760, 1600, and 1230 cm^{-1} , $^1\text{H-NMR}$ (CDCl_3) δ 1.87, 1.90, 1.96, and 1.97 (each 3H, s, $\text{OCOCH}_3 \times 4$), 2.58 and 2.67 (each 3H, s, $\text{COCH}_3 \times 2$), 3.4-5.6 (7H, m), 4.26 (1H, s, $\text{C}_4\text{-OH}$), 18.51 (s, chelated OH), $^{13}\text{C-NMR}$ (pyridine- d_5) δ 195.9, 195.4, 193.7, 191.3, 187.6, 170.7, 170.6, 170.2, 170.1, 106.9, 105.6, and 86.2 (each s), 83.9, 76.5, 75.9, 69.4, and 69.1 (each d), 63.4 (t), 31.5, 29.1, 21.7, 21.0, 20.9, and 20.8 (each q), MS m/z 556 (M^+). Deacetylation of 3 with sodium methoxide in methanol gave the desired compound, 2,6-diacetyl-4-C-(β -D-glucopyranosyl)-4-hydroxycyclohexane-1,3,5-trione (4), mp 168-169 °C, in a 70% yield. $^{13}\text{C-NMR}$ ($\text{DMSO}-d_6$) δ 193.9, 193.6, 193.2, 191.9, 188.4, 108.2, 106.9, and 85.9 (each s), 83.9, 80.4, 78.0, 69.3, and 69.1 (each d), 60.7 (t), 24.2 (q).

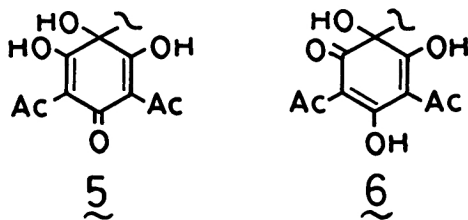
The C-glucoside structure of 3 or 4 was confirmed from the $^{13}\text{C-NMR}$ spectra of their glucosyl groups.⁵⁾ The large coupling constant (10 Hz) of 1-proton in the $^1\text{H-NMR}$ spectrum (pyridine- d_5) of 3 confirms the β -configuration of the C-glucosyl bond. Further, the characteristic enol proton signal of 3 observed in the very low field at 18.51 ppm strongly supports the enolized β -triketone structure as carthamin²⁾ and other analogs.⁶⁾

The riddle of the hydrolysis of carthamin described at the beginning was clearly solved by the acid hydrolysis of 4, that is, 4 was hydrolyzed with 10% hydrochloric acid to give 1 and glucose in spite of its C-glucoside structure.⁷⁾ In the above glucosylation of 1, no O-glucoside has been isolated.

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References

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- 3) The bis-enol structures, 5 or 6, are assumed for these triketones, 3 or 4, from their spectral data.



- 4) This compound (mp 234-235 °C) was obtained by the C-acetylation of 1,2,3,5-benzenetetrol with boron trifluoride-acetic acid complex.
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- 7) A small amount of 2,3,4,6-tetrahydroxyacetophenone was also obtained in this hydrolysis.

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