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The Structure of Safflomin C, a Constituent of Safflower

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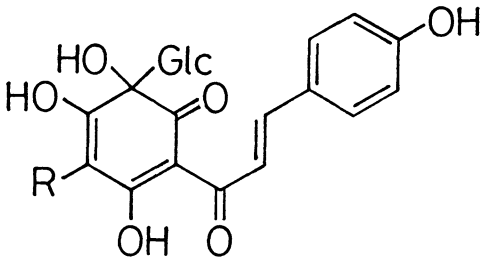
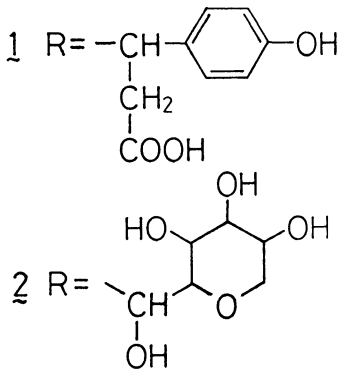
The structure of safflomin C, a yellow constituent of the flowers of Safflower (Carthamus tinctorius L.), was investigated.

Recently, we have reported the structure of safflomin A (2),[1] a yellow coloring matter of the flowers of safflower (Carthamus tinctorius L.). In this communication, we wish to report the structure of safflomin C (1) (Scheme 1.), the analogous yellow constituent obtained from safflower with 2, on the basis of its spectral data and the behavior of its derivatives.





Scheme 1.

Safflomin C (1), yellow powder, mp 300 °C (dec.), $FeCl_3$-dark green, Mg-HCl test-negative, MS m/z 615 $(M+H)^+$, IR (KBr) ν 3400 (br.), 1700, 1613, 1595, 1510, 1400, 1230, 1162, 1068, 920, and 825 cm^{-1}, ^{1}H-NMR (C_5D_5N) δ 8.33 and 8.04 (each 1H, d, J=15.94 Hz), 7.92 and 7.19 (each 2H, d, J=8.42 Hz), 7.47 and 6.85 (each 2H, d, J=8.43 Hz), 5.77 (1H, t, J=7.32 Hz, >C<u>H</u>-CH_2-), 4.68 (1H, d, J=9.53 Hz), 4.47 (1H, dd, J=8.42 and 8.84 Hz), 4.31 (1H, d, J=9.89 Hz), 4.05 and 3.83 (each 1H, dd, J= 7.32 and 15.40 Hz, >CH-C<u>H</u>$_2$-), 3.98 (4H, m), was obtained from the fresh petals of safflower by the adsorption on polyamide and repeated column chromatography on silica gel, Toyopearl gel, and cellulose in a 0.046% yield.[2]

The electronic spectrum of 1 was similar to those of 2 and its analogous

compound, 3-p-hydroxycinnamoyl-5-methylfilicinic acid (3),[3] in the wave length about 300 to 450 nm, but, the additional absorption bands at 220-300 nm were observed as shown in Fig. 1.

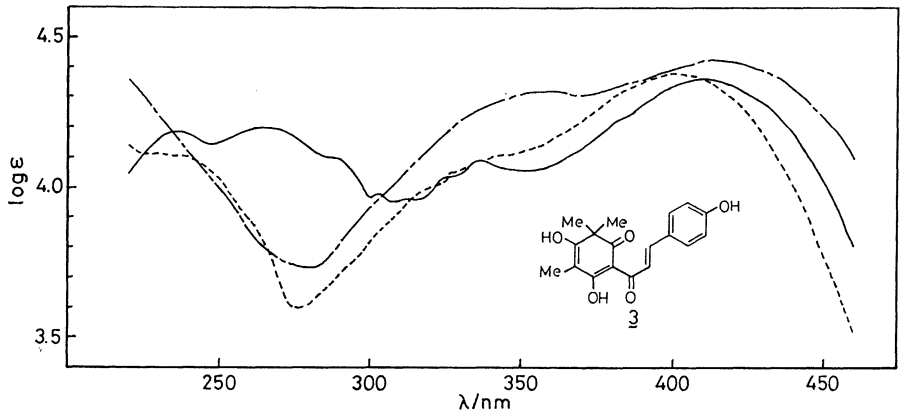


Fig. 1. The electronic spectra of safflomin A (2) (------), 3-p-hydroxycinnamoyl-5-methylfilicinic acid (3) (-·-·-·-), and safflomin C (1) (———) in ethanol.

In analogy with safflomin A and carthamin,[4] 1 affords glucose by acid hydrolysis and gives p-hydroxybenzaldehyde by alkali-degradation.

Further, it is assumed that 1 has a glucosyl, p-substituted cinnamoyl, and p-substituted phenyl group and a characteristic enol proton (δ 18.53) from the comparison of the ^{1}H-NMR spectrum of 1 with that of 2 as shown in Table 1.

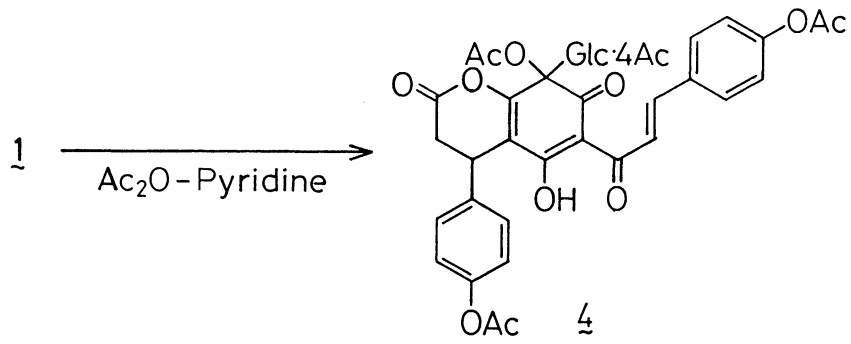
Table 1. Chemical shifts (δ) and coupling constants of safflomin A (2) and 1 in DMSO-d_6 using tetramethylsilane as an internal standard

Safflomin C (1)	Safflomin A (2)
2.8-3.8 (ca. 9H, m), 4.53 (1H,t,J=8.0 Hz)	2.8-5.5 (ca. 14H, m, glucosyl ×2)
6.60 and 7.09, 6.82 and 7.53 (each 2H,	6.79 and 7.43 (each 2H, d, J=8.5 Hz,
d, J=8.4 and 8.8 Hz, p-substituted	p-substituted phenyl)
phenyl ×2), 7.27 and 7.59 (each 1H, d,	7.33 and 7.47 (each 1H, d, J=16.0 Hz,
J=16.0 Hz, -CH=CH-)	-CH=CH-)
18.53 (1H, s, OH)	18.70 (1H, s, OH)

From the above electronic and ^{1}H-NMR spectral data of 1 and 2, the presence of p-hydroxycinnamoylcyclohexadienone skeleton which has a novel C-glucosyl group was expected for the structure of 1.

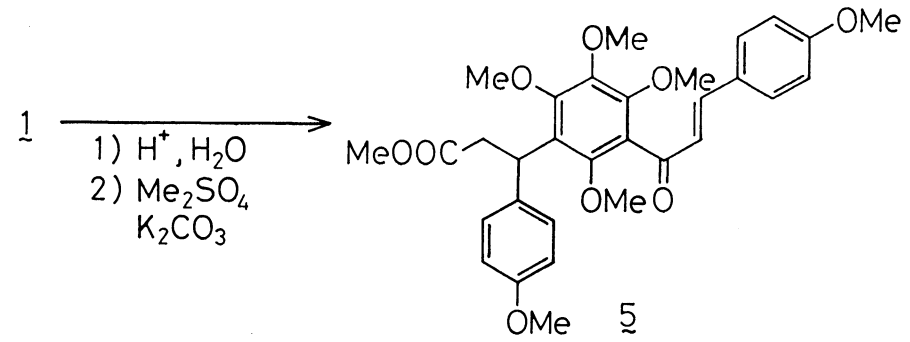
Acetylation of 1 with acetic anhydride-pyridine affords heptaacetate (4) as a yellow crystal, mp 195-196 °C, MS m/z 890 (M^+), IR (KBr) ν 1802, 1758, 1620, 1515, 1428, 1373, 1228, 1200, 1167, 1100, 1040, and 906 cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ 17.87 (1H, s), 8.17 and 7.96 (each 1H, d, J=15.87 Hz), 7.66 and 7.16 (each 2H, d, J=8.55 Hz), 7.34 and 7.16 (each 2H, d, J=8.55 Hz), 5.43 (1H, t, J=9.76 Hz), 5.15 (1H, t, J=8.85 Hz), 4.87 (1H, t, J=9.16 Hz), 4.44 (1H, t, J=4.88 Hz), 4.10 (1H, d, J=9.76 Hz), 4.03 (1H, d, J=10.31 Hz), 3.60 (1H, m), 3.64 (2H, q,

J=6.80 and 10.30 Hz), 3.03 (2H, d, J=4.88 Hz), 2.30, 2.29, 2.18, 2.06, 2.01, 2.00, and 1.72 (each 3H, s), ^{13}C-NMR ($CDCl_3$) δ 189.7, 188.4, 183.5, 170.4, 170.3, 169.2, 168.9, 168.2, 163.2, 158.3, 153.0, and 150.4 (each s), 145.8 (d), 137.1 and 132.3 (each s), 130.3, 127.7, 122.6, 122.3, and 121.0 (each d), 116.1 and 108.0 (each s), 79.8 (d), 79.7 (s), 76.0, 74.2, 68.8, 67.8 (each d), 62.1 (t), 35.6 (t, >CH-$\underline{C}H_2$-), 34.5 (d, >$\underline{C}$H-CH_2-), 21.1, 20.8, 20.6, 20.5, 20.4, and 20.2, each q).



Scheme 2.

The structure 4 (Scheme 2) was proposed for this heptaacetate on the basis of its spectral data. The IR spectrum of 4 exhibited its absorption band at 1802 cm^{-1} which was not appeared in 1. This band was assigned to carbonyl group of γ-δ-unsaturated-δ-lactone formed during acetylation.



Scheme 3.

Hydrolysis of 1 with dilute ethanol containing phosphoric acid affords its aglycone which was methylated with dimethylsulfate-potassium carbonate in acetone to give hexamethoxychalcone (5) (Scheme 3) as a pale yellow viscous oil.

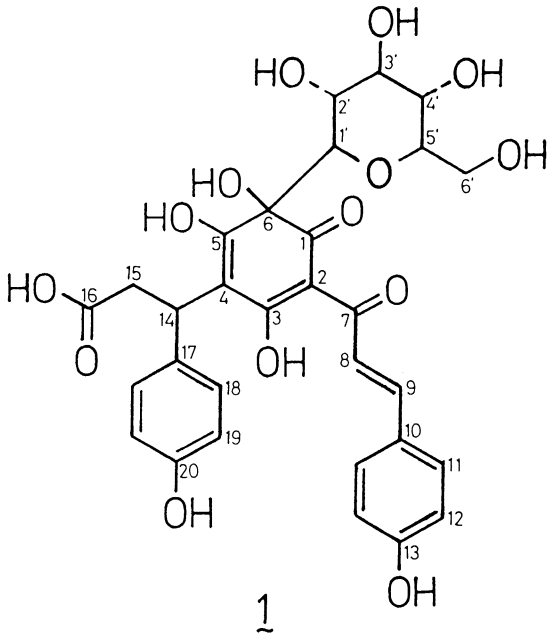
Compound 5, MS m/z 550 (M^+), IR (CCl_4) ν 1740, 1645, and 1600 cm^{-1}, ^{1}H-NMR (CCl_4) δ 7.44 and 6.76 (each 2H, d, J=8.5 Hz), 7.09 and 6.68 (each 2H, d, J=8.5 Hz), 7.09 and 6.68 (each 1H, d, J=16.0 Hz), 4.87 (1H, t, J=8.0 Hz), 3.74 (3H, s), 3.72 (6H, s), 3.66, 3.56, 3.50, and 3.43 (each 3H, s), 3.03 (2H, m), ^{13}C-NMR($CDCl_3$) δ 194.6, 173.2, 162.2, 158.2, 154.1, 151.7, 150.6, and 146.5 (each s), 146.4 (d), 135.9 (s), 130.8 and 128.8 (each d), 127.7 and 127.2 (each s), 126.4 (d), 124.6 (s), 114.7 and 113.8 (each d), 63.1, 62.1, 61.0, 60.9, 55.6, 55.5, and 55.4 (each q), 38.1 (t, >CH-$\underline{C}H_2$-), 36.5 (d, >$\underline{C}$H-CH_2-).

The chalcone structure 5 was given for this methylated aglycone of 1 on the basis of the above spectral data.[5] The ^{13}C-NMR spectrum of 1 and its assignments are shown in Table 2. Finally, both p-substituted phenyl groups of 14-position in 1 and 5 were supported by the observation of the long range coupling between 14-H and 18-H in their ^{1}H-^{1}H 2D COSY spectra.

Consequently, we proposed the structure 1 for safflomin C from the above-mentioned results. The absolute configuration of 1 is now under investigation.

Table 2. ^{13}C-NMR data of 1 in pyridine-d_5 using tetramethylsilane as an internal standard

Carbon No.	δ	Carbon No.	δ
1	197.0(s)	17	136.6(s)
2	108.4(s)	18	130.5(d)[a]
3	184.6(s)	19	116.5(d)[a]
4	110.2(s)	20	156.8(s)
5	180.5(s)	1'	88.7(d)
6	85.0(s)	2'	71.6(d)
7	188.9(s)	3'	80.3(d)
8	139.4(d)	4'	70.7(d)
9	122.1(d)	5'	81.6(d)
10	127.9(s)	6'	63.0(t)
11	129.7(d)[a]		
12	115.8(d)[a]		
13	160.6(s)		
14	37.2(d)		
15	39.9(t)		
16	176.0(s)		



1

a) These assignments may be reversed.

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References

1) J. Onodera, H. Obara, M. Osone, Y. Maruyama, and S. Sato, Chem. Lett., 1981, 433; J. Onodera, S. Sato, and H. Obara, ibid., 1981, 887.
2) The details of the extraction method of 1 will be reported elsewhere.
3) H. Obara, J. Onodera, S. Abe, and T. Saito, Bull. Chem. Soc. Jpn., 53, 289 (1980).
4) H. Obara and J. Onodera, Chem. Lett., 1979, 201.
5) The synthesis of 5 is now in progress.

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