[Chem. Pharm. Bull. 12 (3) 316 ~ 326]

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46. Seigo Fukushima, Yukio Akahori, and Akira Ueno: Studies on Benzochromones. VII.*1) Ultraviolet Spectra of Benzochromones and Related Compounds.

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Furochromones, *i.e.* khellin, visnagin, khellinol, khellol and khellol glucoside show similar ultraviolet absorption spectra.[1] According to Roberts, *et al.*,[2] the ultraviolet spectra of rubrofusarin, norrubrofusarin monomethyl ether, which are already assigned to linear benzochromone derivatives are quite different from those of eleutherinol and flavasperon which belong to angular benzochromones; the ultraviolet spectra of linear benzochromones have characteristic fine structure in the near 300 mμ region and in contrast those of angular ones lack it. Fennel, *et al.*[3] pointed out that the ultraviolet spectrum of fonsecin which belongs to linear benzochromone shows fine structure in the range of 320 to 330 mμ. Schmid, *et al.*[4] studied the ultraviolet spectra of several benzochromones as model compounds of eleutherinol and found small bathochromic shift resulting from the replacement of methyl group at 2-position of the γ-pyrone ring with carboxyl group. This observation is not in accordance with Roberts' and Fennel's results that the fine structure at 300~320 mμ appears in the ultraviolet spectra of not only linear series but also angular series.

A series of benzochromones have been prepared in our laboratory as reported previously, and the present paper deals with the investigation of their ultraviolet spectra.

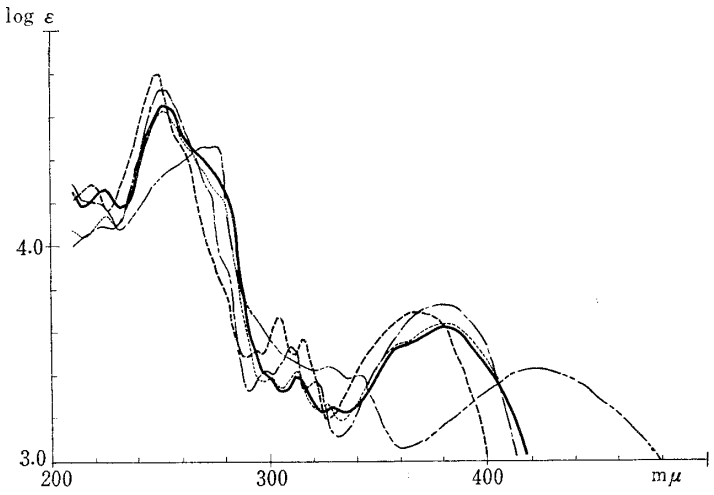
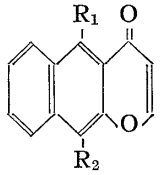


Fig. 1.



		R_1	R_2
I	———	H	H
II	·····	H	OH
III	—·—·—	OH	OH
IV	– – – –	MeO	H
V	—·—·—	MeO	MeO

Result and Discussions

1) 2-Methyl-6,7-benzochromones (linear benzochromones)

The main absorptions of these compounds are located at 220, 250, and 380 mμ, and the fine structure appears at near 300 mμ. The fine structure of each compound is consisted of three absorption peaks of which intervals are almost regularly 12 to 14 mμ. It is, therefore, considered that the fine structure is due to the benzenoid band displaced from 250mμ with increasing of conjugation system. Substituents on the aromatic ring afford regular spectral changes in wave length and

*1 Part VI: This Bulletin, **12**, 312 (1964).
*2 Oshika, Shizuoka (福島清吾, 赤堀幸男, 上野 明).
1) G. Illing: Arzneimittel Forschung, **7**, 497 (1957).
2) B.W. Bycroft, T.A. Dobson, J.C. Roberts: J. Chem. Soc., **1962**, 40.
3) O.L. Galmarini, F.H. Stodola, K.B. Paper, O.F. Fennell: Nature, **195**, 502 (1962).
4) H. Schmid, H. Seiler: Helv. Chim. Acta., **35**, 1990 (1952).

the enhanced effect is observed in the longer wave length region. Therefore, comparison was made on the longest absorption maxima.

Replacement of methoxyl group at 8-position in 2-methyl-5,8-dimethoxy-6,7-benzochromone (V) with hydrogen, *i.e.* IV, results in hypsochromic shift of 14 mμ. Introduction of two hydroxyl groups at 5- and 8-positions of 2-methyl-6,7-benzochromone, *i.e.* III,

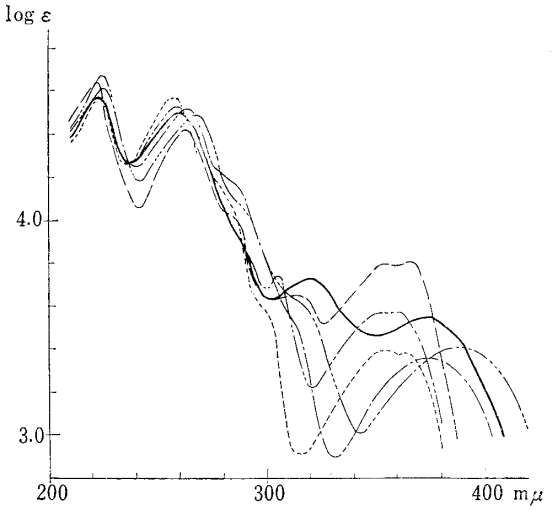


Fig. 2.

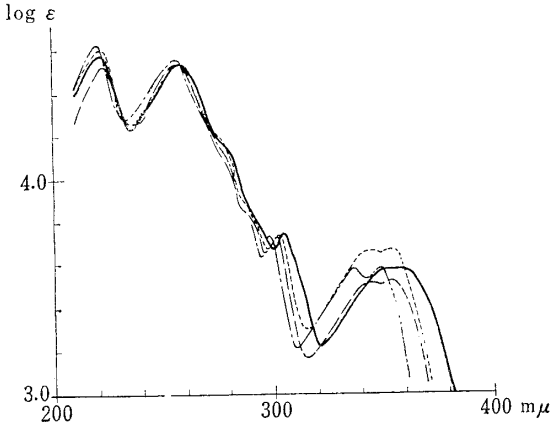
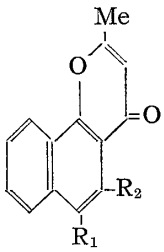
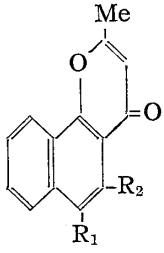


Fig. 3.



		R_1	R_2
XV:	------	OH	H
XVI:	-·-·-·-	H	OH
XVII:	·····	H	MeO
XVIII:	———	OH	MeO
XIX:	—··—··	MeO	MeO
XX:	—···—···	MeO	OH



		R_1	R_2
XXI:	------	AcO	MeO
XXII:	·····	MeO	AcO
XXIII:	-·-·-·-	AcO	AcO
XIX:	———	MeO	MeO

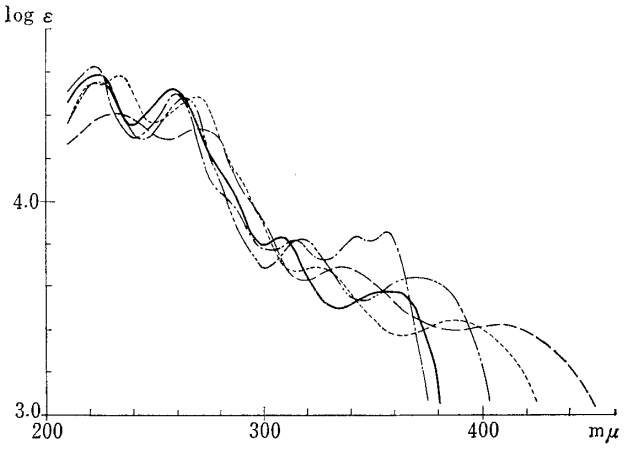


Fig. 4.

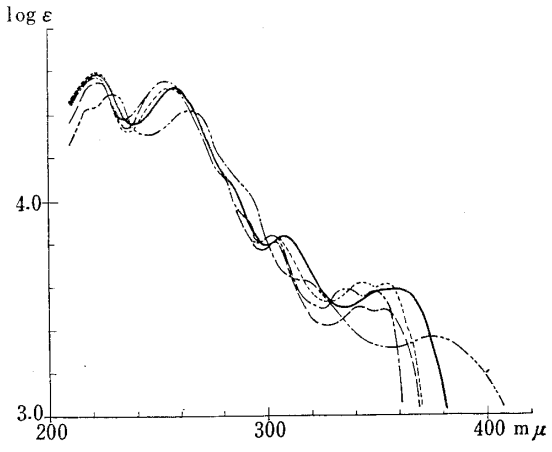
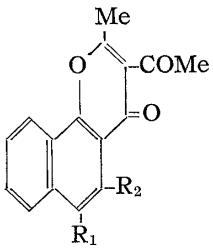
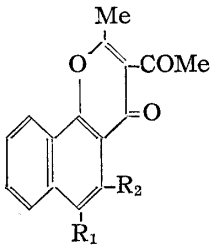


Fig. 5



		R_1	R_2
XXVIII:	-·-·-·-	MeO	H
XXIX:	·····	MeO	OH
XXX:	—··—··	OH	MeO
XXXI:	———	MeO	MeO
XXXII:	------	OH	OH



		R_1	R_2
XXXI:	———	MeO	MeO
XXXIII:	·····	MeO	AcO
XXXIV:	------	AcO	MeO
XXXV:	-·-·-·-	AcO	AcO
XXXVI:	—··—··	AcO	OH

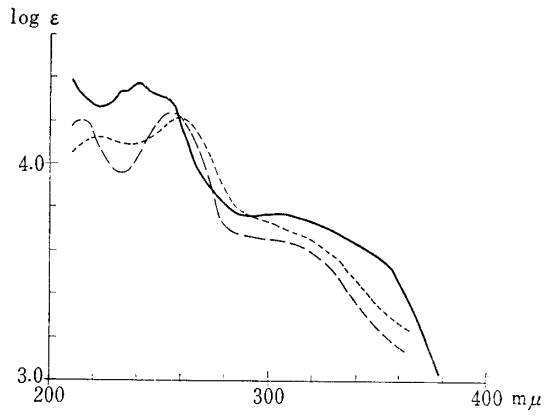
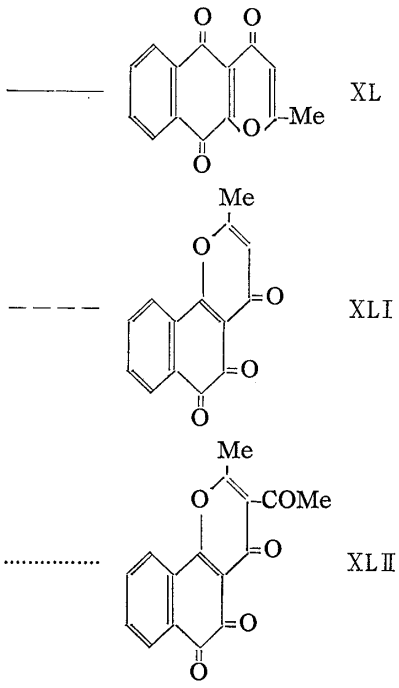


Fig. 6.



displaces the band to longer wave length, and the strong bathochromic effect is adequately explained to be due to formation of the *ortho*-quinoid by contribution of the free hydroxyl group at 5-position, as already known in the cases of *o*-hydroxybenzaldehyde and its analogues.[5]

The interrelation of the ultraviolet spectra of the three compounds is in accordance with the empirical evidences.[6]

In contrast, replacement of hydrogen atom at 8-position in 2-methyl-6,7-benzochromone (I) with hydroxyl group, *i.e.* II, shows no spectral change, and no remarkable change is found when the spectra of 2-methyl-6,7-benzochromone (I) and 2-methyl-8-hydroxy-6,7-benzochromone (II) are compared with that of 2-methyl-5,8-dimethoxy-6,7-benzochromone (V). The compounds (I and II) unexpectedly have absorption bands at 16 mμ longer position than that of 2-methyl-5-methoxy-6,7-benzochromone (IV) and the anomalous phenomenon may be attributed to the nature of hydrogen at 5-position of the aromatic ring, common in the compounds (I and II). Furthermore, anomalous effect of free hydroxyl group at the 8-position may also be considered, although the reason is not clear.

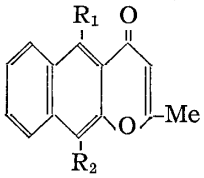
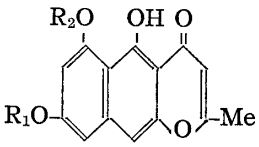
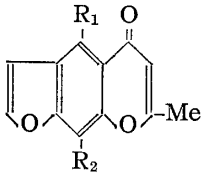
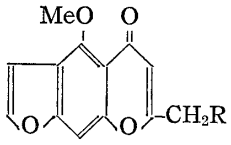
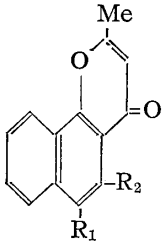
Existences of two K-bands at 225 and 280 mμ, of fine structure at 300 mμ and of other band in longer wave length region in rubrofusarin[1] (VI), norrubrofusarin[1] (VII), rubrofusarin monomethyl ether[1] (VIII) and fonsecin[2] (IX), are completely in accordance with the results obtained from synthetic compounds in the present study. Concerning absorption bands in longer wave length region, the bands of natural compounds are in longer region than those of synthetic compounds, and the reason can be denoted to the increasing of oxygen functions, especially free hydroxyl group at *peri*-positon of carbonyl oxygen in the γ-pyrone ring.

Among the natural compounds, the structure of rubrofusarin was confirmed by X-ray crystal analysis. The structures of the synthetic compounds, except 2-methyl-5-methoxy-6,7-benzochromone (IV), are undoubted because the routes of their syntheses have no unambiguous point.

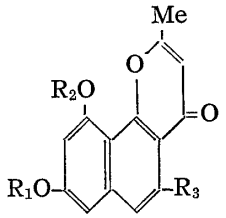
In natural furochromones, replacement of methyl group at 2-position of visnagin (XI) with carbonol group, *i.e.* khellol (XIII) or its glucoside (XIV), shows no remarkable change on their ultravoilet spectra. Thus khellin (X), visnagin (XI), khellol (XIII) and

5) K. Sone : J. Am. Chem. Soc., **75**, 5207 (1953); L. N. Ferguson : Chem. Revs. **43**, 385 (1948).
6) K. Hirayama : Zikken Kagaku Koza, **1**, 151, 214 (1957); R. A. Friedel, M. Orchin : "Ultraviolet Spectra of Aromatic Compounds." John Wiley & Sons, Inc., New York, (1951).

TABLE I.

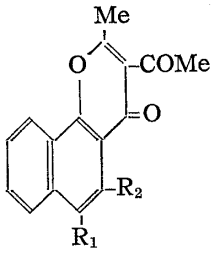
Compounds R1	R2	R3	λmax (log ε)					References
A) 6,7-Benzochromone derivatives (linear benzochromones)								
								
I	H	H	225 (4.25)	251 (4.66)	267[a] (4.40)	280[a] (4.25)	300[a] (3.40)	
			314 (3.40)	328 (3.25)	356[a] (3.50)	380 (3.61)		
II	H	OH	225 (4.16)	251 (4.63)	270[a] (4.36)	279[a] (4.25)	301 (3.38)	
			314 (3.43)	328 (3.26)	356[a] (3.55)	382 (3.64)		
III	OH	OH	220[a] (4.19)	255[a] (4.32)	269 (4.46)	275 (4.46)	312[a] (3.47)	
			323 (3.43)	341 (3.40)	427 (3.41)			
IV	MeO	H	218 (4.29)	248 (4.80)	260[a] (4.45)	278[a] (3.84)	293 (3.51)	
			304 (3.68)	316 (3.56)	366 (3.69)			
V	MeO	MeO	221 (4.10)	251 (4.72)	270[a] (4.30)	278[a] (3.95)	297 (3.41)	
			308 (3.53)	321 (3.36)	380 (3.72)			
								
VI	Me	H	225 (4.45)	278 (4.68)	326 (3.51)	406 (3.74)		2)
VII	H	H	225 (4.45)	250[a] (4.29)	280 (4.64)	330 (3.48)	414 (3.74)	2)
VIII	Me	Me	226 (4.47)	275 (4.73)	329 (3.45)	345 (3.46)	387 (3.67)	2)
IX	H	Me	233 (4.42)	275 (4.50)	321 (3.86)	332 (3.90)	400 (3.94)	3)
B) Furochromones								
								
X	MeO	MeO	220[a] (4.21)	248 (4.54)	260[a] (4.30)	282 (3.66)	332 (3.67)	
XI	MeO	H	220[a] (4.2)	250 (4.6)	290[a] (3.6)	340 (3.7)		1), [b]
XII	OH	MeO	250 (4.5)	260 (4.6)	300[a] (3.6)	360 (3.4)		1), [b]
								
XIII	OH		220 (4.2)	250 (4.6)	290[a] (3.7)	330 (3.7)		1), [b]
XIV	O-gl.[c]		220[a] (4.1)	250 (4.6)	290 (3.7)	330 (3.7)		1), [b]
C) 2-Methyl-7,8-benzochromone derivatives (angular benzochromones)								
								
XV	OH	H	221 (4.64)	263 (4.42)	283[a] (4.02)	304 (3.66)	365 (3.81)	

XVI	H	OH	224 (4.67)	265 (4.51)	280[a] (4.21)	310[a] (4.62)	375 (3.36)	
XVII	H	MeO	213 (4.57) 355 (3.38)	258 (4.56)	273[a] (4.26)	286[a] (4.01)	299[a] (3.60)	
XVIII	OH	MeO	221 (4.56)	260 (4.50)	285[a] (3.93)	320 (3.73)	374 (3.55)	
XIX	MeO	MeO	222 (4.57) 353 (3.61)	259 (4.53)	277[a] (4.17)	293[a] (3.80)	306 (3.76)	
XX	MeO	OH	225 (4.61)	268 (4.47)	290[a] (4.03)	315[a] (3.65)	389 (3.40)	
XXI	AcO	MeO	222 (4.53) 344 (3.48)	257 (4.52) 352 (3.49)	278[a] (4.09)	288[a] (3.85)	301 (3.70)	
XXII	MeO	AcO	221 (4.60) 343 (3.65)	259 (4.52) 353 (3.66)	278[a] (4.14)	290[a] (3.83)	302 (3.73)	
XXIII	AcO	AcO	220 (4.62) 299 (3.74)	248[a] (4.50) 320[a] (3.36)	256 (4.55) 335 (3.57)	277[a] (4.13) 348 (3.57)	287[a] (3.86)	
XXIV	MeO	H	220 (4.40) 340 (3.83)	260 (4.46) 348 (3.82)	276[a] (4.12)	290[a] (3.74)	308 (3.72)	4)
XXV	H	H	218 (4.62) 330 (3.95)	255 (4.56)	268[a] (4.33)	308[a] (3.42)	325 (3.68)	4)



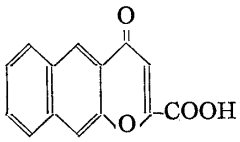
XXVI	H	H	Me	240 (4.62)	273 (4.48)	362 (4.00)		2), 4)
XXVII	Me	Me	OH	241 (4.58)	282 (4.35)	370 (3.67)		2)

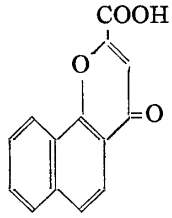
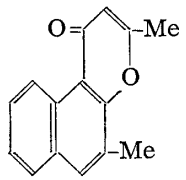
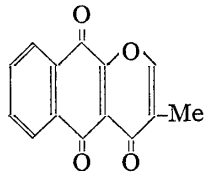
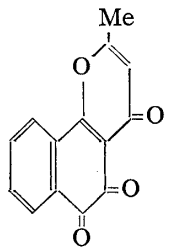
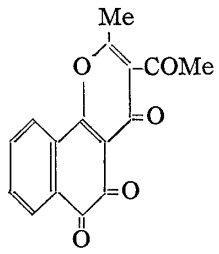
D) 3-Acetyl-2-methyl-7,8-benzochromone derivatives



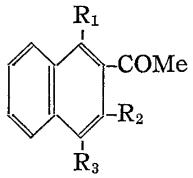
XXVIII	MeO	H	221 (4.62) 356 (3.85)	260 (4.49)	285[a] (3.99)	313 (3.81)	343 (3.83)
XXIX	MeO	OH	220 (4.55) 323 (3.69)	228[a] (4.56) 390 (3.44)	233 (4.57)	270 (4.48)	295[a] (4.07)
XXX	OH	MeO	223 (4.55)	265 (4.47)	280[a] (4.06)	320 (3.85)	372 (3.65)
XXXI	MeO	MeO	224 (4.58)	258 (4.53)	285[a] (4.03)	309 (3.83)	356 (3.57)
XXXII	OH	OH	233 (4.40)	274 (4.33)	336 (3.69)	407 (3.41)	
XXXIII	MeO	AcO	222 (4.59) 355 (3.60)	255 (4.52)	280[a] (4.12)	305 (3.82)	342 (3.61)
XXXIV	AcO	MeO	223 (4.55) 354 (3.49)	254 (4.55)	280[a] (4.12)	304 (3.86)	343 (3.50)
XXXV	AcO	AcO	222 (4.57) 302 (3.83)	253 (4.55) 320[a] (3.51)	260[a] (4.49) 335 (3.56)	279[a] (4.17) 350 (3.56)	288[a] (3.92)
XXXVI	AcO	OH	218[a] (4.40) 315[a] (3.64)	230 (4.50) 376 (3.35)	261 (4.41)	270[a] (4.38)	285[a] (4.18)

E) Miscellaneous

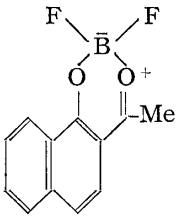
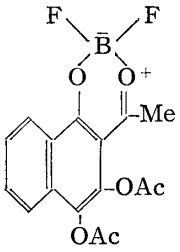
XXXVII			250 (4.7)	285[a] (4.0)	308 (3.7)	320 (3.7)	385 (3.7)	4), [b]

XXXVIII		260 (4.7)	280[a] (4.5)	296 (4.0)	328 (3.7)	344 (3.7)	4), [b]
XXXIX		228 (4.4)	260 (4.3)	270[a] (4.2)	308 (3.9)		4), [b]
XL		233[a] (4.32)	241 (4.37)	253[a] (4.31)	270[a] (3.92)	305 (3.78)	
XLI		216 (4.25)	260 (4.24)	310 (3.63)			
XLII		220 (4.12)	258 (4.22)	320[a] (3.65)			

F) Polyhydroxy-2-acetylnaphthalene derivatives



XLIII	OH	OH	AcO	223 (4.38)	265 (4.21)	275[a] (4.19)	292 (4.19)	325[a] (3.53)
XLIV	OH	AcO	AcO	219 (4.51)	244[a] (4.27)	258 (4.38)	268[a] (4.31)	284[a] (3.86)
				296[a] (3.74)	308[a] (3.46)	378 (3.70)		
XLV	AcO	AcO	AcO	223 (4.54)	240[a] (4.38)	250[a] (4.13)	277[a] (3.77)	284 (3.82)
				295[a] (3.71)	330 (3.25)			
XLVI	MeO	AcO	AcO	223 (4.63)	243[a] (4.35)	253[a] (4.24)	275[a] (3.74)	286 (3.78)
				296[a] (3.67)	330 (3.27)			
XLVII	MeO	MeO	AcO	229 (4.73)	250[a] (4.06)	285 (3.71)	295[a] (3.63)	326 (3.14)
XLVIII	MeO	OH	MeO	226 (4.63)	237[a] (4.56)	258 (4.49)	299 (3.77)	314[a] (3.51)
				344 (3.26)	396[a] (3.15)			
XLIX	MeO	MeO	OH	212 (4.40)	240 (4.47)	260[a] (3.78)	302 (3.63)	332 (3.49)
L	OH	MeO	MeO	223 (4.57)	265 (4.45)	274 (4.44)	290[a] (3.90)	300[a] (3.75)
				314[a] (3.30)	396 (3.64)			
LI	OH	OH	H	222 (4.41)	263[a] (4.27)	275 (4.31)	286[a] (4.20)	300[a] (4.00)
				312 (3.70)	403 (3.43)			
LII	OH	MeO	H	221 (4.60)	261 (4.46)	271 (4.44)	285[a] (4.00)	296 (3.98)
				305[a] (3.82)	389 (3.49)			

LIII	MeO	OH	H	224 (4.54) 304[a] (3.62)	256 (4.39) 336 (3.09)	264[a] (4.33) 398 (3.09)	285[a] (3.79)	294 (3.73)	
LIV	MeO	MeO	H	228 (4.73) 316[a] (3.11)	250[a] (4.21) 330 (3.23)	268[a] (3.75)	277 (3.72)	287[a] (3.57)	
LV	OH	H	H	265 (4.5)	285 (3.7)	295 (3.7)	308 (3.4)	370 (3.7)	7), [b]
LVI				265 (4.5)	285 (3.7)	295 (3.7)	310 (3.4)	370 (3.7)	7), [b]
LVII				260 (4.5) 370 (3.8)	270 (4.5)	285 (3.8)	295 (3.8)	310 (3.6)	7), [b]

a) inflexion point
b) values taken from figure
c) glucose

khellol glucoside (XIV) gave similar ultraviolet spectra, and khellinol (XII) shows bathochromic shift due to the free hydroxyl group at the 5-position.

2) 2-Methyl-7,8-benzochromones (angular benzochromones)

In the ultraviolet spectra of angular benzochromones, there is no fine structure which observed in linear benzochromones, but several shoulders, in addition to a small peak at 300 mμ, appear on the slope of K-band located at 260 mμ. The two K-bands are located at 220 mμ and 260 mμ, and the second band at 260 mμ shifts to longer wave length by 10 mμ in linear compounds. The relative intensities of these two K-bands show marked difference in angular and linear series; in angular compounds molecular extinctions of the shorter and the longer wave length K-bands are almost equal, while in linear compounds molecular extinction of the longer wave length K-band is approximately two times that of the shorter wave length K-band. The ultraviolet spectra of angular benzochromones are collected in Table I, and their interrelations are shown in Fig. 8.

Among six compounds, *i.e.* 2-methyl-5-hydroxy-7,8-benzochromone (XVI), 2-methyl-5,6-dimethoxy-7,8-benzochromone (XIX), 2-methyl-5-hydroxy-6-methoxy-7,8-benzochromone (XX), 2-methyl-5-methoxy-6-acetoxy-7,8-benzochromone (XXI), 2-methyl-5-acetoxy-6-methoxy-7,8-benzochromone (XXII) and 2-methyl-5,6-diacetoxy-7,8-benzochromone (XXIII), the relations between their structure and spectra are similar to those in linear benzochromones as mentioned above.

The ultraviolet spectrum of 2-methyl-6-methoxy-7,8-benzochromone[5] (XXIV) is identical with that of 5-methoxy isomer (XVII). This result is quite reasonable, but introduction of free hydroxy groups affords unexpected results.

Introduction of free hydroxyl group at 6-position of 2-methyl-5-methoxy-7,8-benzochromone (XVII), *i.e.* XVIII, shows bathochromic shift of 20 mμ which is fairly larger than in usual cases. It is notable that 2-methyl-6-hydroxy-7,8-benzochromone (XV) and 2-methyl-5-methoxy-7,8-benzochromone (XVII) absorb at longer wave length than 5,6-dimethoxy derivative (XIX).

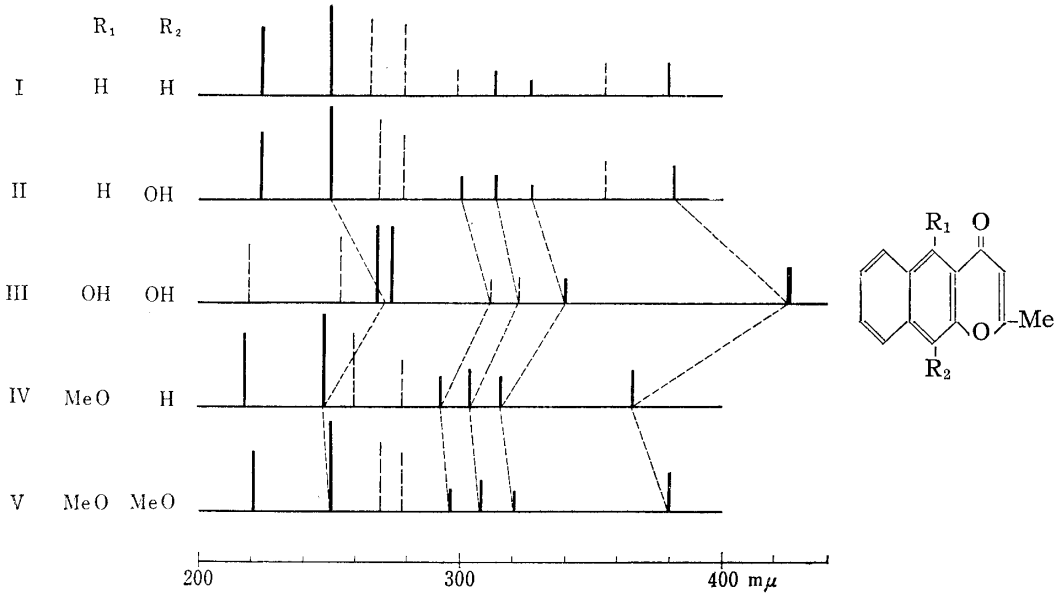


Fig. 7.

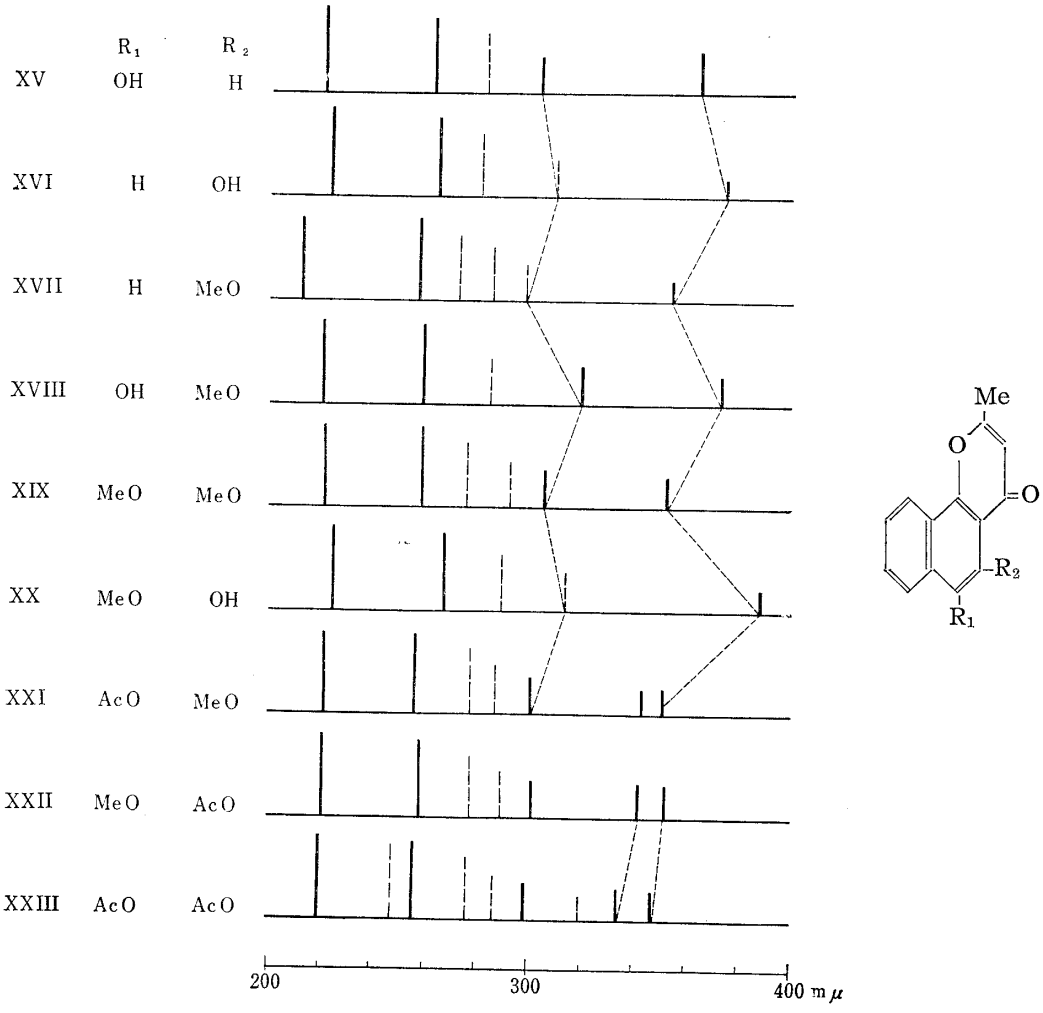


Fig. 8.

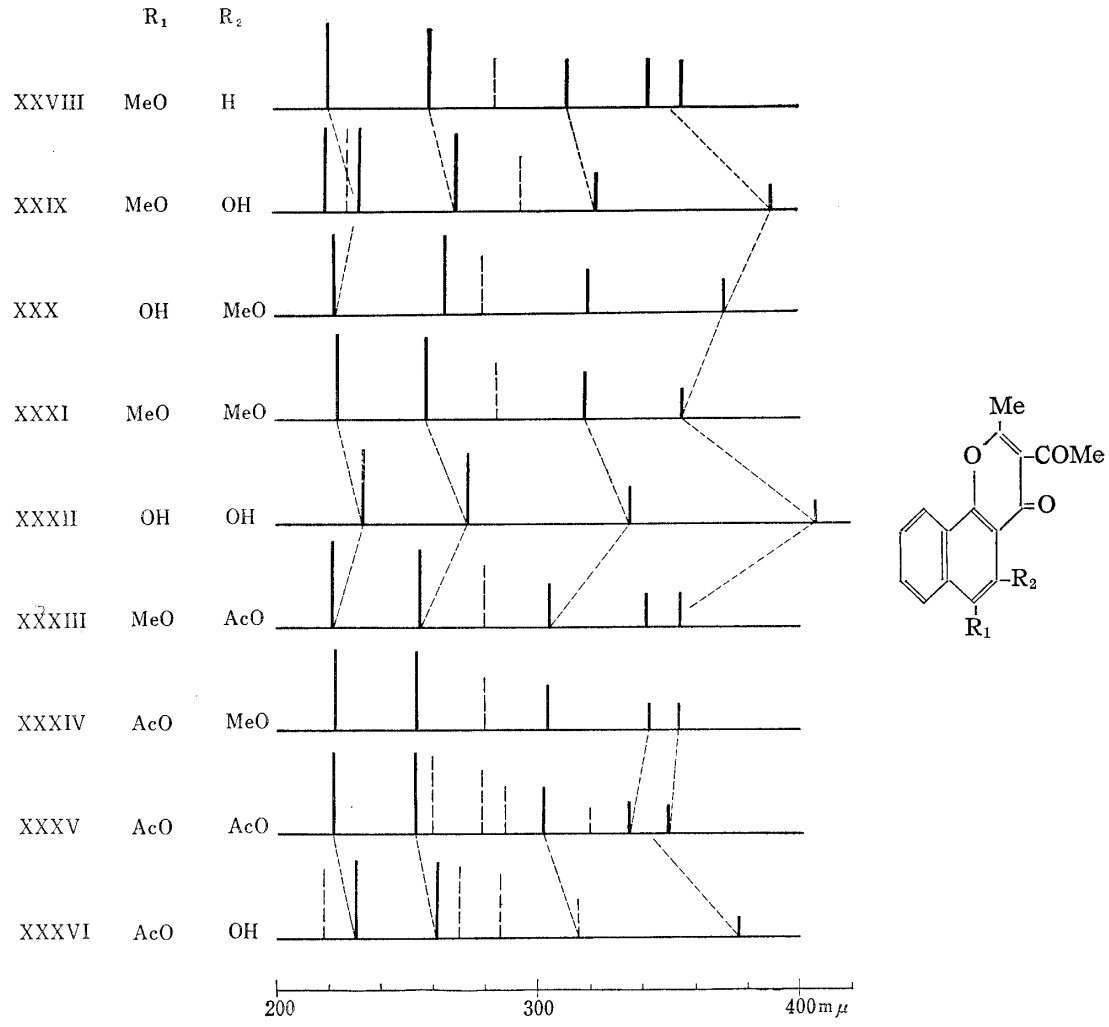


Fig. 9.

Although these three compounds (XV, XVII, and XVIII) show agreement with respect to the direction of shift, they absorb at extraordinary longer wave length when compared with the other six compounds in this series, *i.e.* XIX, XX, XXI, XXII, XXIII, and XVI. From these facts, it is suggested that free hydroxyl group at 6-position and hydrogen atoms at 5- and 6-position have somewhat anomalous effects on the band displacement. This assumption can be supported by the fact that the ultraviolet spectrum of the parent compound, 2-methyl-7,8-benzochromone[4] (XXV), shows the identity with that of dimethoxy derivative (XIX).

The spectra of natural compounds, eleutherinol (XXVI) and flavasperone (XXVII) give reasonable results, when compared with those of synthetic compounds.

The structures of all compounds which were cited in the above discussion have been unambigously established by their synthetic routes and reactions with only one exception of 2-methyl-5-methoxy-7,8-benzochromone (XVII).

The ultraviolet spectra of the compound (XVII) and its isomer (IV) show the characteristic features of angular and linear benzochromones, respectively.

Alkali degradation of the compound (XVII) affords 2-acetyl-3-methoxy-1-naphthol (LII), and partial methylation of 2-acetyl-1,3-naphthalenediol (LI) yields its isomer, 1-methoxy-2-acetyl-3-naphthol (LIII). The infrared and ultraviolet spectra of LII and LIII reasonably support the structures described above. These findings give powerful reasons to assign the structures of the compounds (IV and XVII) to linear and angular, respectively.

The ultraviolet spectrum of 2,8-dimethyl-5,6-benzochromone[4] (XXXIX) shows marked change comparing with that of 2-methyl-7,8-benzochromone (XXV). This effect may be contributed to the difference of ring fusion.

3) 2-Methyl-3-acetyl-7,8-benzochromones (angular 3-acetyl benzochromones)

The ultraviolet spectra of the compounds are quite similar to those of angular benzochromones described in section 2. The effects of nuclear substituents are completely in accordance with the cases described above. The relations between structural and spectral changes are shown in Fig. 9, and it was found that application of the empirical rules[6] is always adequate to explain the each process except only one case of 2-methyl-3-acetyl-5-methoxy-6-hydroxy-7,8-benzochromone (XXX).

The cause of the irregular property of this compound may be considered to be as same as in the case of section 2.

Dihydroxy compounds (III and XXXII) in the diluted solution are fairly unstable under the usual condition, and afford the spectra identical with those of the corresponding quinones, respectively. To avoid the air oxidation, the spectra of these compounds are measured as rapidly as possible, but the accuracy of the data cannot be freed from doubt.

4) Quinones

The spectra of quinones, XL, XLI, and XLII, show characteristic and rather monotonous shapes, and they can be easily distinguished from those of linear benzochromones.

5) Polyhydroxy-2-acetylnaphthalenes

Polyhydroxy-2-acetylnaphthalenes were used for preparation of benzochromones, and some of naphthalene derivatives were obtained by degradation of benzochromones to identify their structures. The ultraviolet spectra of these naphthalene derivatives were measured and collected in Table I.

Etherification and esterification of the free hydroxyl groups give the striking changes on their ultraviolet spectra, and their interrelations are quite complicated.

It is, however, to be noted that 2-acetyl-1-naphthol (LV) and 2-acetyl-3,4-diacetoxy-1-naphthol (XLIV) afforded borondifluoride complexes (LVI) and (LVII), respectively, and that there is no spectral change between the starting materials and the complexes in both of the series.[7] In present study, the spectra of polyhydroxy-2-acetylnaphthalene derivatives are considerably sensitive to replacement of the phenolic hydrogen with alkyl or acyl groups.

Conclusions

Concerning with ultraviolet spectra of benzochromones, the following conclusions are obtained.

1) The ultraviolet spectra of linear and angular benzochromones show three remarkable differences; the fine structure near 300 mμ, relative intensity of two K-bands and the longest wave length absorption maximum.

2) In both of the series, replacement of substituents on the aromatic ring affords the regular shift on their spectra with only a few exception. On the other hand, replacement of substituents on the γ-pyrone ring gives only slight changes. And these changes on the spectra by replacement of substituents are too small to compare with the difference between linear and angular series.

7) D. J. Cram : J. Am. Chem. Soc., **71**, 3953 (1949).

These conclusions indicate that the electronic state of these compounds is mainly dependent upon the type of the ring fusion, and it is closely analogous to the case of polycyclic aromatic compounds.[8] Concerning the biological activity of polycyclic aromatic compounds, it is known that carcinogenic activity is found in some of angular series and not in linear series. It is of interest whether or not the similar relation between ring system and biological activity will be found in these benzochromone series.

Experimental

Apparatus and condition: Hitachi Recording Spectrophotometer ESP-2U; period 1, photomultiplier sensitivity 1, scale AB 0~1 and 1~2, scanning speed 4 and 2.
Solvent: 99% EtOH. Samples: analytical grade.

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Summary

The ultraviolet spectra of benzochromones and the related compounds were measured and compared with those of natural benzochromones. The spectra of linear benzochromones are distinguished from those of angular compounds by their characteristic absorption bands. In each series, regular shift were observed by replacement of substituents.

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8) W. V. Mayneord, E. M. F. Roe: Proc. Roy. Soc. (London), **A 152**, 299 (1935); **A 158**, 634 (1937).

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47. Haruyuki Ito: Synthesis of Nitro Compounds by Means of Oxidation of Acylamino Compounds. IX.*1 On the Reaction Mechanism.

(*Shizuoka College of Pharmacy**2)

A new reaction which affords nitro compounds by hydrogen peroxide oxidation of acylamino compounds has been described and developed by Kosuge.[1] In the part IV[2] of this series, the reaction was assumed to proceed with an initial oxidation of the acylamino group to acylamine N-oxide, followed by the hydrolysis of the acyl group to a free amine N-oxide due to the low electron density of carbon-nitrogen bond with an N-oxide formation and the amine N-oxide is oxidized to a nitro compound with an additional hydrogen peroxide as shown in Chart 1.

*1 Part VIII. T. Kosuge, S. Miyashita: This Bulletin, 2, 397 (1954).
*2 Oshika, Shizuoka (伊藤晴之).
1) T. Kosuge: Kenkyu Nenpo (Faculty of Pharm., Univ. of Kanazawa) 2, 3 (1952).
2) *Idem*: *Ibid.*, 2, 22 (1952).