HETEROCYCLES, Vol 16, No 6, 1981

THE FORMATION OF MORACENIN D FROM KUWANON G

Taro Nomura*, Toshio Fukai, and Eriko Sato

Faculty of Pharmaceutical Sciences, Toho University,
2-2-1, Miyama, Funabashi-Shi, Chiba 274, Japan

Kazutaka Fukushima

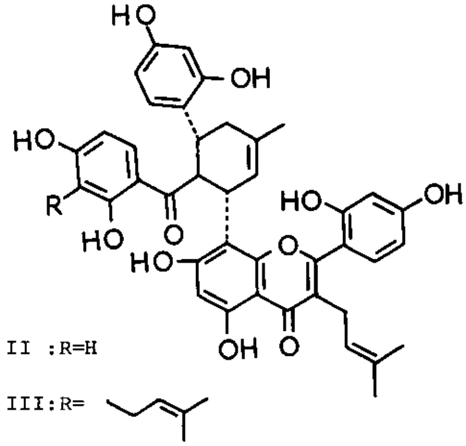
Research Institute for Chemobiodynamics, Chiba University,
1-8-1, Inohana-Cho, Chiba-Shi, Chiba 280, Japan

From the ethyl acetate extract of the root bark of the cultivated mulberry tree (a variety of Morus alba L.), a novel flavone derivative, moracenin D, containing condensed dihydrochalcone partial structure was isolated. The structure was shown to be I on the basis of the formation of moracenin D (I) from kuwanon G (II).

In the previous communications,[1,2] our group reported that two new hypotensive flavone derivatives named kuwanon G (=moracenin B[3]=albanin F[4]) and H (=moracenin A[5] =albanin G[4]) were isolated from the root bark of the cultivated mulberry tree (a variety of Morus alba L.), and that the structures were shown to be II[1,4] and III,[2,4] respectively. On the other hand, Oshima et al. proposed the structures II'[3] and III'[5] for moracenin B and A, respectively. In this paper, we report the isolation of moracenin D[6] from the Morus root bark and propose the new structure (I) for moracenin D on the basis of the formation of moracenin D from kuwanon G (II).

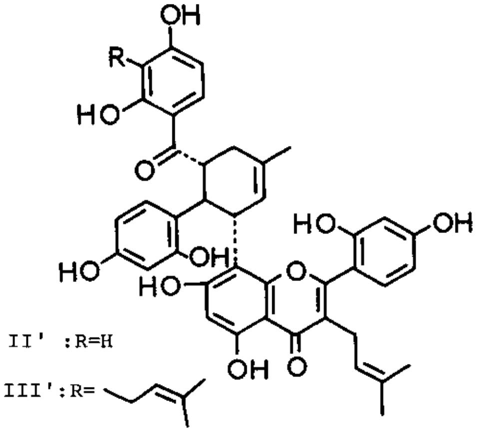
The dried root bark of the cultivated mulberry tree (a variety of Morus alba L.) was extracted successively with n-hexane, benzene, and ethyl acetate. The ethyl acetate extract was fractionated sequentially by the polyamide column chromatography, and by the preparative thin layer chromatography over silica gel, resulting in the isolation of the compound (I) in 1.0×10^{-3}% yield from the dried root bark.

The compound (I), amorphous powder,[7] $[\alpha]_D^{18}$ -419°(c=0.16 in methanol), gave the FD-MS spectrum which showed the molecular ion peak at m/e 710, and showed the cmr spectrum which indicates the presence of forty carbons [fourteen aliphatic



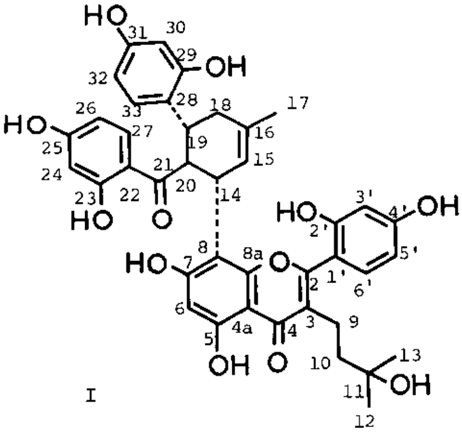
II :R=H

III:R=

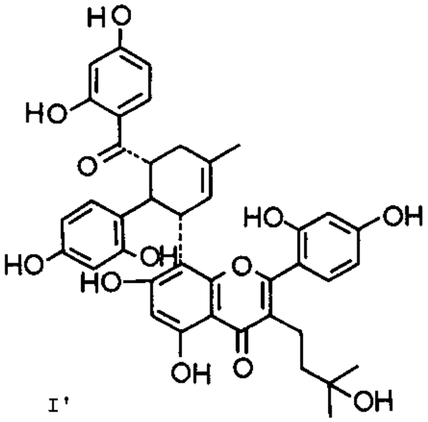


II' :R=H

III':R=



I



I'

Table 1. Cmr Chemical Shifts in CD_3CN

	moracenin D[6]	I		moracenin D	I		moracenin D	I
C-2	156.3 s	157.0	C-6'	131.2 d	132.0	C-22	114.5 s	115.6
C-3	121.5 s	122.6	C-9	20.0 t	21.0	C-23	164.0 s	164.9
C-4	182.5 s	183.6	C-10	41.9 t	42.9	C-24	102.8 d	103.8
C-4a	104.7 s	105.8	C-11	70.2 s	71.1	C-25	164.7 s	165.8
C-5	154.9 s	156.0	C-12	28.2 q	29.1	C-26	107.3 d	108.4
C-6	97.5 d	98.4	C-13	28.1 q	29.1	C-27	132.7 d	133.8
C-7	160.0 s	161.1	C-14	37.6 d	38.6	C-28	121.5 s	122.6
C-8	107.0 s	108.0	C-15	122.9 d	123.9	C-29	155.8 s	156.7
C-8a	160.0 s	161.1	C-16	133.2 s	134.2	C-30	102.0 d	102.9
C-1'	112.4 s	113.4	C-17	22.0 q	23.1	C-31	155.8 s	156.7
C-2'	160.2 s	161.1	C-18	37.1 t	38.0	C-32	107.0 d	108.0
C-3'	102.6 d	103.6	C-19	37.6 d	38.6	C-33	128.8 d	129.5
C-4'	161.0 s	161.8	C-20	47.0 d	47.9			
C-5'	107.1 d	108.0	C-21	208.8 s	209.9			

carbons(CH_3x3, $-CH_2-$x3, -CH<x3, $>C=C<^{O}$x1, >C=CH-x1, ⋟C-Ox1), twenty-four aromatic carbons(CHx10, Cx5, C-Ox9), and two carbonyl carbons], so that the composition of the compound (I) was supported to be $C_{40}H_{38}O_{12}$. The compound (I) showed the following color reactions: Mg-HCl test (red), Zn-HCl test (orange), $FeCl_3$ test (dark purple), and showed the following spectra: ir ν_{max}^{KBr} cm^{-1}: 3300, 1665(sh), 1650, 1620; uv λ_{max}^{MeOH} nm(log ε): 209(4.85), 230(sh 4.54), 265(4.50), 280(sh 4.30), 316(4.17); $\lambda_{max}^{MeOH+AlCl_3}$: 211(4.87), 274(4.55), 308(4.31), 354(4.06); ms m/e 710[8], 692, 600, 582, 438, 420, 354, 137, 110, pmr(δ in CD_3COCD_3), 1.12(6H,s,$C_{11}-CH_3$x2), 1.50(3H,br s,$C_{16}-CH_3$), 1.50-1.83(2H,m,C_{10}-Hx2), 1.80-2.20(2H,m,C_{18}-Hx2, overlapping with the signals of solvent), 2.34-2.67(2H,m,C_9-Hx2), 3.40-3.90(1H,m,C_{19}-H), 4.37(1H,br d,J=10 Hz,C_{14}-H), 4.65(1H,t,J=10,C_{20}-H), 5.16 (1H,br s,C_{15}-H), 5.90(1H,dd,J=2 and 8,C_{26}-H), 5.96(1H,s,C_6-H), 6.01(1H,d,J=2,C_{24}-H), 6.13(1H,dd,J=2 and 8,C_{32}-H), 6.20(1H,d,J=2,C_{30}-H), 6.54(1H,dd,J=2 and 8,$C_{5'}$-H), 6.64(1H,d,J=2,$C_{3'}$-H), 6.77(1H,d,J=8,C_{33}-H), 7.29(1H,d,J=8,$C_{6'}$-H or C_{27}-H), 7.38(1H,d,J=8,$C_{6'}$-H or C_{27}-H), 7.50-9.60(6H,OHx6), 12.80(1H,s,C_5-OH or C_{23}-OH), 12.82(1H,s,C_5-OH or C_{23}-OH). These findings indicate that the compound (I) is possibly moracenin D which was obtained from Morus root bark, for which the structure I' was proposed by Oshima et al.[6] The identification of the compound (I) with moracenin D was carried out by the comparison of the cmr spectrum of the compound (I) with that of moracenin D[6] (Table 1).

To elucidate the structure of moracenin D, the formation of moracenin D from kuwanon G (II) was carried out as described bellow. A solution of II in H_2O-dioxane(1:1) containing 10% H_2SO_4 was kept at 85° for 2 hr, and moracenin D was obtained in 34% yield.[9] The reaction product was identified with moracenin D by ir and pmr spectroscopy. As our group proposed the structure II for kuwanon G, our group proposed the structure I for moracenin D.

ACKNOWLEDGEMENT We are grateful to Dr. J. Uzawa, The Institute of Physical and Chemical Research, for cmr spectral measurement.

REFERENCES AND FOOTNOTES

1 T. Nomura and T. Fukai, Chem. Pharm. Bull., 1980, **28**, 2548.

2 T. Nomura, T. Fukai, and T. Narita, Heterocycles, 1980, **14**, 1943.

3 Y. Oshima, C. Konno, H. Hikino, and K. Matsushita, Tetrahedron Letters, 1980, **21**, 3381.

4 M. Takasugi, S. Ishikawa, S. Nagao, T. Masamune, A. Shirata, and K. Takahashi, Chem. Letters, 1980, 1577.

5 Y. Oshima, C. Konno, H. Hikino, and K. Matsushita, Heterocycles, 1980, 14, 1287.

6 Y. Oshima, C. Konno, H. Hikino, and K. Matsushita, Abstracts of Papers, "23nd Symposium on the Chemistry of Natural Products", Nagoya, October 25, 1980, p 544.

7 Although only one spot was detected on tlc, this compound could not be isolated as crystaline form.

8 This molecular ion could be detected only in FD-MS.

9a T. Saitoh and S. Shibata, Chem. Pharm. Bull., 1969, 17, 729; b M. Komatsu, T. Tomimori, K. Hatayama, and N. Mikuriya, Yakugaku Zasshi, 1970, 90, 463; c T. Nomura, T. Fukai, and M. Katayanagi, Chem. Pharm. Bull., 1978, 26, 1453.

Received, 16th February, 1981