CHEMISTRY LETTERS, pp. 433-436, 1981.

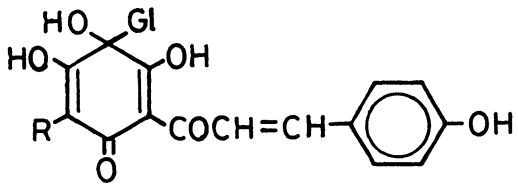
THE STRUCTURE OF SAFFLOMIN-A, A COMPONENT OF SAFFLOWER YELLOW

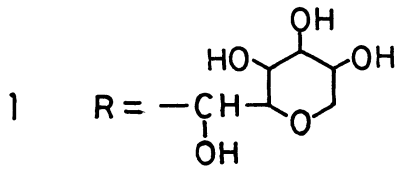
Jun-ichi ONODERA, Heitaro OBARA*, Masahide OSONE, Yasunobu MARUYAMA, and Shingo SATO
Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa 992

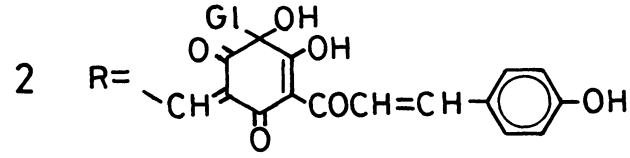
The structure of safflomin-A, a yellow component of the flowers of Safflower (Carthamus tinctorius L.), was investigated.

Safflower yellow,[1] the yellow coloring matter of the flowers of Safflower (Carthamus tinctorius 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 ($\log \varepsilon$ = 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-p-hydroxy-cinnamoyl-5-methylfilicinic acid (3)[5] as shown in Fig. 1.

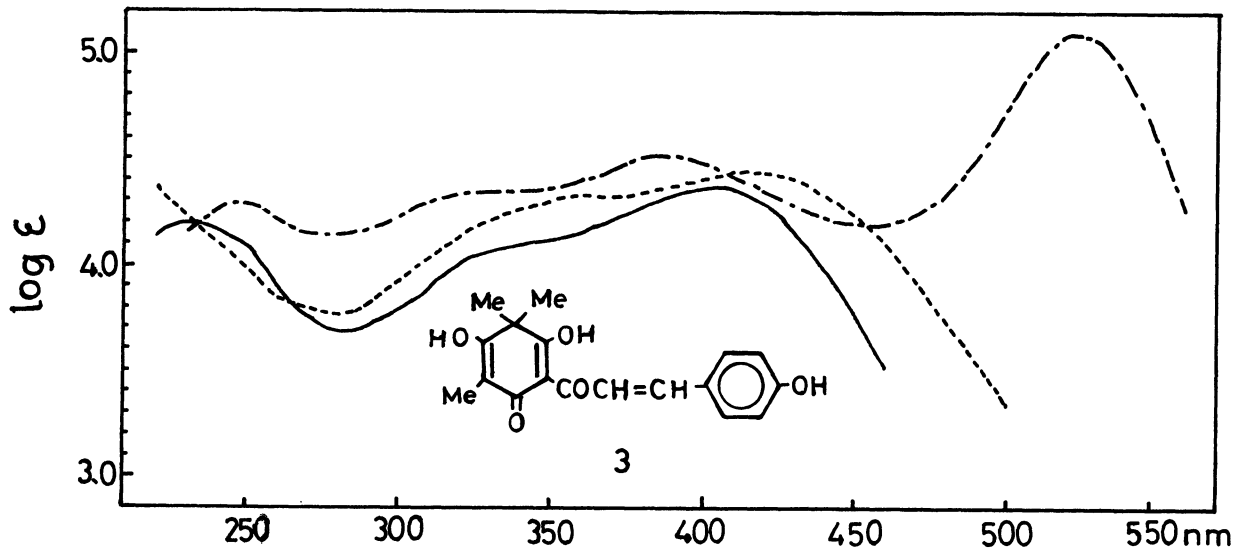


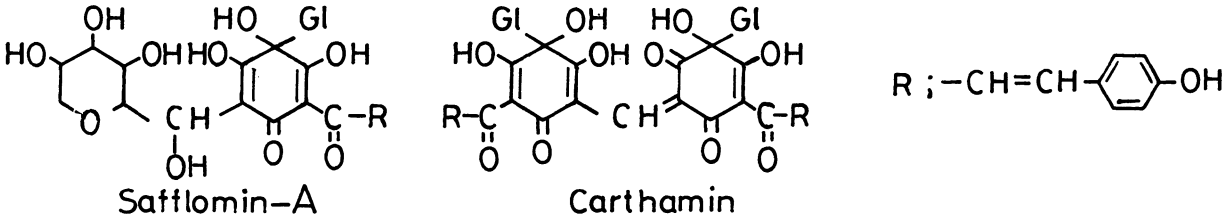
Fig. 1. The electronic spectra of safflomin-A (——), 3-p-hydroxycinnamoyl-5-methylfilicinic acid (3) (---), and carthamin (—·—·) in ethanol.

As shown in Table 1, the presence of a p-hydroxycinnamoyl group[6] and a characteristic 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 p-hydroxycinnamoyl group is expected from the peak area at 2.8-5.5 ppm in 1.

Table 1. Chemical Shifts (δ) and Coupling Constants (Hz) of Safflomin-A and Carthamin in DMSO-d_6 using Tetramethylsilane as an internal standard.

Safflomin-A (1)	Carthamin (2)
2.8-5.5 (ca.14H, m, glucosyl × 2)	2.8-4.8 (ca.14H, m, glucosyl × 2)
6.79 and 7.43 (each 2H, d, J=8.5, p-substituted phenyl)	6.87 and 7.60 (each 4H, d, J=8.5, p-substituted phenyl × 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- × 2)
———	8.42 (1H, s, -CH=)
18.70 (1H, s, OH)	19.00 (1H, s, OH)

The comparison of the ^{13}C-NMR spectrum of 1 with that of carthamin (2) provided a significant information regarding two C-glucosyl groups[7] 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.



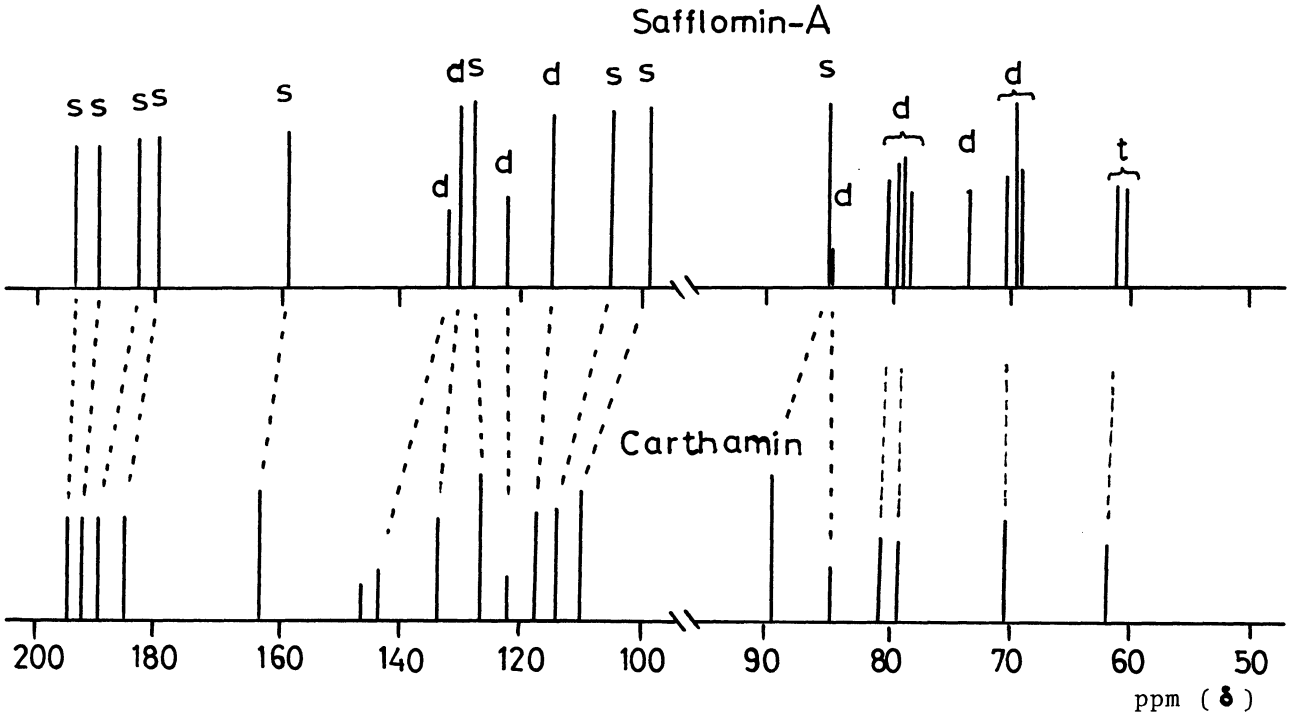
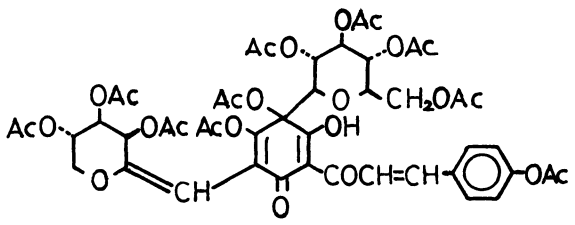


Fig. 2. The ^{13}C-NMR spectra of safflomin-A (1) and carthamin (K salt)[3] in DMSO-d_6. The letter t, d, and s show the triplet, doublet, and singlet in the offresonance ^{1}H-decoupling spectra, respectively.

Acetylation of 1 with acetic anhydride-pyridine gave an unsaturated decaacetate (4), yellow crystals, mp 113-116°C, UV λ_{max} (EtOH) 398, 272, and 245 nm, IR (KBr) 1745, 1665, and 1615 cm^{-1} (C=O, C=C), ^{1}H-NMR ($CDCl_3$) δ 1.84, 1.87, 1.98, 2.00, 2.14, 2.17, 2.22, and 2.27 (each 3H, s, -OAc ×8), 1.93 (6H, s, -OAc ×2), 3.4-5.5 (12H, m), 7.14 and 7.66 (each 2H, d, J=8.5Hz, p-substituted phenyl), 7.88 and 8.24 (each 1H, d, J=16Hz, -CH=CH-), 6.92[8] (1H, s, -CH=), 18.22[8] (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]

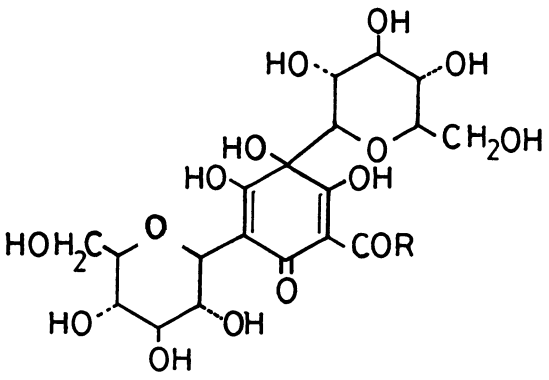


4

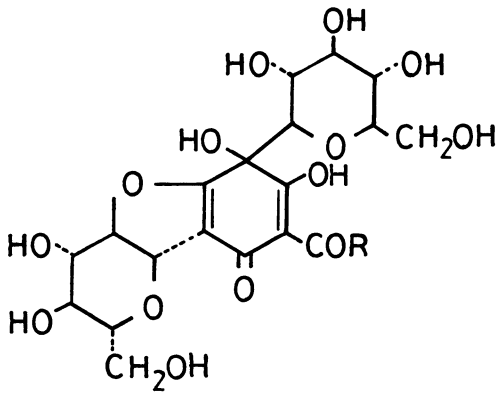
Although the acid hydrolysis of 1 gave glucose and its aglycon, the results will be reported and discussed elsewhere.[10)]

References and Notes

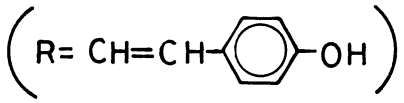
1) A. Schlieper, Justus Liebigs Ann. Chem., 58, 357 (1846).
2) These substances, which we should now call safflomin-A and safflomin-B, have been hitherto named by us SY-1 and SY-2, respectively.[11,12,13)] The details of the structure of safflomin-B will be published elsewhere.
3) H. Obara and J. Onodera, 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.



5



6



10) Recently, Wada et al.,[11)] proposed the structure 6 for the yellow pigment of the flowers of Safflower, Sp_2, on the basis of its spectral data. Although the direct comparison of 1 with Sp_2 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.

(Received December 12, 1980)