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SYNTHESIS OF 2-[[3-HYDROXY-5-[3-(4-HYDROXYPHENYL)-1-OXO-2-PROPENYL]-3-METHYL-2,4,6-TRIOXOCYCLOHEX-1-YL]METHYLENE]-4-HYDROXY-6-[3-(4-HYDROXYPHENYL)-1-OXO-2-PROPENYL]-4-METHYL-1,3,5-TRIOXOCYCLOHEXANE, AN ANALOG OF CARTHAMIN[1)]

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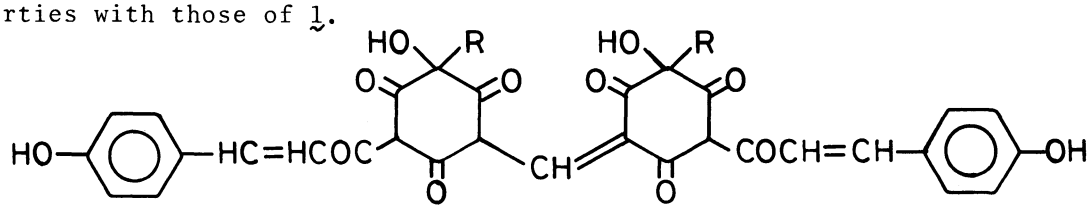
The synthesis of 2-[[3-hydroxy-5-[3-(4-hydroxyphenyl)-1-oxo-2-propenyl]-3-methyl-2,4,6-trioxocyclohex-1-yl]methylene]-4-hydroxy-6-[3-(4-hydroxyphenyl)-1-oxo-2-propenyl]-4-methyl-1,3,5-trioxocyclohexane, an analog of carthamin, was investigated.

In 1979, we proposed the revised structure 1 for carthamin, the red pigment of the flowers of Safflower (Carthamus tinctorius L.).[2)] However, no synthetic studies of 1 have reported yet. In this communication, we wish to report the synthesis of an analog of 1, the title compound (2), and the comparison of its properties with those of 1.

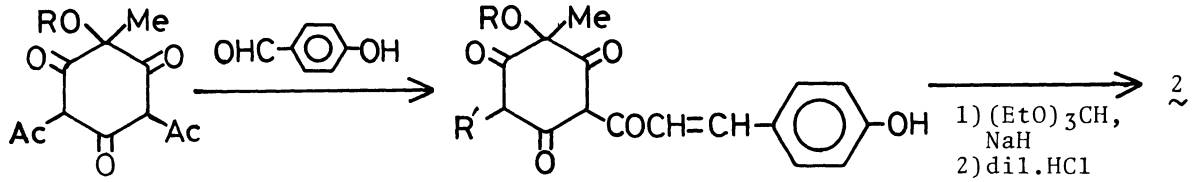


1 R=Glu
2 R=Me

Methylation of 2,6-diacetyl-1,3,4,5-benzenetetrol[3)] with methyl iodide in the presence of sodium hydride in dimethyl sulfoxide gave 2,6-diacetyl-4-hydroxy-4-methylcyclohexane-1,3,5-trione (3)[4)] in a 57% yield. Condensation of 3 with p-hydroxybenzaldehyde in piperidine afforded 4[5)] in a 15% yield. Since deacetylation of 4 with dilute alkali was unsuccessful probably due to instability of the resulting humulone-like product, 5 to alkali,[6)] the hydroxyl group at the 4-position of 4 was protected before alkaline treatment. Compound 6[7)] thus obtained from 3 in a 83% yield was condensed with p-hydroxybenzaldehyde in piperidine to give 7[8)] in a 17% yield. Deacetylation of 7 by warming with 5% aqueous sodium carbonate afforded 8 as a viscous oil in a 15% yield. The structure of 8 was confirmed by spectral data of 5[9)] obtained from the former by treatment with dilute hydrochloric acid. The target 2[10,11)] was obtained from 8 by treatment with triethyl orthoformate and sodium hydride followed by deprotection of the resulting product with dilute hydrochloric acid. The over-all yield of 2 from 7 was 2%.

The electronic spectrum of 2 was very similar to those of carthamin and 2-[[5-[3-(4-hydroxyphenyl)-1-oxo-2-propenyl]-3,3-dimethyl-2,4,6-trioxocyclohex-1-yl]-methylene]-6-[3-(4-hydroxyphenyl)-1-oxo-2-propenyl]-4,4-dimethyl-1,3,5-trioxocyclohexane (9)[12)] as shown in Fig. 1. Cotton and silk were dyed pink-red with 2 in a

similar manner to carthamin.



3 R=H 4 R=H, R'=Ac 5 R=R'=H
6 R=THP 7 R=THP, R'=Ac 8 R=THP, R'=H

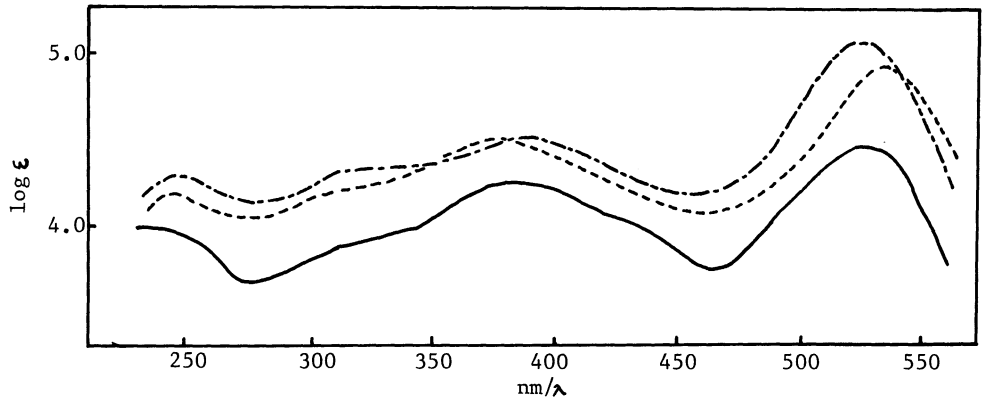


Fig.1. The electronic spectra of 2 (——), 9 (·····), and carthamin (-·-·-) in ethanol.

References

1) Since the direction of enolization is either not fixed or known with any certainty, all compounds are shown in keto form in this report.
2) H. Obara and J. Onodera, Chem. Lett., 1979, 201.
3) H. Obara, Y. Matsui, S. Namai, and Y. Machida, Chem. Lett., 1984, 1397.
4) Compound 3; mp 139-140 °C, MS m/z 240 (M^+), ^{1}H-NMR ($CDCl_3$) δ 1.62 (3H, s, CH_3), 2.62 and 2.74 (each 3H, s, $COCH_3$×2), 4.10 (1H, br-s, OH), 18.90 (1H, s, chelated OH).
5) Compound 4; mp 220-222 °C, MS m/z 344 (M^+), ^{1}H-NMR (C_5D_5N) δ 1.94 (3H,s, CH_3), 2.85 (3H, s, $COCH_3$), 7.24 and 7.72 (each 2H, d, J=8 Hz, aromatic protons), 8.10 and 8.45 (each 1H, d, J=16 Hz, -COCH=CH-). ^{13}C-NMR (DMSO-d_6) δ 26.9 and 27.6 (each q), 78.0, 104.6, and 106.8 (each s), 116.2 and 117.5 (each d), 125.5 (s), 131.4 and 146.4 (each d), 161.6, 184.3, 188.0, 195.3, 197.0, and 198.5 (each s).
6) H. Obara, Y. Machida, S. Namai, and J. Onodera, Chem. Lett., 1985, 1393.
7) Compound 6; viscous oil, ^{1}H-NMR ($CDCl_3$) δ 1.27-1.93 (9H, m), 2.66 and 2.74 (each 3H, s, $COCH_3$×2), 3.35 and 3.76 (each 1H, m), 4.73 (1H, br-s).
8) Compound 7; mp 236-237 °C, ^{1}H-NMR (acetone-d_6) δ 1.36-1.70 (9H, m), 2.65 (3H, s, $COCH_3$), 6.99 and 7.70 (each 2H, d, J=8 Hz), 8.10 (2H, s).
9) Compound 5; mp 165-167 °C, MS m/z 302 (M^+), ES λ_{max} (EtOH) 405 nm (ε =21400), ^{1}H-NMR (C_5D_5N) δ 1.95 (3H, s), 7.07 and 7.64 (each 2H, d, J=8 Hz), 8.13 and 8.67 (each 1H, d, J=16 Hz).
10) Compound 2; mp >300 °C, ES λ_{max} (EtOH) 385 and 524 nm (ε =17000 and 29500). ^{1}H-NMR (C_5D_5N) δ 1.96 and 2.10 (total 6H, each s), 7.08 and 7.65 (each 4H, d, J=8 Hz), 8.14 and 8.61 (each 2H, d, J=16 Hz), 9.14 (1H, s).
11) The configurations of hydroxyl and methyl groups at 3- and 4-positions of 2 have not determined yet.
12) H. Obara, J. Onodera, and F. Shirasaki, Chem. Lett., 1980, 1095.

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