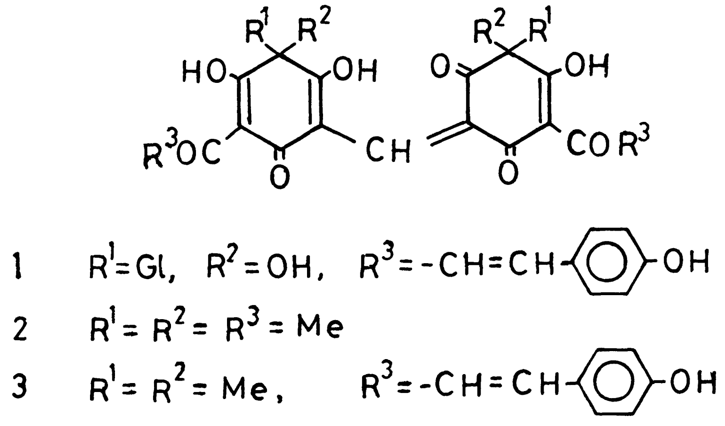
CHEMISTRY LETTERS, pp. 1095-1098, 1980. © The Chemical Society of Japan 1980

SYNTHESIS OF DEHYDRO-3,3'-BIS(p-HYDROXYCINNAMOYL)-5,5'-METHYLENEDIFILICINIC ACID, AN ANALOG OF CARTHAMIN

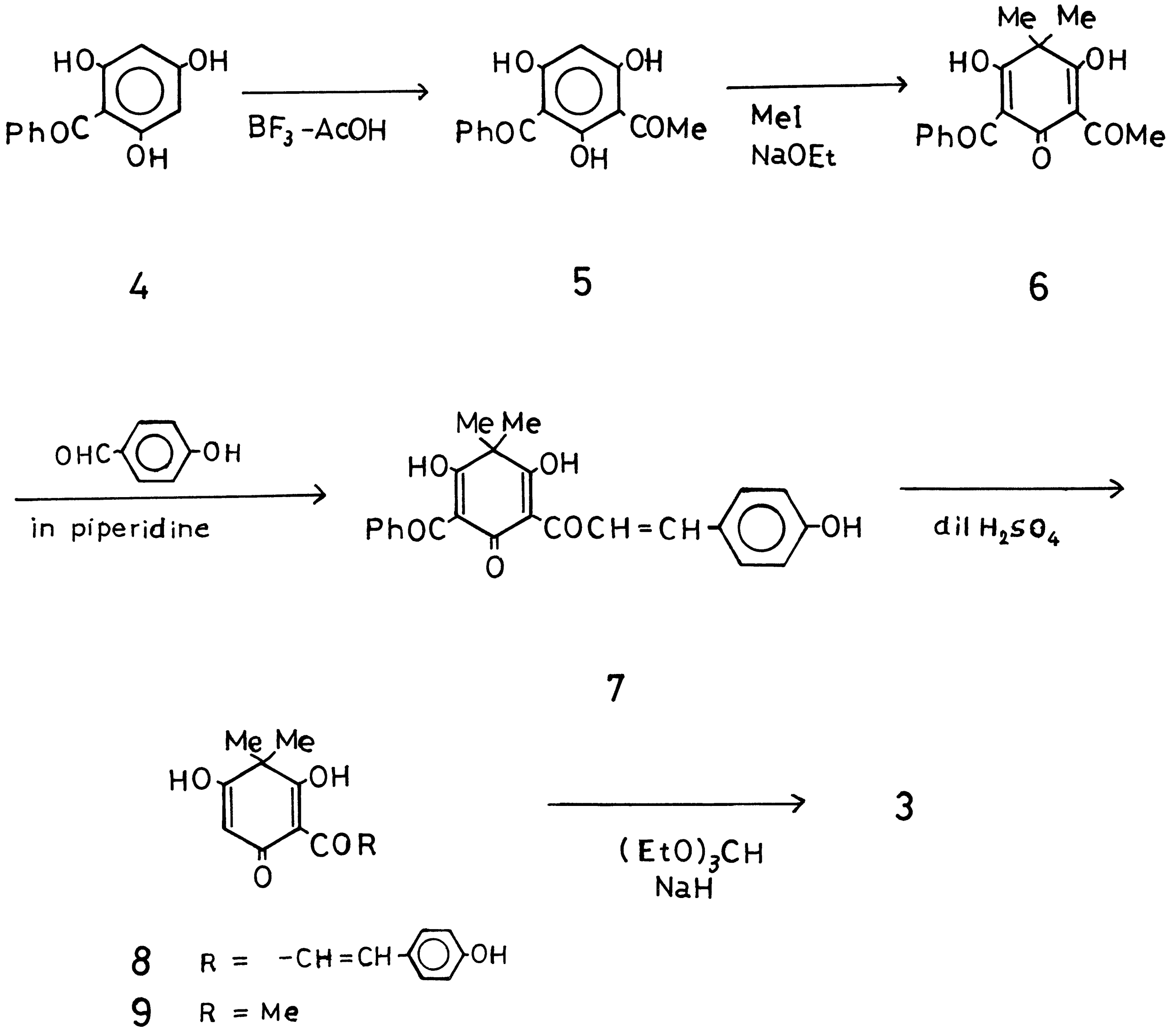
Heitaro OBARA, Jun-ichi ONODERA, and Fumio SHIRASAKI
Department of Applied Chemistry, Faculty of Engineering,
Yamagata University, Yonezawa 992

In connection with the studies on the structure of carthamin (1), dehydro-3,3'-bis(p-hydroxycinnamoyl)-5,5'-methylenedifilicinic acid, an analog of 1, was synthesized from 2-benzoylphloroglucinol through five steps and its properties were compared with those of 1.

In the previous papers,[1,2] we have reported the synthesis of dehydro-3,3'-diacetyl-5,5'-methylenedifilicinic acid (2), an analogous compound of carthamin (1).[1,3] In this communication, we wish to report the synthesis of dehydro-3,3'-bis(p-hydroxycinnamoyl)-5,5'-methylenedifilicinic acid (3), a more analogous compound of 1, and the comparison of its behaviors with those of 1.



2-Acetyl-4-benzoylphloroglucinol (5), mp 145-146°C (from dil methanol), was prepared by the C-acetylation of 2-benzoylphloroglucinol (4)[4] with boron trifluoride-acetic acid complex in a 76% yield. C-Methylation of 5 with methyl iodide in the presence of sodium ethoxide by reference to the literature[5.6] gave 3-acetyl-5-benzoyl-



filicinic acid (6), mp 91-92°C (from ligroin), in a 42% yield. Condensation of 6 with p-hydroxybenzaldehyde in piperidine afforded 3-benzoyl-5-(p-hydroxycinnamoyl)-filicinic acid (7), mp 224-225°C (from benzene), UV_{max} (EtOH) 405 nm (log ε = 4.5), MS, m/e 404 (M^+), in a 64% yield. Debenzoylation of 7 by heating with dilute sulfuric acid in ethanol gave 3-(p-hydroxycinnamoyl)filicinic acid (8), mp 204-206°C (from benzene-ethyl acetate), UV_{max} (EtOH) 395 nm (log ε = 4.5), IR (KBr) 3200 br, 1650, 1618, 1593, 1520, 1500, 1480, 1435, 1415, 1308, 1288, 1233, 1169, 1108, 1047, 982, and 830 cm^{-1}, PMR (pyridine-d_5) δ 1.55 (6H, s, -Me × 2), 7.09 and 7.68 (each 2H, d, J=9Hz, p-substituted phenyl), 7.33 (1H, s, C_5-H), 8.20 and 8.77 (each 1H, d, J=16Hz, -CH=CH-), MS, m/e 300 (M^+), 181, and 147.

Dehydro-3,3'-bis(p-hydroxycinnamoyl)-5,5'-methylenedifilicinic acid (3) was obtained from 8 by the following method. Into a solution of 8 (120 mg) in triethyl orthoformate (60 ml) was added sodium hydride (120 mg) at room temperature. The reaction mixture was poured into cold dilute hydrochloric acid and extracted with ethyl acetate. The ethyl acetate was removed *in vacuo* and the residue was recrystallized from methanol to give 3 (49 mg, 20%), mp 230°C (dec), UV$_{max}$ (EtOH) 377 and 535 nm (log ε = 4.5 and 4.9), IR (KBr) 3250 br, 1620, 1600, 1580, 1515, 1470, 1435, 1410, 1285, 1215, 1167, 1105, 1072, 1032, 985, 965, and 826 cm^{-1}, PMR (pyridine-d$_5$) δ 1.58 (12H, s, -Me × 4), 7.10 and 7.68 (each 4H, d, J=9Hz, *p*-substituted phenyl × 2), 8.19 and 8.70 (each 2H, d, J=16Hz, -CH=CH- × 2), 8.80 (1H, s, =CH-).

This compound 3 didn't give a molecular ion peak in its EI-MS spectrum, but a maximum fragment ion peak was observed at m/e 593 $(M - OH)^+$ in its FD-MS spectrum.7)

Previously,2) we had reported the synthesis of dehydro-3,3'-diacetyl-5,5'-methylenedifilicinic acid (2) by the condensation of 3-acetyl-5-formylfilicinic acid with acetylfilicinic acid (9) in 1% aqueous potassium hydroxide solution. We found that this compound 2 was also obtained from 9 by the above method.

Interestingly, cotton or silk could be dyed pink-red with 3 in a similar manner as carthamin (1). The electronic spectrum of 3 was also very analogous to that of 1 (Fig. 1). These behaviors of compound 3 support the structure of 1 proposed by us.1)

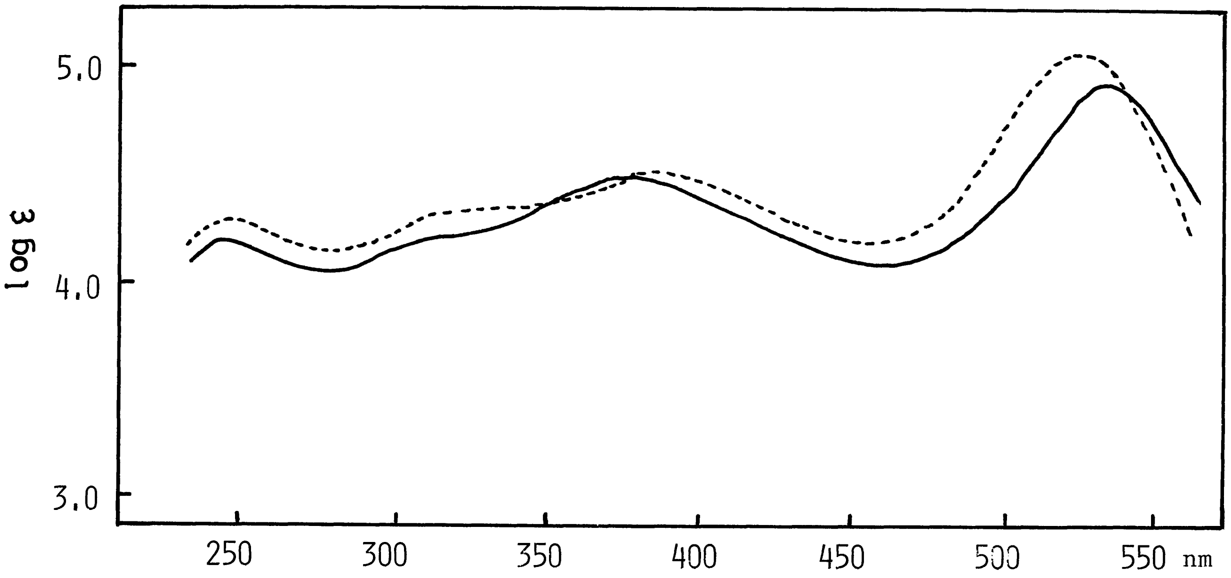


Fig. 1. The electronic spectra of 3 (———) and carthamin (-----) in ethanol.

Acknowledgment The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. The authors wish to express their thanks to Mr. Shoji Tanji of the Laboratories of Kaken Kagaku Co., Ltd., for obtaining the FD-MS spectrum. We also would like to thank Mr. Kazuaki Sato for the measurement of the electronic spectra and the microanalyses.

References and Notes

1) H. Obara and J. Onodera, Chem. Lett., 1979, 201.

2) H. Obara, J. Onodera, and T. Saito, Bull. Chem. Soc. Jpn., 53, 289 (1980).

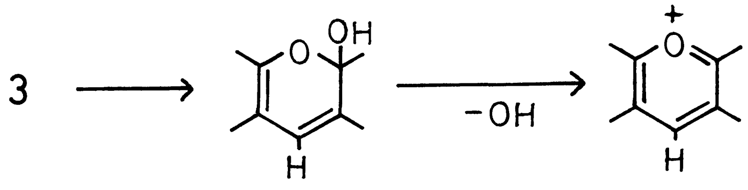
3) C. Kuroda, Nippon Kagaku Zasshi, 51, 237 (1930); C. Kuroda, J. Chem. Soc., 1930, 752; H. Obara and J. Onodera, Chem. Lett., 1978, 643; J. Onodera, T. Saito, and H. Obara, Chem. Lett., 1979, 1327.

4) K. W. Rosenmund and M. Rosenmund, Chem. Ber., 61, 2609 (1928).

5) K. Hoefer and W. Riedl, Justus Liebigs Ann. Chem., 656, 127 (1962).

6) T. Meikle and R. Stevens, J. Chem. Soc., Perkin I, 1978, 1309.

7) It is thought that this maximum fragment ion (11) forms from 3 *via* its hemiacetal (10) as follows.



m/e 593

10 11

(Received July 4, 1980)