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KUWANON F, A NEW FLAVANONE DERIVATIVE FROM THE ROOT BARK OF THE CULTIVATED MULBERRY TREE (MORUS ALBA L.)

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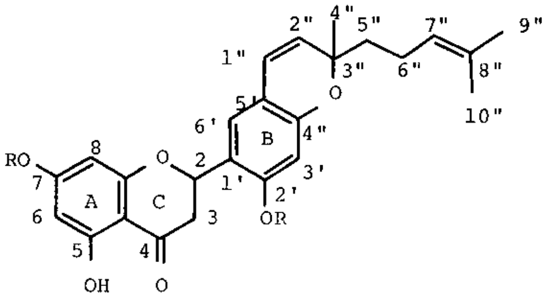
A new flavanone derivative containing 2-methyl-2-(4-methylpent-3-enyl)chromene ring named kuwanon F was isolated from the root bark of the cultivated mulberry tree (a variety of Morus alba L.). The structure was shown to be I on the basis of spectral and chemical data.

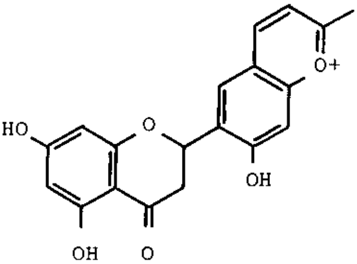
The structures were reported[1-7] of a series of prenylflavonoids isolated from the root bark of Morus alba L., a plant of Moraceae family. In the course of our studies on the constituents of Morus alba L., a flavanone derivative, kuwanon F (I), was isolated from the benzene extract. In this paper, we report the isolation and structure determination of I.

The dried root bark (10 Kg) of the cultivated mulberry tree (a variety of Morus alba L.), collected in Saitama Prefecture, was finely cut and extracted with n-hexane and then with benzene. The benzene extract (60 g) was dissolved in ether. The solution was extracted successively with 5 % aqueous sodium bicarbonate, 5 % aqueous sodium carbonate, and 5 % aqueous sodium hydroxide solution. The 5 % aqueous sodium carbonate solution was treated as usual[3,4,6] and extracted with ether. From the ether solution, a mixture of phenolic materials (6.4 g) was obtained, and was chromatographed on silica gel using benzene-methanol (99.5:0.5) as an eluent to give a mixture of phenolic materials which contained I and other unidentified phenolic compounds. From this mixture, I (17 mg) was isolated by preparative TLC.

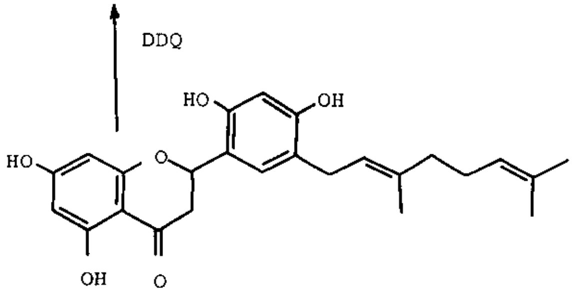
Kuwanon F (I), $C_{25}H_{26}O_6$,[8] amorphous powder,[9] uv [λ_{max}^{MeOH} nm(log ε): 225(4.49), 287.5(4.19), 320(sh 3.93); $\lambda_{max}^{MeOH+AlCl_3}$: 222.5(4.56), 310(4.33), 375(3.54); $\lambda_{max}^{MeOH+NaOMe}$: 319.5(4.50)], $[\alpha]_D^{20}$ +0.5° (c=1.1 in methanol), gave an intense



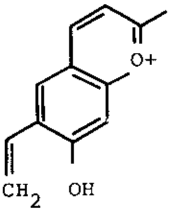
(I): R=H, (Ia): R=COCH$_3$



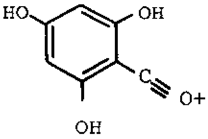
(III)



(II)



(IV)



(V)

reddish violet color with methanolic ferric chloride and was both positive in the magnesium-hydrochloric acid test and the sodium borohydride test,[10] but negative in the zinc-hydrochloric acid test. Kuwanon F gave the absorption bands for hydroxyl, conjugated carbonyl, and benzene ring in the ir spectrum [$\nu_{max}^{CHCl_3}$: 3600, 3250(br), 1650, 1630(sh), 1600(sh)]. Treatment of I with acetic anhydride in pyridine at room temperature for five min yielded a diacetate (Ia), $C_{29}H_{30}O_8$ (M^+ 506), amorphous powder,[9] which gave a reddish violet color with the methanolic ferric chloride test. These findings show that I is a flavanone derivative which has at least three hydroxyl groups, and that one hydroxyl group is hydrogen bonded. This assumption was substantiated by the ^1H nmr spectrum (pyridine-d_5) of I in which the signals were observed at δ 3.08(1H, dd, J=3 and 18 Hz, C_3-H, cis), 3.42(1H, dd, J=13 and 18 Hz, C_3-H, trans), 6.17(1H, dd, J=3 and 13 Hz, C_2-H), 12.80(1H, s, C_5-OH, disappeared on addition of D_2O).

The ^1H nmr spectrum of I showed the meta-coupled doublet (J=1.5 Hz) at δ 6.46(C_6-H) and δ 6.53(C_8-H), which indicated that A ring was unsubstituted at the 6- and the 8-positions.[11] The arrangement of substituents in the B ring was assumed by the ^1H nmr spectrum of I: two singlet signals at δ 6.81(1H,s, $C_{3'}$-H) and δ 7.50(1H, s, $C_{6'}$-H) supported that the B ring of I was substituted in the 2'-, the 4'-, and the 5'-positions. The biogenetic analogy to other prenylflavonoids which have been isolated from Morus alba L.,[1-7] suggests that B ring has the 2'-, 4'-dioxygenated pattern. The presence of 2-methyl-2-(4-methylpent-3-enyl)chromene ring as a partial structure was supported by the ^1H nmr spectrum of I as follows: δ 1.44(3H, s, $C_{3''}$-CH_3),1.54, 1.65(each 3H, s, $C_{8''}$-CH_3x2), 1.75-2.42(4H, m, $C_{5''}$-Hx2 and $C_{6''}$-Hx2), 5.17(1H, br t, J=7 Hz, $C_{7''}$-H), 5.53(1H, d, J=10 Hz, $C_{2''}$-H), 6.56(1H, d, J=10 Hz, $C_{1''}$-H).[12,13]

The mass spectrum of I showed the fragments[14] at m/e 404($C_{25}H_{24}O_5$), 339 ($C_{19}H_{15}O_6$, base peak, III),[13,15] 321($C_{19}H_{13}O_5$), 213($C_{13}H_9O_3$), 187($C_{12}H_{11}O_2$, IV),[13,15] 161($C_{10}H_9O_2$), 153($C_7H_5O_4$, V).[16] The significant peak at m/e 339 indicates the loss of a isohexenyl group from the molecular ion. The characteristic peak at m/e 187 suggests the presence of one hydroxyl group and 2-methyl-2-(4-methylpent-3-enyl)chromene ring in the ring B of the flavanone nucleus.[13,15] In order to corroborate the structure of I, I was derived from kuwanon E (II)[7] by oxidation with DDQ(2,3-dichloro-5,6-dicyanobenzoquinone).[13,17] The ir and ^1H nmr spectrum of the product are in fair agreement with those of I.

From the consideration of above results, we propose the formula (I) for the structure of kuwanon F.

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8 High resolution mass spectrum of the compound gave a satisfactory result.

9 Although only one spot was detected on TLC, this compound could not be isolated as crystalline form.

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