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The Light Resistance of the Complex Salts of Flavones and Flavonols

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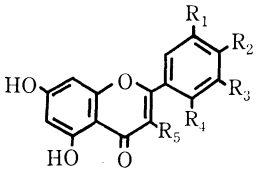
In a previous paper,[1] we showed that flavones, in contrast to flavonols (3-hydroxyflavones), show a high degree of resistance to light, and made clear that dyes from the plants *Arthraxon hispidus*,[2] *Reseda luteola*, and *Miscanthus tinctorius*[3] are superior to dyes from other grasses in their resistance to light because they contain flavones, such as arthraxin, luteolin, and tricin.

Since silk threads normally soaked in a mordant of lye made from leaves and stems of trees, such as *Eurya ochacea* and *Camellia japonica*, after being dyed with dyes from the above-mentioned plants, we examined the light resistance of the complex salts of flavones and flavonols by following the time change in the UV spectra of the following complexes substances: quercetin (**1**), morin (**2**), arthraxin (**3**), luteolin (**4**), and tricin (**5**).

Because of the similarity in the molecular structures of these substances, their molecular extinction coefficients will be considered to be approximately equal.



1 R_1, R_2, R_5=OH R_3,R_4=H
2 R_2,R_4,R_5=OH R_1,R_3=H
4 R_1,R_2=OH R_3,R_4,R_5=H
5 R_2=OH R_1,R_3=OMe R_4,R_5=H

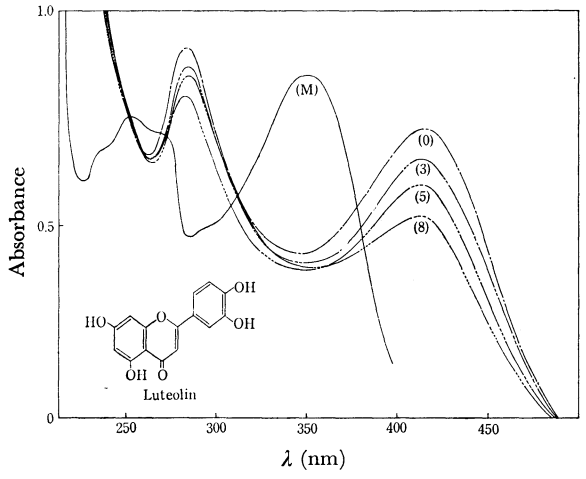


Fig. 1. Time change during irradiation of the spectrum of luteolin complex formed with *Camellia* lye.
(M): Methanol solution of luteolin, (0): 0 hr irradiation, (3): 3 hr irradiation, (5): 5 hr irradiation, (8): 8 hr irradiation.

We can, therefore, measure the light resistance of the substances by means of the decrease in the ratio of the absorption intensity.

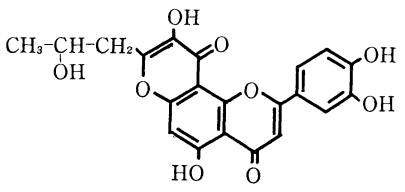


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TABLE 1. DECREASE RATIO OF INTENSITY OF BAND I AFTER FIVE-HOUR IRRADIATION

	Flavonol		Flavone		
	Quercetin (371)[a]	Morin (370)	Arthraxin (340)	Luteolin (350)	Tricin (350)
Lye of plant *Camellia*[5]	53% (438)	57 (403)	30 (403)	19 (415)	24 (375)
Lye of plant *Eurya*	51 (443)	54 (395)	12 (408)	15 (412)	20 (377)
Na_2CO_3	100 (385)	75 (395)	24 (401)	20 (395)	37 (418)
$AlCl_3$	92 (456)	38 (420)	31 (408)	22 (425)	17 (392)
Al_2O_3	100 (380)	75 (392)	16 (353)	3 (360)	24 (367)
CuO(NaOHaq)	100 (425)	100 (455)	15.3 (415)	25 (405)	15 (425)

$$\text{Decrease ratio} = \frac{\text{Intensity at 0 hr} - \text{Intensity at 5 hr}}{\text{Intensity at 0 hr}} \times 100\%$$

a) λ max of band I of the samples and their complexes are shown in the respective parentheses.

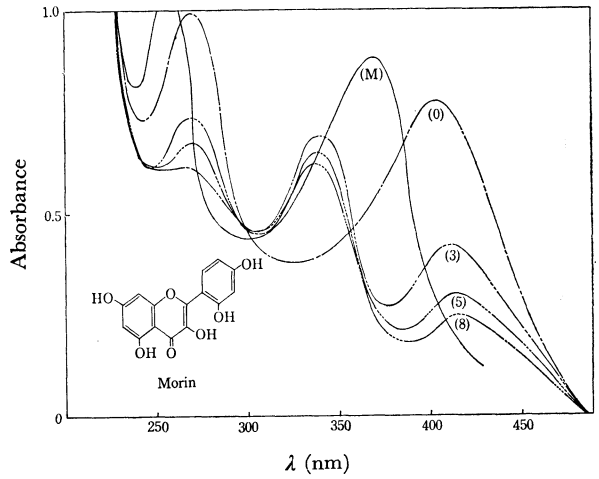

Fig. 2. Time change during irradiation of the spectrum of morin complex formed with *Camellia* lye.
(M): Methanol solution of morin, (0) 0 hr irradiation, (3): 3 hr irradiation, (5): 5 hr irradiation, (8): 8 hr irradiation.

1) M. Kaneta and N. Sugiyama, This Bulletin, **44**, 3211 (1971).
2) M. Kaneta and N. Sugiyama, *ibid.*, **42**, 2084 (1969).
M. Kaneta and N. Sugiyama, *J. Chem. Soc., C*, **1971**, 1892
3) M. Kaneta and N. Sugiyama, This Bulletin, **45**, 528 (1972).

Fifty ml portions of methanol solutions of the samples were prepared so as to show approximately equal absorption intensities of Band I, with Band I defined as the peak absorption band in the 350—450 nm region. To each solution, we then added a few drops of a saturated solution of salts (Na_2CO_3, $AlCl_3$) or lye of leaves and stems of *Eurya ochacea*, and *Canellia japonica* in order to make a complex.[4] The methanolic solutions of the complexes were irradiated under the same conditions with an immersion-type Taika HLV-A 200-W high-pressure mercury lamp through a quartz glass tube under bubbling air. The UV spectrum of an aliquot was then recorded at intervals of 1, 2, 3, 5, 8, 12, and 24 hr.

The results tabulated in Table 1 indicate that the complex salts of flavones, in contrast with flavonol-salt complexes, show a high power of resistance to the light when air is bubbled into the methanol solution. This result also agrees with the observations reported in a previous paper,[1] so it becomes clear that flavones are more stable than flavonols (3-hydroxyflavone) to irradiation both in the free state and in the complex-salt state.

4) For information about the "complexes" of flavones and flavonols, the reader is referred to T. J. Mabry, K. R. Markham and M. B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, New York (1970), p. 51.

5) The main metals contained in these plants were found to be Na, K, Ca, Mn, Al, Fe, and Cu by Mr. Ryokichi Negishi, Kanagawa Prefectural Industrial Experiment Station.