

At present we have no positive data to go upon identification of radical structures. It is noticeable, however, that the observed effects of DNA on free radical production from 4-NQO and from 4-HAQO were in the opposite direction, one being accelerative and the other retardative. As to this, we are of the preliminary opinion that the opposite effects of DNA might be interpreted consistently in terms of charge transfer between DNA and N-oxide compounds. During the course of an investigation on the *in vitro* interaction of 4-NQO and related carcinogens with cellular materials, we have found that charge transfer occurs from the base moiety of DNA to 4-NQO⁹⁾ as well as from the former to 4-HAQO.¹⁰⁾ So that it may be quite possible that DNA, through its tendency to push electrons toward N-oxide compounds, accelerated reductive radical production from 4-NQO and retarded oxidative radical production from 4-HAQO.

With a view to attaining more concrete picture of the present results, studies are being continued and further details will be published later.

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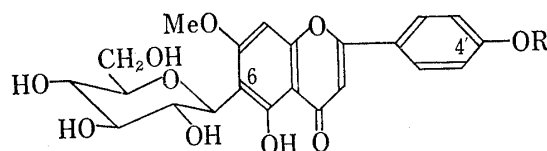
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Experiments showing the Identity of Swertisin and Flavocommelitin

Flavocommelitin is an aglycone of a pale yellow flavonoid component involved in commelinin,¹⁾ *i.e.*, a blue crystalline metallo-anthocyanin previously isolated by one of us (K.H.) from the blue *Commelina* flowers. According to K. Takeda, *et al.*,²⁾ the sugar-free moiety of this flavonoid was shown to be 6-C-glucopyranosylgenkwanin (I), and its glycoside, flavocommelin, is 4'-O-glucoside (II) of flavocommelitin, as shown by the following formula. In the mean time, however, it was found that the same structure had already been assigned by the two of the present authors (M.K. and T.T.) to swertisin,³⁾ a pale yellow substance isolated from the herb of *Swertia japonica* MAKINO by T. Nakaoki⁴⁾ in 1927.



Swertisin *viz.* flavocommelitin (I: R=H),
Flavocommelin (II: R=glucose residue).

- 1) S. Mitsui, K. Hayashi, and S. Hattori, *Proc. Japan Acad.*, **35**, 169 (1959); *Botan. Mag.* (Tokyo), **72**, 325 (1959).
2) K. Takeda, S. Mitsui, and K. Hayashi, *Botan. Mag.* (Tokyo), **79**, 578 (1966).
3) M. Komatsu and T. Tomimori, *Tetrahedron Letters*, **1966**, 1611; *Chem. Pharm. Bull.* (Tokyo), **15**, 263 (1967).
4) T. Nakaoki, *J. Pharm. Soc. Japan*, **47**, 144 (1927).

Unfortunately, the literatures cited above show that a slight inconsistency may be noted in some of the physical constants between swertisin and flavocommelitin. In order to settle the confusion in the literature, the present authors have made, in conjunction with the two different laboratories, an attempt to make a careful comparison on these two specimens in question.

The results of comparative experiments are arranged in Tables I and II. As a consequence, both specimens have proved to be identical, inasmuch as the usual characteristics are concerned, *e.g.*, the melting point tests, *Rf* values, ultraviolet and infrared absorption spectra, *etc.* Moreover, hexa-O-acetyl derivatives of both compounds, when prepared in the same way as described previously,²⁾ have also established the identity of both derivatives and also of

TABLE I. Comparison of the Purified Specimens of Swertisin and Flavocommelitin

	Swertisin	Flavocommelitin
Melting point (after recrystallization from water)	243° (decomp.)	243° (decomp.)
UV-absorption maxima in EtOH	273, 338 m μ	273, 338 m μ
UV-absorption maxima in EtOH + AlCl ₃	282, 304, 354, 380 ^{a)} m μ	282, 304, 354, 380 ^{a)} m μ
<i>Rf</i> values ^{b)} obtained by irrigation with		
15% AcOH	0.59	0.59
30% AcOH	0.73	0.73
<i>n</i> -BuOH/AcOH/H ₂ O (4:1:5, v/v)	0.60	0.60
AcOH/HCl/H ₂ O (30:3:10, v/v)	0.88	0.88

a) point of inflection

b) Estimated on Toyo No. 51 filter paper by the ascending method at *ca.* 19°.

TABLE II. Comparison of Hexa-O-acetyl Derivatives of Swertisin and Flavocommelitin

	Hexa-O-acetyl swertisin	Hexa-O-acetyl flavocommelitin
Melting point (after recrystallization from acetone-petroleum ether)	182° (mixed mp 182°)	182°
UV-absorption maxima in EtOH	243 ^{a)} , 261, 308 m μ	243 ^{a)} , 261, 308 m μ
<i>Rf</i> values ^{b)} obtained by irrigation with		
<i>n</i> -BuOH/AcOH/H ₂ O (4:1:5, v/v)	0.88	0.88
15% AcOH	0.54	0.53
30% AcOH	0.89	0.89

a) point of inflection

b) Estimated on Toyo No. 51 filter paper by the ascending method at *ca.* 19°.

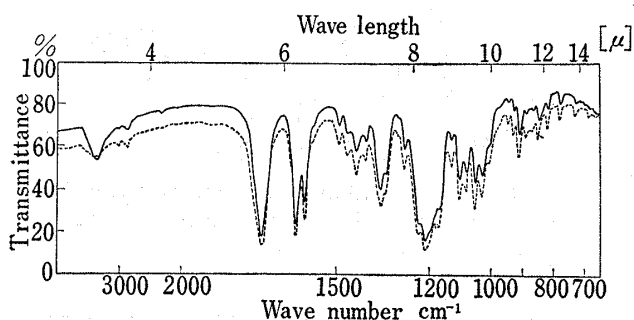


Fig. 1. Infrared Absorption Spectra of Hexa-O-acetyl Derivatives of Swertisin and Flavocommelitin in KBr

----- swertisin
 ————— flavocommelitin

their mother substances (*cf.*, Table II and Fig. 1). In nuclear magnetic resonance spectrum, both derivatives exhibit the same pattern of characteristic signals (*cf.*, previous data³⁾).

Now that the identity of swertisin and flavocommelitin has been sufficiently established, the name 'flavocommelitin' should be eliminated from the literature as a matter of priority. Of course, the name 'isoflavocommelitin,' *i.e.*, an acid-converted isomer, should also be replaced by 'iso-swertisin.' But the term

'flavocommelin' may be retained in the literature as a designation of 4'-O-glucoside of swertisin.

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