Tetrahedron. Vol. 24, pp. 6053 to 6073. Pergamon Press 1968. Printed in Great Britain

ELECTRONIC SPECTRA OF SUBSTITUTED NAPHTHOQUINONES*

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(*Received in USA* 8 *March* 1968; *accepted for publication* 13 *May* 1968)

Abstract—Echinoderms elaborate many closely related structural pigments (spinochromes) based on a naphthoquinone skeleton. As an aid to structural elucidation of these compounds the electronic spectra of a large number of substituted naphthoquinones were examined. The bands in the 240–600 mμ region of the electronic spectra of 1,4-naphthoquinone, juglone, and naphthazarin have been assigned to either benzenoid or quinoid electronic excitations and the effect of substitution on the position of these bands has been systematically studied. As a result, a number of empirical correlations have been derived that are useful in the structure determination o f unknown pigments.

CONCURRENTLY with a systematic NMR.[1] ESR.[2] and mass spectrometric[3] investigation of substituted naphthoquinones we also studied the electronic spectra of this class of compounds. Very few such data have been recorded in the literature[4, 5] and we needed electronic spectral data of these compounds to facilitate our structural elucidation of echinoderm pigments.[6, 7] Even though electronic absorption spectroscopy has severe limitations as a structural tool, we were nevertheless able to derive a number of empirical correlations. As a result, the structures of some unknown pigments could be predicted from an examination of their electronic spectra and chromatographic behavior.[7] We first studied the spectra of naphthoquinones; we then examined the spectra of juglone derivatives; we finally undertook a detailed examination of the spectra of naphthazarins. This report summarizes our findings.

1,4-*Naphthoquinones.* The diagnostic features of the electronic spectrum of a 1,4-naphthoquinone which is *unsubstituted* in the benzenoid ring are (1) intense benzenoid and quinoid electron-transfer[8] (E.T.) bands in the 240–290 mμ region (ε 13,000–25,000), (2) a benzenoid E.T. band at about 335 mμ of medium intensity (ε 2600–3200), (3) a quinoid E.T. band in the 330–450 mμ region of low to medium intensity that is generally only observed for 2,3-disubstituted compounds, and finally (4) a broad local excitation[8] (L.E.) band of low intensity (ε < 100) in the 400–500 mμ region attributable to the n → π* transition of the quinone carbonyls.

In the spectrum of 1,4-naphthoquinone (**1**, Fig. 1), the peaks at 245 (ε 22,100) and 251 mμ (ε 23,450) are due to benzenoid E.T. processes and shift only slightly with

* This investigation was supported by PHS Research grant GM 10413 from the Institute of General Medical Sciences.

† Grantee of the East-West Center, 1963–66.

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§ NDEA Fellow, 1960–63; NIH Predoctoral Fellow, 1963–64.

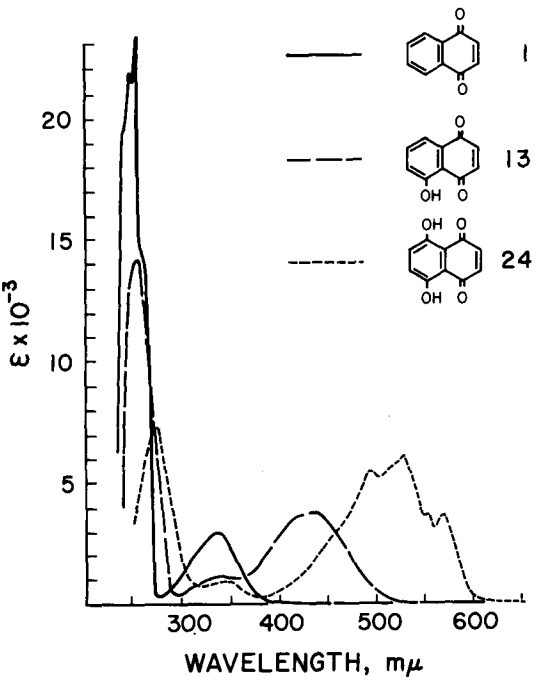
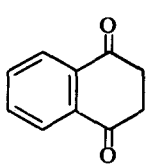


FIG. 1 Electronic absorption spectra of 1,4-naphthoquinone, juglone, and naphthazarin in chloroform.

substitution in the quinoid ring (Table 1). The quinoid E.T. transitions [shoulder at 257 mμ (ε 13,100)], on the other hand, are quite sensitive to substitution in the quinoid ring (Table 1). Note that the benzenoid bands of 2-hydroxy-1,4-naphthoquinone (**3**) appear at essentially the same positions as in **1** itself, but that the quinoid bands have shifted bathochromically to 277 (ε 15,900) and 283 mμ (ε 15,960).

The band at 335 mμ (ε 3040) in the spectrum of 1,4-naphthoquinone (**1**) (Fig. 1) is assigned to a benzenoid E.T. transition and as expected its position appears to be relatively independent of substitution in the quinoid ring (Table 1). Although the quinone carbonyls insulate the aromatic portion from the quinoidal double bond and its substituents, the presence of the double bond does facilitate this excitation. The band position in **1** is bathochromically displaced by 40 mμ from the corresponding E.T. transition for 2,3-dihydro-1,4-naphthoquinone (**12**) [295 mμ (ε 2100) in ethanol[9]].



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The quinoid E.T. transition in the 330–450 mμ region is not usually discernible in the spectra of 1,4-naphthoquinone and its 2-substituted derivatives [see for example

the spectrum of 2-methoxy-1,4-naphthoquinone (**4**, Fig. 2)] because of its low intensity and because it is masked by the larger benzenoid band at 335 mμ. The band cannot be seen in the spectrum of 1,4-naphthoquinone (Fig. 1). In the spectra of 2-hydroxy- (**3**, Table 1) and 2-methoxy-1,4-naphthoquinone (**4**, Fig. 2), however, an appreciable bathochromic shift of the quinoid E.T. band and enhancement of its intensity has been engendered by the electron-releasing substituent to produce an inflection at 380 mμ. In all 2,3-disubstituted derivatives bearing strong electron-donating groups, the bathochromic shift of the quinoid band is sufficient to separate it entirely from the benzenoid band. The spectrum of 2-hydroxy-3-methoxy-1,4-naphthoquinone (**8**, Fig. 2), for example, displays the band at 418 mμ (ε 1320). This transition is not observed in the spectrum of 2-acetoxy-3-methyl-1,4-naphthoquinone (**6**, Table 1).

1,4-Naphthoquinone exhibits a broad L.E. band at about 425 mμ (ε 32) in isooctane; in chloroform this band appears as a shoulder on the much larger 335 mμ band. This transition is attributed to the $n \rightarrow \pi^*$ excitation of the quinone carbonyls.

Juglones. The diagnostic features of the electronic spectrum of a juglone (5-hydroxy-1,4-naphthoquinone) are (1) intense benzenoid and quinoid E.T. bands in the 240–320 mμ region (ε 7000–20,000), (2) a benzenoid E.T. band at about 425 mμ (ε 3000–5000), and (3) a quinoid E.T. band in the 320–420 mμ region (ε 1000–2500).

The benzenoid and quinoid E.T. bands of juglone (**13**) overlap and appear at essentially the same positions as in **1** (Fig. 1). Surprisingly the substitution at C-5 does not produce an appreciable shift of either transition. Substitution at C-6, however, does have an effect on the benzenoid E.T. band as shown in the spectrum of 6-hydroxy-1,4-naphthoquinone (**16**, Table 2), where the benzenoid E.T. band has shifted bathochromically by about 10 mμ and the position of the quinoid E.T. band has remained essentially unaltered. The benzenoid E.T. bands of **13** and **16** are comparable with o-hydroxycarbonyl and p-hydroxycarbonyl chromophores, respectively.[10] Substitution on the quinoid ring with an electron-releasing substituent causes a pronounced shift of the quinoid E.T. band [see the spectra of 2-hydroxyjuglone (**17**, Fig. 3) and 3-hydroxyjuglone (**18**, Fig. 4)] while the position of the benzenoid E.T. band remains essentially unchanged. As expected both benzenoid and quinoid E.T. bands shift bathochromically in the spectra of 3,7-dimethoxyjuglone (**20**, Fig. 5) and spinochrome B [2,3,7-trihydroxyjuglone (**21**), Table 2].

A benzenoid E.T. band of **13** appears in the visible region of the spectrum at 429 mμ (ε 3800); this is a bathochromic shift of almost 100 mμ as compared with the 335 mμ band of **1** (Fig. 1). The band may involve excitation of the non-bounding electrons of the hydroxyl group to the quinone carbonyl antibonding orbitals. Note that a hypsochromic shift occurs when the polarity of the solvent is increased (Table 2). The position of this band is not appreciably affected by further substitution on the benzenoid ring at positions 6 and/or 7 or by substitution in the quinoid ring. Substitution at the other peri position, however, exerts a dramatic effect. In the spectrum of naphthazarin [5,8-dihydroxy-1,4-naphthoquinone (**24**), Fig. 1] the benzenoid E.T. band is bathochromically displaced by about 100 mμ compared with the corresponding band of juglone.

The anionic form of the peri hydroxyl produces a large bathochromic shift of the visible peak (Fig. 5). A smaller red shift is observed when a quinoidal hydroxyl group is present in the molecule (Figs. 3 and 4). It is interesting to note the twinned appearance of the visible peak of 2-hydroxyjuglone (**17**) in strong base.

TABLE 1. ELECTRONIC ABSORPTION SPECTRA[a] OF 2- AND 2,3-SUBSTITUTED 1,4-NAPHTHOQUINONES

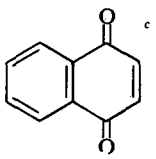
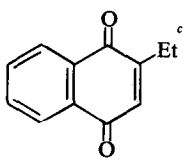
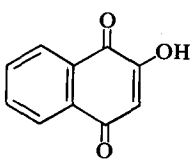
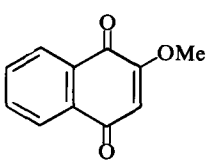
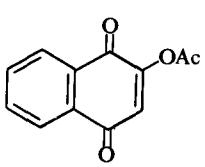
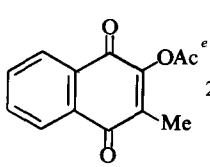
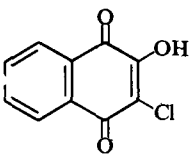
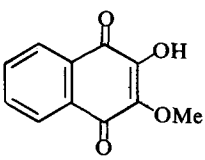
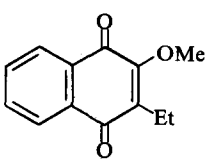
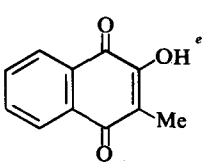
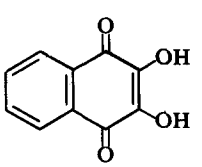
No.	Compound	λ_{max} (ε) of E.T. bands			
		Benzenoid	Quinoid	Benzenoid	Quinoid[b]
1		245 (22,100); 251 (23,450)	sh 257 (13,100)	335 (3040)	
2		245 (18,230); 251 (19,910)	259 (17,860); 268 (16,430)	335 (2680)	
3		244 (15,580); 250 (18,150)	277 (15,900); 283 (15,960)	337 (3020)	sh 380 (750)[d]
4		242 (16,680); 248 (17,950)	274 (16,260); 280 (16,300)	333 (2950)	
5		252 (17,800)	252 (17,800)	341 (3190)	
6		244, 250	264, 269	337	

TABLE 3—*continued*

No.	Compound	λ_{max} (ε) of E.T. bands			
		Benzenoid	Quinoid	Benzenoid	Quinoid[b]
7		252 (21,700)[a]	sh 281 (13,900); 286 (15,100)	340 (2950)	sh 380 (1270)
8		253 (17,790)	273 (13,900); sh 283 (13,280)	337 (2620)	418 (1320)
9		sh 245 (20,700); 252 (22,000)	280 (17,700); sh 288 (15,800)	338 (2990)	sh 388 (860)
10		sh 247, 252	281, sh 287	337	sh 385
11		262 (17,650)[f]	sh 274 (17,000; sh 288 (14,350)	335 (2275)	439 (1470)

[a] The spectra were determined in chloroform.

[b] This quinoid E.T. band for the monosubstituted 1,4-naphthoquinones is generally of low intensity (ε < 100) and masked by the benzenoid E.T. band near 335 mμ.

[c] The spectrum was determined immediately as an anomalous reaction with chloroform occurs on standing.

[d] In methanol: sh 380 mμ (ε 1000).

[e] Molar extinction coefficients were not determined.

[f] Even though no distinct inflections are discernible on the low wavelength side of this band, there is enough absorption at 245–255 mμ to indicate the presence of the more familiar 245 and 250 mμ bands.

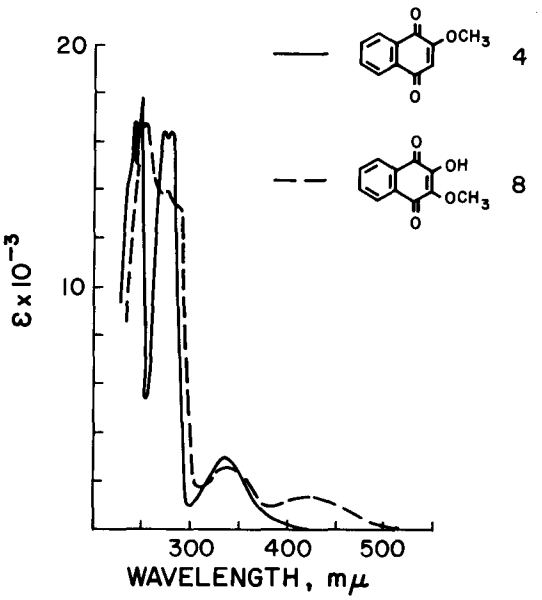


FIG. 2 Electronic absorption spectra of 2-methoxy-1,4-naphthoquinone and 2-hydroxy-3-methoxy-1,4-naphthoquinone.

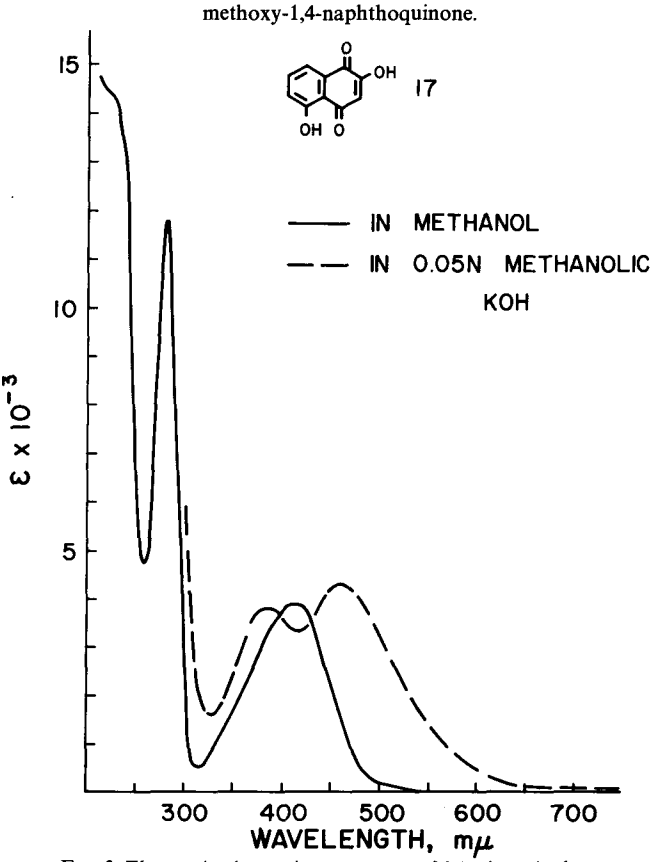


FIG. 3 Electronic absorption spectrum of 2-hydroxyjuglone.

The benzenoid E.T. band of **1** at 335 mμ is very sensitive to peri substitution. Even in 5-acetoxy-1,4-naphthoquinone (**15**) this band is bathochromically shifted by 10 mμ. Substitution at C-6 shows a less pronounced red shift, as in the spectrum of 6-hydroxy-1,4-naphthoquinone (**16**) where the E.T. band is found at 388 mμ. The visible E.T. absorptions of **21** (Table 2) and several other highly substituted juglones[7,11] have twin peaks which are generally centered about 425 mμ.

The band at 337 mμ (ε 1270) in the spectrum of **13** (Fig. 1) is tentatively assigned to a quinoid E.T. transition.

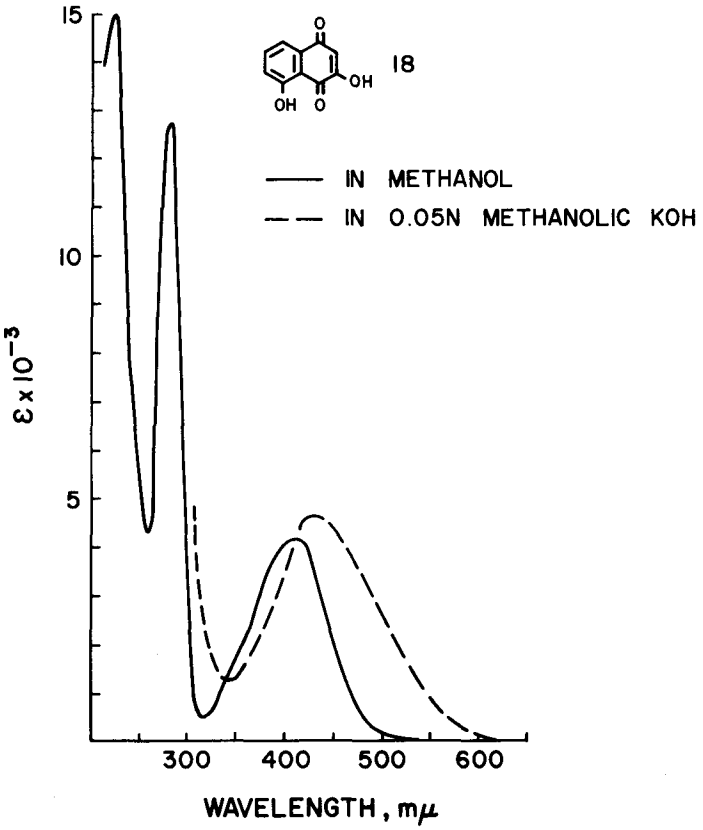
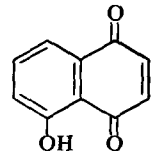
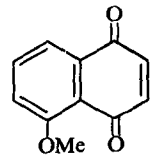
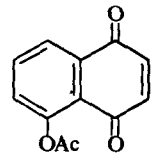
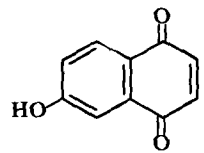


FIG. 4 Electronic absorption spectrum of 3-hydroxyjuglone.

Naphthazarins. The diagnostic features of the electronic spectrum of a naphthazarin (Fig. 1) are (1) a combined benzenoid and quinoid E.T. band in the 270–350 mμ region (ε 5000–10,000), (2) a benzenoid E.T. absorption of multibanded structure centered near 500 mμ (ε 6000–9000) and (3) a small quinoid E.T. band in the 330–500 mμ region (ε 000–1700).

The E.T. band in the 270–350 mμ region apparently is a combination of benzenoid and quinoid $p \rightarrow \pi^*$ excitations, which is not surprising when one considers the tautomeric nature of the naphthazarin system. Unlike 1,4-naphthoquinones and juglones which show two E.T. bands (one benzenoid and one quinoid) in this region, most naphthazarins exhibit only one E.T. band. The position of the E.T. band is important for elucidating the nature of β-substituents on the naphthazarin system.

TABLE 2. ELECTRONIC ABSORPTION SPECTRA OF JUGLONES AND 1,4-NAPHTHOQUINONES SUBSTITUTED ON THE BENZENOID RING

No.	Compound	Solvent	λ_{max}, mμ (ε) of E.T. bands			
			Benzenoid	Quinoid	Benzenoid	Quinoid[a]
13		$CHCl_3$	251 (14,320)	251 (14,320)	429 (3800), sh 415 (3640)	337 (1210)
		MeOH	248 (12,880)	248 (12,880)	422 (3630), sh 407 (3550)	sh 340 (1130)
14		$CHCl_3$	247 (17,590)	247 (17,590)	396 (3320)	sh 324 (1270)
15		$CHCl_3$	244 (17,700); 250 (18,100)	sh 259 (11,650)	345 (2850)	—[b]
16		$CHCl_3$	261 (19,520)	254 (19,900)	388 (2410)	sh 344 (1760)
		MeOH	259 (17,930)	254 (17,700)	374 (2880)	340 (2320)

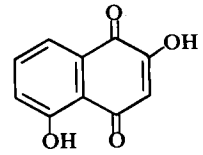
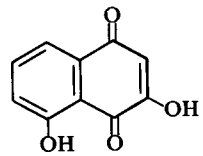
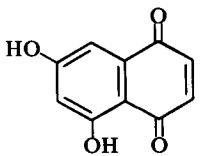
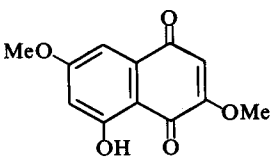
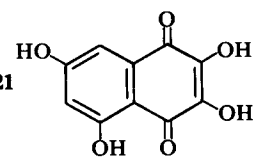
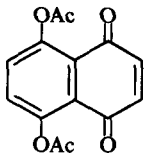
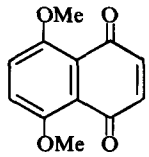
17		$CHCl_3$	240 (9980)	286 (12,600)	430 (3660); 418 (3610)	—[d]
		MeOH	n.d.[c]	282 (11,800)	409 (3920)	
18		$CHCl_3$	240 (7810)	283 (14,000)	419 (4410)	—[d]
		MeOH	n.d.	282 (12,760)	410 (4220)	
19		$CHCl_3$	263 (12,720)	sh 249 (10,920)	436 (3680)	sh 371 (2230)
20		$CHCl_3$	268 (10,900)	300 (15,380)	430 (4430)	—[d]
		MeOH	266 (11,230)	299 (14,520)	423 (4180)	
21		MeOH	270 (15,940)	320 (7790)	387 (2800), 470 (1440)	—[d]

TABLE 2—*continued*

No.	Compound	Solvent	λ_{max}, mμ (ε) of E.T. bands			
			Benzenoid	quinoid	benzenoid	quinoid[a]
22		$CHCl_3$	244 (16,540), 250 (16,620)	sh 259 (10,980)	355 (3190)	—[b]
23		$CHCl_3$ MeOH	255 (13,780) 254 (11,100)	255 (13,780) 254 (11,100)	445 (4340) 448 (4170)	313 (764) 324 (946)

[a] Tentative assignment.

[b] Band is presumably of low intensity (compare with 1,4-naphthoquinone) and masked by the larger benzenoid E.T. transition.

[c] Not determined.

[d] Band not observed. Substituents on quinoid ring should engender a bathochromic shift of the transition and the larger visible band may masking its position.

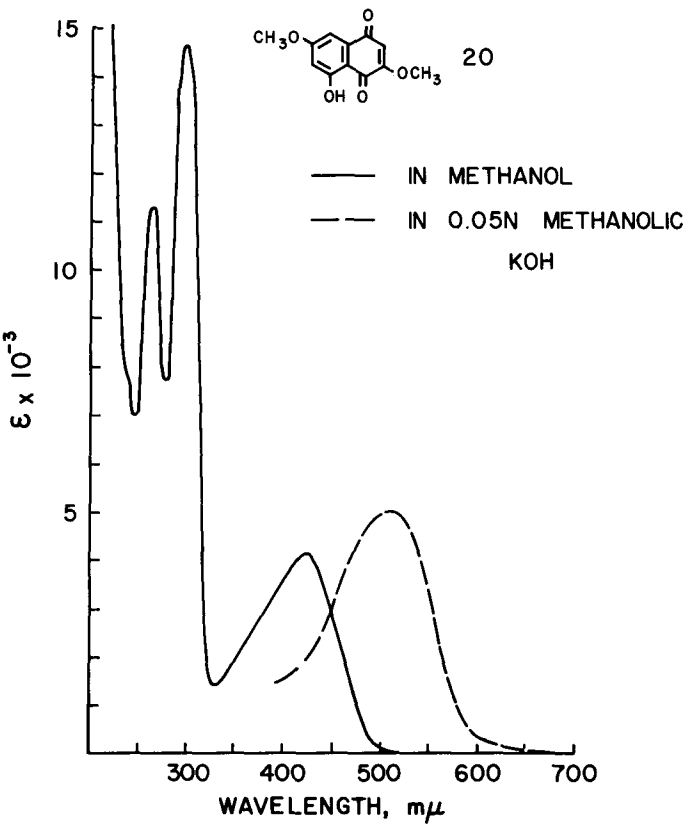
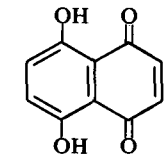
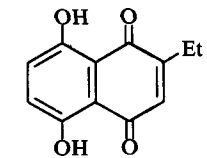
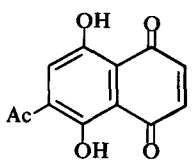
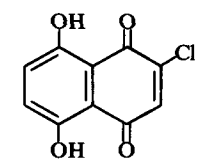


FIG. 5 Electronic absorption spectrum of 3,7-dimethoxyjuglone.

For example it can readily be seen from Table 3 and Fig. 6 that a 20 mμ bathochromic shift of the E.T. band is associated with each β-hydroxyl attached to the naphthazarin nucleus. Methoxy groups also shift the E.T. band dramatically to the red, although for adjacent methoxyls the effect is diminished due to less overlap of the *p*-orbital electrons of the sterically crowded methoxyl groups with the naphthazar in π-system. The p-orbital electrons of an acetylated β-hydroxyl group are not available for transfer to the naphthazarin π-system.[12] The net effect on the position of the E.T. band is therefore comparable to that of an alkyl group. Compare the spectra of 2-ethylnaphthazarin (**25**) and 2-acetoxynaphthazarin (**41**) (Table 3 and Fig. 7). As long as no alkoxyl or O-acyl groups are present, the position of the E.T. band immediately reveals the number of β-hydroxyls attached to the naphthazarin nucleus.

The visible band is attributed to E.T. $p \rightarrow \pi^*$ excitations of the non-bonding electrons of the peri hydroxyls. A blue shift is noted on increasing the polarity of the solvent and the visible band is, as a rule, shifted to shorter wavelengths by electron-donating substituents and to higher wavelengths by electron-withdrawing groups (Table 3). A large bathochromic shift results from the anionic form of the peri hydroxyl (Fig. 8) and only small shifts are engendered from anionic β-hydroxyls.

TABLE 3. ELECTRONIC ABSORPTION SPECTRA OF NAPHTHAZARINS

No.	Compound	Solvent	λ_{max}, mμ (ε) of E.T. bands		
			Benzenoid	Quinoid	Combination
24		$CHCl_3$	564 (3720), 547 (3630), 524 (6050), 490 (5420)	338 (990)	269 (7460)
		MeOH	553 (3070), 514 (5350), 484 (5170)	330 (1270)	267 (7160)
25		$CHCl_3$	553 (3840), 516 (6450), 502 (5920), 486 (5820)	343 (570)	278 (9260)
		MeOH	542 (3060), 508 (5140), 481 (4860)	333 (670)	275 (7220)
26		$CHCl_3$	555 sh (4200), 530 (6220), 508 (5840)	sh 335 (1250)	271 (7280)
27		$CHCl_3$	569 (4140), 526 (6760), 494 (5980)	340 (700)	284 (8560)
		MeOH	sh 555 (3290), 518 (5800), 490 (5580)	330 (840)	281 (7830)

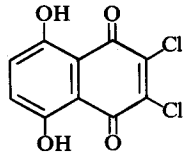
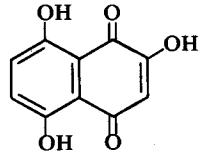
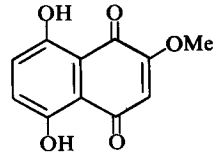
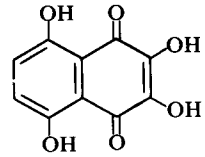
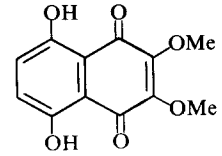
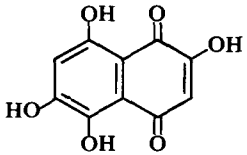
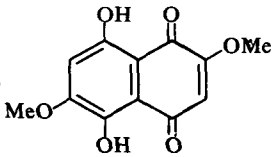
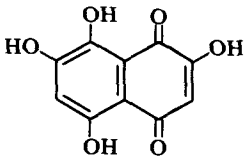
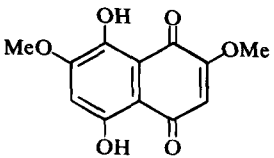
28		$CHCl_3$	569 (4950), 528 (7540), 494 (6270)	359 (680)	294 (8880)
29		$CHCl_3$	543 (4000), 528 (4640), 506 (6280), sh 496 (6160), 481 (5520)	sh 390 (1140)	292 (8130)
		MeOH	534 sh (3320), 519 sh (4310), 498 sh (5850), 488 (5960), 475 (5640)	sh 390 (1700)	290 (8560)
30		$CHCl_3$	540 (4150), 522 (4710), 503 (6980), sh 494 (6760), 475 (6300)	sh 380 (860)	291 (10,790)
		MeOH	sh 530 (3590), sh 513 (4660), 494 (6470), sh 486 (6430), 472 (6150)	sh 380 (1120)	288 (9700)
31		$CHCl_3$	524 (4420), 511 (4490), 488 (6280), sh 478 (5960), 463 (5560)		302 (4570) 288 (4630) 249 (15,680)
32		$CHCl_3$	533 (4370), 499 (7070), 473 (6410)		295 (7920)
		MeOH	sh 525 (4050), 494 (6680), 472 (6360)		292 (7350)

TABLE 3—*continued*

No.	Compound	Solvent	λ_{max}, mμ (ε) of E.T. bands		
			Benzenoid	Quinoid	Combination
33		$CHCl_3$	532 (4180), sh 520 (3660), 494 (5670) 465 (4550)		310 (8920) 267 (4780)
		MeOH	527 (3920), 514 (3580), 489 (5450), 562 (4560)	371 (1710)	310 (8640) 260 (5220)
34		$CHCl_3$	529 (6470), sh 518 (5500), 492 (8790), 464 (6710)		307 (10,520)
		MeOH	523 (5880), 488 (8070), 461 (6380)		303 (9150)
35		$CHCl_3$	558 (3290), 520 (5380), 490 (4800)		316 (7630) 269 (7320)
		MeOH	552 (3350), 515 (5520), 488 (5150)		315 (7460) 267 (7820)
36		$CHCl_3$	550 (5140), 532 (4850), 511 (8040), 499 (6950) 479 (6720)		309 (8580) 286 (7920)
		MeOH	543 (4570), 506 (7330), sh 491 (6700), 478 (6540)		307 (7370) 280 (7420)

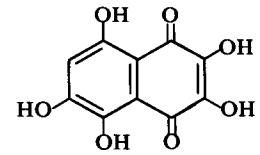
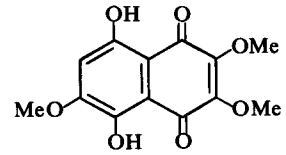
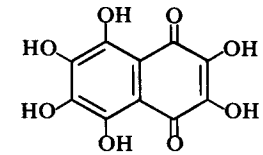
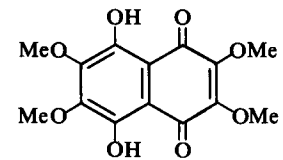
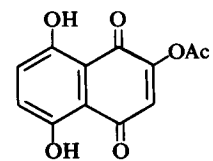
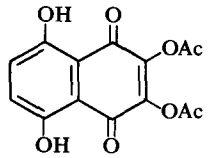
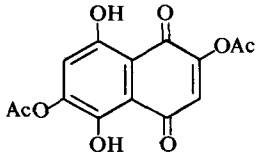
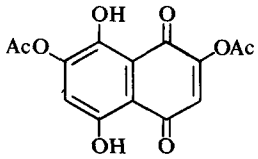
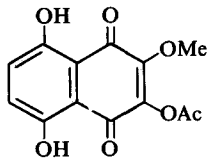
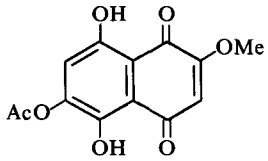
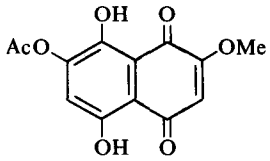
37		$CHCl_3$	559 sh (1430), 519 sh (3570), 494 (4170), 469 (3950)		323 (5610) 259 sh (9030)	
		MeOH	512 sh (3590), 488 (4090), 468 (4020)		321 (5170) 259 sh (9220)	
38		$CHCl_3$	529 (5400), 496 (7710), sh 474 (6580)		314 (8710)	
		MeOH	sh 518 (5420), 492 (7460), sh 478 (6750)		312 (7910)	
39		MeOH	498 sh (4350), 475 (6060), 459 sh (5350)		357 (7660)	
40		$CHCl_3$	531 (5450), 496 (7940), 469 (6680)		328 (8500)	
		MeOH	524 (5260), 493 (7440), 468 (6580)		325 (7440) 235 (21,400)	
41		$CHCl_3$[a]	560, 544 sh, 519, 488, 460 sh	340	280	

TABLE 3—*continued*

No.	Compound	Solvent	λ_{max}, mμ (ε) of E.T. bands		
			Benzenoid	Quinoid	Combination
42		$CHCl_3$[b]	553, 542 sh, 513, 481, 547 sh	sh 370	286
43		$CHCl_3$[b]	552, 513, 483, 453 sh	365	280
44		$CHCl_3$[b]	556, 516, 486, 460 sh	366	283

45		$CHCl_3$	537 (3950), 501 (6090), 486 sh (5600), 479 (5490)	sh 380 (960)	293 (7970)
46		$CHCl_3$[c]	528 sh (4040), 515 sh (4900), 493 (6940), 485 sh (6870)	sh 370 (880)	295 (11,000)
47		$CHCl_3$[c]	535 sh (3710), 521 sh (4680), 501 (6580), 492 (6610), 475 (6270)	sh 370 (820)	295 (10,150)

[a] The qualitative spectrum is compared with that of 2-ethylnaphthazarin (**25**) in Fig. 7.
[b] The shape of the qualitative spectrum is very similar to that of 2-ethylnaphthazarin (**25**).
[c] The shape of the spectrum is very similar to that of 2-methoxynaphthazarin (**30**).

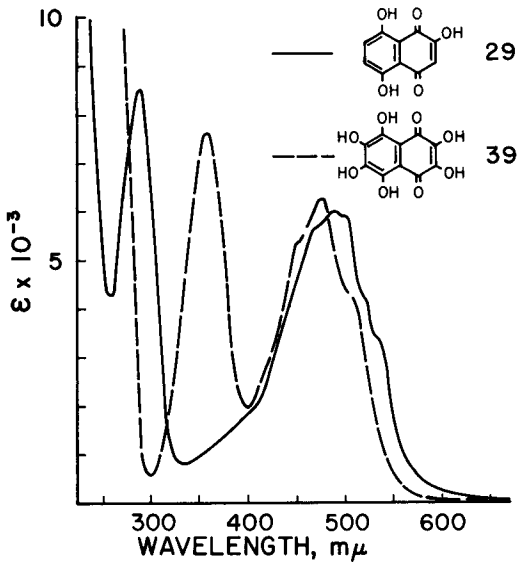


FIG. 6 Electronic absorption spectra of naphthopurpurin and spinochrome E (2,3,6,7-tetrahydroxynaphthazarin) in methanol.

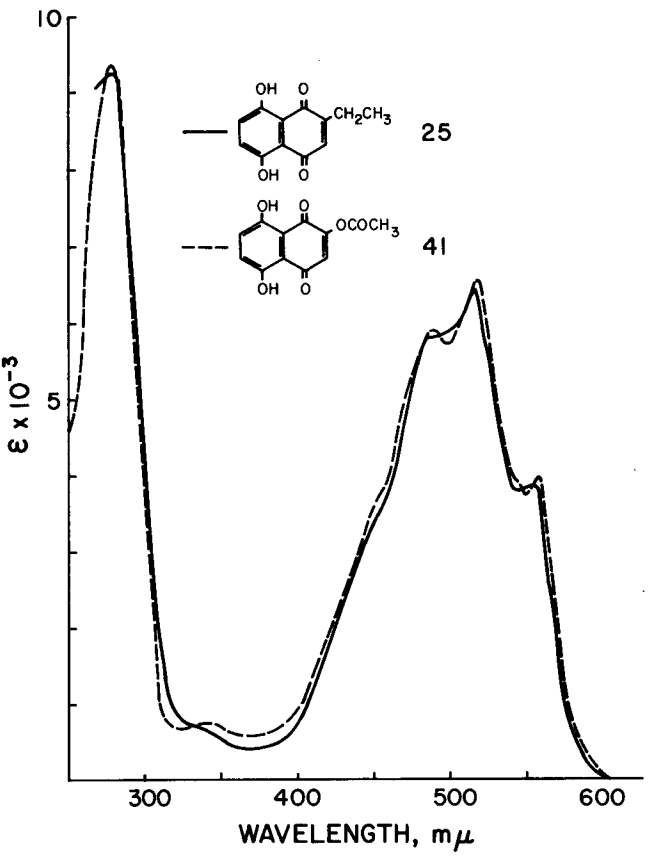


FIG. 7 Electronic absorption spectra of 2-ethylnaphthazarin and 2-acetoxynaphthazarin.

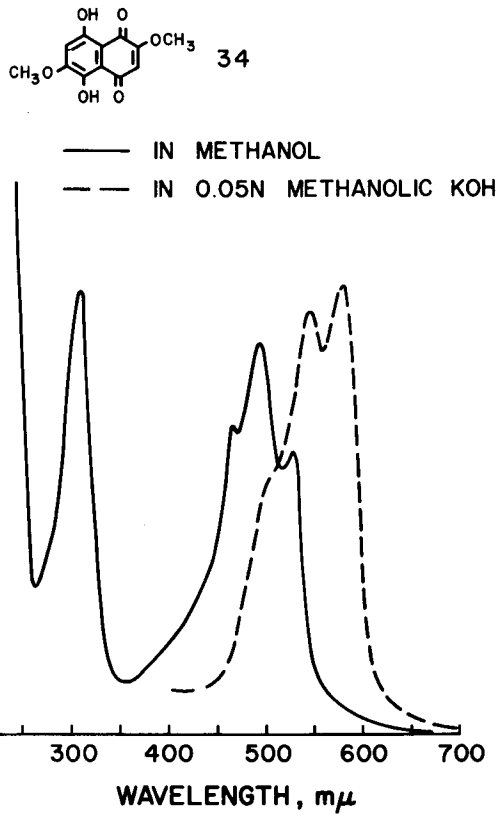


FIG. 8 Electronic absorption spectrum of 2,6-dimethoxynaphthazarin.

The multibanded structure of the visible absorption is the most important criterion for ascertaining the relative positions of substituents on the naphthazarin system. Compare for example the spectra of the three isomeric dihydroxynaphthazarins (Fig. 9).

The small band in the valley between the visible band and the intense E.T. band is assigned to a quinoid E.T. band. It can always be seen in the spectra of monosubstituted naphthazarins and/of naphthazarin itself (Table 3). An expected bathochromic shift is observed when the group is electron-releasing. The quinoid E.T. band of 6-acetylnaphthazarin (**18**) is essentially unshifted since the acetyl is located on a predominantly benzenoid ring.[5] Further substitution with electron-releasing groups usually causes a large enough bathochromic shift of the quinoid E.T. band that it becomes obscured by the much larger visible band.

EXPERIMENTAL[13]

Preparation of acetoxynaphthazarins.

Ketene gas was passed through a soln of 20–25 mg naphthapurpurin in 15 ml benzene for 5 min. The reaction was monitored by TLC on deactivated silica gel.[14] When the starting material had almost disappeared, the mixture was evaporated *in vacuo* and the residual gummy solid was applied to thick layer plates of deactivated silica gel. An initial TLC purification in benzene followed by one in chloroform led

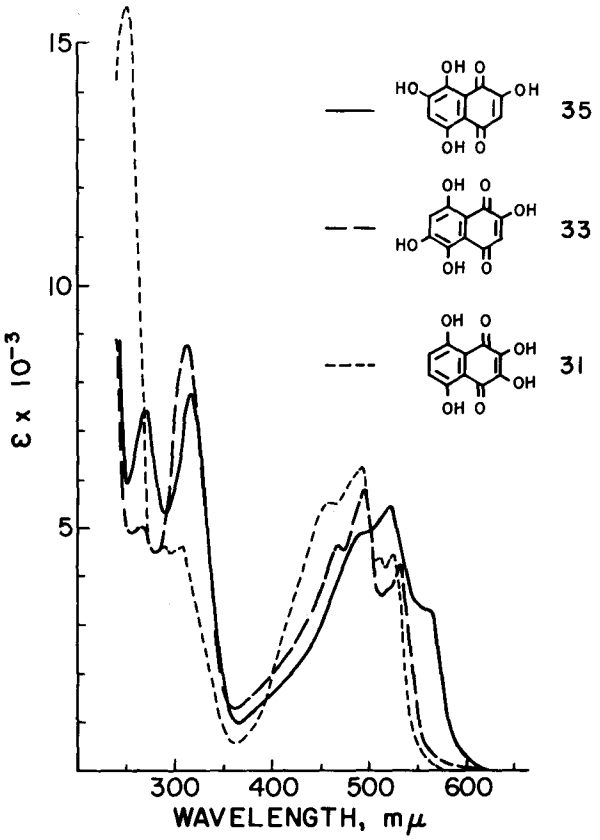


FIG. 9 Electronic absorption spectra of 2,3-, 2,6-, and 2,7-dihydroxynaphthazarin.

to pure acetoxynaphthazarin. The desired product was red and generally moved faster on TLC plates than the yellow periacetylated by-products. The acetoxynaphthazarin was crystallized from isooctane. The following derivatives were prepared from the corresponding hydroxy compounds: 2-acetoxynaphthazarin, m.p. 132–133°; 2,3-diacetoxynaphthazarin, m.p. 158–160°; 2,6-diacetoxynaphthazarin, m.p. 161–162°; 2,7-diacetoxynaphthazarin, m.p. 166–167°; 2-methoxy-3-acetoxynaphthazarin, m.p. not determined; 2-methoxy-6-acetoxynaphthazarin, m.p. 178–179°; and 2-methoxy-7-acetoxynaphthazarin, m.p. not determined. The NMR spectral data, except for 2-methoxy-3-acetoxynaphthazarin, have been reported elsewhere.[5]

The Charrier and Tocco reaction[15] *of* 1,5-*dinitro*-2,6-*dimethoxynaphthazarin*

To a well-stirred mixture of 5 g 1,5-dinitro-2,6-dimethoxynaphthalene in 100 g conc H_2SO_4, 3·5 g powdered S in 120 g fuming H_2SO_4 (30–33%) was added dropwise at such a rate that the temp was not allowed to exceed 40°. The dark purple soln, after an additional hour's stirring, was poured onto 1 kg ice and the mixture was filtered.

A. *Isolation of* 2,6-*dimethoxynaphthazarin.* The above filtrate was boiled for 30 min and then extracted with benzene. The product was chromatographed on an 80 cm × 5 cm column of deactivated silica gel and the second band (orange) which was eluted with benzene yielded 100 mg 2,6-dimethoxynaphthazarin (2%), dark red needles from acetone, m.p. 295–296°. Only traces of other compounds were present.

B. *Isolation of* 3,7-*dimethoxyjuglone.* The above filtrate was extracted several times with ether and the product was chromatographed on an 80 cm × 5 cm column of deactivated silica gel. Separation was achieved with benzene and six bands were eluted. The first band (yellow) after vacuum sublimation and crystallization from chloroform-isooctane yielded 50 mg 3,7-dimethoxyjuglone (1%) as small orange needles, m.p. 248–250° with subl.[16]

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[7] R. E. Moore, H. Singh and P. J. Scheuer, *J. Org. Chem.* **31**, 3645 (1966).
[8] For an explanation of our nomenclature see: A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products* p. 8. Macmillan, New York, N.Y. (1964).
[9] R. H. Thomson, *J. Chem. Soc.* 1737 (1950).
[10] See Ref. 8, p. 101.
[11] R. E. Moore, H. Singh, C. W. J. Chang, and P. J. Scheuer, *J. Org. Chem.* **31**, 3638 (1966).
[12] See Ref. 8, p. 91.
[13] M.ps taken on a Fisher–Johns block and uncorrected. UV visible spectra on a Cary 14 recording spectrophotometer.
[14] I. Singh, R. E. Moore, C. W. J. Chang, R. T. Ogata and P. J. Scheuer, *Tetrahedron* **24**, 2969 (1968).
[15] C. Charrier and G. Tocco, *Chem. Zentr.* **94**, 1159 (1923); [*Gazz. chim. ital.* **53**, 431 (1923).
[16] NMR data reported in Ref. 5.