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

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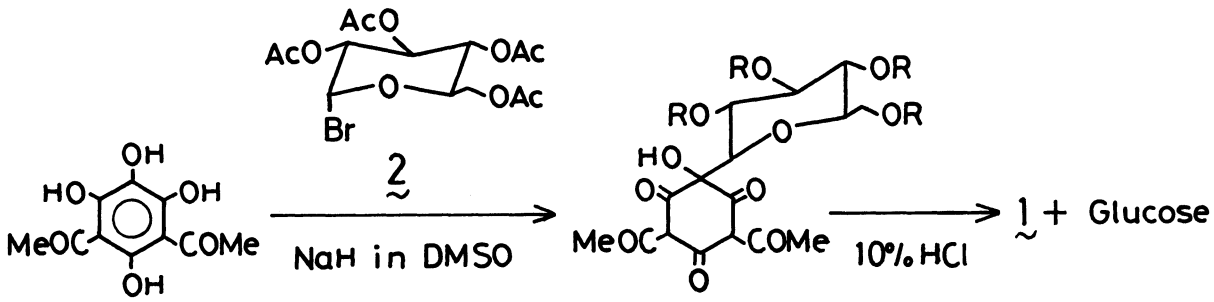
2,6-Diacetyl-4-C-(β-D-glucopyranosyl)-4-hydroxycyclohexane-1,3,5-trione was obtained by the deacetylation of 2,6-diacetyl-4-C-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-4-hydroxycyclohexane-1,3,5-trione which prepared by the C-glucosylation of 2,6-diacetyl-1,3,4,5-benzenetetrol with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl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



1

3 R = Ac

4 R = H

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}H-NMR ($CDCl_3$) δ 1.87, 1.90, 1.96, and 1.97 (each 3H, s, $OCOCH_3$×4), 2.58 and 2.67 (each 3H, s, $COCH_3$×2), 3.4-5.6 (7H, m), 4.26 (1H, s, C_4-OH), 18.51 (s, chelated OH), ^{13}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}C-NMR (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}C-NMR spectra of their glucosyl groups.[5] The large coupling constant (10 Hz) of 1-proton in the ^{1}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 carthamin[2] and other analogs.[6]

The riddle of the hydrolysis of carthamin described at the biggining 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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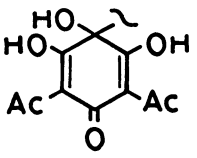
References

1) C. Kuroda, Nippon Kagaku Zasshi, 51, 237 (1930); C. Kuroda, J. Chem. Soc., 1930, 752, H. Obara, J. Onodera, and F. Yamamoto, Chem. Lett., 1973, 915.
2) H. Obara and J. Onodera, Chem. Lett., 1979, 201.
3) The bis-enol structures, 5 or 6, are assumed for these triketones, 3 or 4, from their spectral data.



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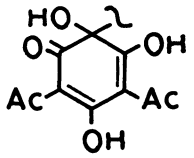

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4) This compound (mp 234-235 °C) was obtained by the C-acetylation of 1,2,3,5-benzenetetrol with boron trifluoride-acetic acid complex.
5) K. R. Markham and V. M. Chari, "Carbon-13 NMR Spectroscopy of Flavonoids," in "The Flavonoids: Advances in Research," ed by J. B. Harborne and T. J. Mabry, Chapman and Hall Ltd., London and New York (1982), p. 45.
6) S. Forsen and M. Nilsson, Acta Chem. Scand., 13, 1383 (1959); S. Forsen, M. Nilsson, and C. A. Wachtmeister, ibid., 16, 583 (1962); D. De. Keukeleile and M. Verzele, Tetrahedron, 26, 385 (1970).
7) A small amount of 2,3,4,6-tetrahydroxyacetophenone was also obtained in this hydrolysis.

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