THE STRUCTURE OF SAFFLOMIN-A, A COMPONENT OF SAFFLOWER YELLOW

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The structure of safflomin-A, a yellow component of the flowers of Safflower (<u>Carthamus</u> <u>tinctorius</u> L.), was investigated.

Safflower yellow,¹⁾ the yellow coloring matter of the flowers of Safflower (<u>Carthamus tinctorius</u> L.), has been hitherto known as an unstable water-soluble yellow glycoside. However, the structure of this pigment has not been elucidated yet. Recently, we have obtained two components, safflomin-A and safflomin-B,²⁾ of this pigment, by the repeated column chromatography.

In this communication, we wish to propose the structure 1 for safflomin-A on the basis of the comparison of its spectral data with those of carthamin $(2)^{3}$ and the behavior of its derivatives.







Safflomin-A (1), yellow powder, mp 300°C (dec), FeCl_3 - dark-green, Mg-HCl test - negative, UV_{max} (EtOH) 227 and 403 nm (log ε = 4.19 and 4.37), IR (KBr) 3350 (br), 1595, 1500, 1435, 1230, 1160, 1071, 980, 920, and 820 cm⁻¹, was obtained from the fresh flowers in a 0.02% yield.⁴⁾ The structure of this compound 1 was derived from the following results.

The IR spectrum of 1 was similar to that of carthamin. However, the UV spectrum of 1 showed striking resemblance to that of an analogous compound, $3-\underline{p}$ -hydroxy-cinnamoyl-5-methylfilicinic acid (3)⁵⁾ as shown in Fig. 1.



Fig. 1. The electronic spectra of safflomin-A (-----), 3-p-hydroxycinnamoy1-5-methylfilicinic acid (3) (---), and carthamin (-----) in ethanol.

As shown in Table 1, the presence of a <u>p</u>-hydroxycinnamoyl group⁶ and a character istic enol proton (18.70 ppm) in 1 was observed in analogy with those of carthamin (2). Further, the presence of two glucosyl groups based on one <u>p</u>-hydroxycinnamoyl group is expected from the peak area at 2.8-5.5 ppm in 1.

Safflomin-A (1)	Carthamin (2)
2.8-5.5 (<u>ca</u> .14H, m, glucosyl X 2)	2.8-4.8 (<u>ca</u> .14H, m, glucosyl X 2)
6.79 and 7.43 (each 2H, d, J=8.5, <u>p</u> -substituted pheny1)	6.87 and 7.60 (each 4H, d, J=8.5, <u>p</u> -substituted phenyl X 2)
7.33 and 7.47 (each 1H, d, J=16.0, -CH=CH-)	7.46 and 7.60 (each 2H, d, J=16.0, -CH=CH-X2)
	8.42 (1H, s, -CH=)
18.70 (1H, s, OH)	19.00 (1H, s, OH)

Table 1. Chemical Shifts ($\boldsymbol{\xi}$) and Coupling Constants (Hz) of Safflomin-A and Carthamin in DMSO-d₆ using Tetramethylsilane as an internal standard.

The comparison of the 13 C-NMR spectrum of 1 with that of carthamin (2) provided a significant information regarding two C-glucosyl groups⁷⁾ in 1 as shown in Fig. 2. From the signals at high field region (60-86 ppm), it should be predictable that one glucosyl group is almost identical with that of carthamin, but, another one is different from it.



Fig. 2. The ¹³C-NMR spectra of safflomin-A (1) and carthamin (K salt)³⁾ in DMSO-d₆. The letter t, d, and s show the triplet, doublet, and singlet in the offresonance ¹H-decoupling spectra, respectively.

Acetylation of 1 with acetic anhydridepyridine gave an unsaturated decaacetate (4), yellow crystals, mp 113-116°C, UV max (EtOH) 398, 272, and 245 nm, IR (KBr) 1745, 1665, and 1615 cm⁻¹ (C=O, C=C), ¹H-NMR (CDC1₃) δ 1.84, 1.87, 1.98, 2.00, 2.14, 2.17, 2.22, and 2.27 (each 3H, s, -OAc \times 8), 1.93 (6H, s, -OAc \times 2), 3.4-5.5 (12H, m), 7.14 and 7.66 (each 2H, d, J=8.5Hz, p-substituted pheny1), 7.88 and 8.24 (each 1H, d, J=16Hz, -CH=CH-), 6.92⁸) (1H, s, -CH=), 18.22⁸) (1H, s, -OH),



along with dodecaacetate (mp 150-152°C). The structure 4 was assigned for the above decaacetate from the studies of its spectra and elemental analyses.⁹⁾

Although the acid hydrolysis of 1 gave glucose and its aglycon, the results will be reported and discussed elsewhere. $^{10)}\,$

References and Notes

- 1) A. Schlieper, Justus Liebigs Ann. Chem., 58, 357 (1846).
- 2) These substances, which we should now call safflomin-A and safflomin-B, have been hitherto named by us SY-1 and SY-2, respectively.^{11,12,13} The details of the structure of safflomin-B will be published elsewhere.
- 3) H. Obara and J. Onodera, Chem. Lett., 1979, 201.
- 4) The details of the extraction method of 1 will be reported elsewhere.
- 5) H. Obara et al., Bull. Chem. Soc. Jpn., 53, 289 (1980).
- 6) The alkali degradation of 1 give p-hydroxybenzaldehyde in analogy with carthamin.
- 7) These C-glucosyl groups are supported from the absence of signals near 100 ppm due to O-glucoside.
- 8) It can be assumed that these two signals are due to the decaacetate moieties.
- 9) The structure 5 can be also considered against the structure 1, but, it can not accept from the formation of such unsaturated decaacetate.



- 10) Recently, Wada et al.,¹¹⁾ proposed the structure 6 for the yellow pigment of the flowers of Safflower, Sp₂, on the basis of its spectral data. Although the direct comparison of 1 with Sp₂ has not been accomplished yet, it is assumed that both compounds are identical.
- 11) M. Wada et al., 23th Symposium of the Chemistry of Natural Products, Nagoya, October 1980, Symposium papers, p. 538.

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