
ULTRAVIOLET SPECTRA, METHOXY AND METHYLENEDIOXY GROUPS OF SOME AROMATIC COMPOUNDS AND ALKALOIDS. IV.***THE EFFECT OF HYDROXYL, METHOXYL AND METHYLENEDIOXY GROUPS ON THE ULTRAVIOLET SPECTRA OF AROMATIC COMPOUNDS CONJUGATED WITH AN OXO-GROUP OR WITH AN α,β -DOUBLE BOND IN THE SIDE CHAIN**

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In this paper, the ultraviolet spectra of hydroxy, methoxy and methylenedioxy derivatives of benzene, benzoic acid, benzaldehyde, acetophenone and propiophenone, 1-indanone, 1,2-indanedione, propenylbenzene, *cis*- and *trans*-cinnamic acids as well as those of the benzaldehyde, acetophenone and indanone oximes have been studied. The spectra have been recorded in dioxane, ethanol or in ethanolic sodium hydroxide and their relationship to the structure of the individual substances is being discussed.

In the previous papers¹⁻³, the effect of the methoxyl and methylenedioxy groups on the ultraviolet spectra of aromatic and heteroaromatic compounds was described.** The present work has been designed to study the variously substituted hydroxybenzenes and their methyl ethers, the aromatic hydroxy or methoxy oxo compounds and the propenyl derivatives, the derivatives of *cis*- and *trans*-cinnamic acids, the oximes of benzaldehydes substituted by methoxyl or methylenedioxy groups and the oximes of substituted indanones. Many of the above mentioned substances have been studied earlier by other authors⁵⁻¹⁴, however, in the majority of cases not systematically. Therefore, where a sufficient quantity of the material was available, we repeated the measurements and compared the results obtained by using the technique described^{2,3}. An attempt has been made to deduce general empirical rules for the relationship which exists between the studied aromatic compounds and their ultraviolet spectra.

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** Having completed this paper, we learned to know that in the paper⁴ the effect of methoxyl and methylenedioxy groups on the ultraviolet spectra of some aromatic and tetrahydroisoquinoline compounds has also been dealt with, however, only as far as the longest wavelengths are concerned.

RESULTS

Benzene Derivatives

The spectra of hydroxybenzene and 1,2- and 1,3-dihydroxybenzene exhibit two bands in the region between 290–215 nm (Table I). The longer wavelength bands of these three compounds are practically of the same intensity. On ionization, both the longer and the shorter wavelength band are shifted to the red. 1,4-Dihydroxybenzene shows a more intensive band at 295 nm which on ionization shifts⁵ to the blue by 22 nm. The longer wavelength bands of 1,2,3- and 1,3,5-trihydroxybenzene (which do not carry hydroxyl groups in *para*-position to each other) undergo a blue shift compared to those of 1,2- and 1,3-dihydroxybenzene. Ionization of these substances results in a red shift by about 80 nm. In 1,2,4-trihydroxybenzene, the intensity of the longest wavelength bands is somewhat decreased in contrast to that of 1,4-dihydroxybenzene and, after ionization, the blue shift is smaller than that of 1,4-dihydroxybenzene. In neutral and alkaline media the methyl ethers of these substances (except the 1,2,4- and 1,3,5-trisubstituted compounds) produce absorption bands at practically the same wavelengths as those of the non-ionized hydroxy compounds.

Aromatic Oxo-Compounds, Substituted by Hydroxyl and Methoxyl Groups

Our study of these compounds rests upon the papers by Doub and Vandenberg⁸ and on our paper². We could confirm that in compounds substituted by a hydroxyl or a methoxyl group in the position 4 to the carbonyl group⁹, the band in the region between 300–250 nm is not uniform but that it consists of a secondary and a first primary band⁸ which more or less coalesce in various solvents.

Derivatives of benzoic acid: The spectra of the hydroxy and those of the methoxy-substituted acids in dioxane and in ethanol (Table II) are identical; the difference in the position of the secondary band is within the range of ± 9 nm. Only the secondary band of 2,6-dihydroxybenzoic acid undergoes a larger shift to the blue (19 nm) compared to that recorded in dioxane. There is a great similarity between the spectra of hydroxy and those of methoxy derivatives of benzoic acid substituted in the positions 2,4 and 3,4 where one of the substituents is in the *para*-position to the electron accepting oxygen group. The spectrum consists of a secondary band at c. 295 nm (substituent in the position 2 or 3) and of the sum of the first primary band of the compound substituted in the position 2 or 3 and of the secondary plus first primary band of the compound substituted in the position 4 (c. 260 nm) (Fig. 1). The relative distance between the secondary and the first primary band is smaller than 50 nm in all the compounds having one of the substituents in position 4. Contrary to the first primary band, the largest red shift is displayed by the secondary band of hydroxy compounds whose substituents are located in the position 2,5. It is smaller when the substituents are in the positions 2,3 and smallest when they are in the positions 3,5.

On the basis of the blue or the red shift of the secondary and the first primary band in ethanolic-alkaline medium, the position of the hydroxyl group in monohydroxy acids can be determined. On ionization, the secondary and the first primary band of 2-hydroxy acids undergo a blue shift whereas those of 3- and 4-hydroxy acids a red shift. These two bands of the ionized dihydroxy acids, except the secondary band of the 2,5- and 2,6-dihydroxybenzoic acids, shift to the red. On ionization, the largest red shift is exhibited by the secondary band of 3,4-dihydroxybenzoic acid (from 293 nm to 424 nm). In contrast to the spectra in ethanol, those of mono- and dimethoxy derivatives of benzoic acid in ethanolic-alkaline medium display a blue shift of the secondary and the first primary band. An exception is the secondary band of 4-methoxybenzoic acid whose position does not change (Table I in ref.²). The bands of the esters of methoxy acids

TABLE I
 Ultraviolet Data of Substituted Benzenes

Substituent	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
Unsubstituted	243 (140)	247 (100)	207 (5 800)s	247 (95)	<i>a</i>	<i>a</i>
	249 (214)	253 (105)	243 (140)	252 (100)		
	255 (227)	259 (95)	249 (220)	259 (83)		
	261 (186)		255 (225)	260 (191)		
1-HO	220 (5 500)	240 (270)	219 (5 900)	239 (250)	239 (9 780)	262 (870)
	268 (1 530)s	278 (1 400)	266 (1 510)s		290 (2 820)	
	274 (2 040)		273 (1 910)			
	281 (1 660)		280 (1 450)s			
1,2-(HO) ₂	218 (6 170)	244 (160)	218 (6 310)	212 (6 030)	241 (6 610)	223 (4 790)
	231 (2 820)s		278 (2 890)	244 (250)	292 (4 170)	271 (3 750)
	279 (2 900)		284 (2 460)s		406 (1 230)	367 (1 170)
	286 (2 090)s					
1,3-(HO) ₂	221 (6 760)	244 (160)	207 (12 000)	244 (310)	239 (7 250)	228 (6 030)
	269 (1 660)s	281 (1 820)	219 (7 080)s	280 (1 950)	288 (2 950)	261 (725)
	277 (2 300)		271 (2 000)s			
	283 (2 000)		276 (2 400)			
		283 (2 090)				
1,4-(HO) ₂	227 (5 890)	252 (130)	225 (6 170)	210 (4 270)	225 (4 270)s	261 (4 950)
	296 (3 470)		295 (3 160)	251 (316)	245 (5 130)	
					273 (5 020)	
					380 (850)s	
1,2,3-(HO) ₃	225 (7 250)s	248 (300)	209 (15 900)	249 (500)	240 (4 170)	297 (3 100)
	268 (790)		225 (7 080)s		265 (3 800)s	
			268 (890)		354 (4 080)	
					430 (3 020)s	
1,2,4-(HO) ₃	252 (12 600)	221 (3 160)	243 (12 900)	217 (4 020)	243 (12 600)	275 (934)
	327 (3 020)	287 (660)	310 (2 760)	277 (1 000)	307 (2 690)	
1,3,5-(HO) ₃	224 (6 460)s	247 (245)	210 (16 600)	247 (300)	227 (14 800)	240 (10 300)
	268 (490)	270 (400)	225 (6 170)s	271 (430)	254 (17 000)	294 (620)
	273 (417)		256 (398)s		270 (1 450)s	
	277 (310)s		269 (500)		354 (6 760)	
			273 (440)			
			276 (350)s			

TABLE I
 (Continued)

Substituent	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
1-(CH ₃ O)	220 (5 020) 268 (1 290)s 273 (1 780) 280 (1 410)	239 (200) 277 (1 230)	219 (5 760) 267 (1 450)s 273 (1 780) 278 (1 480)s	240 (300)	^a	^a
1,2-(CH ₃ O) ₂	228 (6 760) 275 (2 760) 283 (2 240)s	246 (250)	225 (7 600) 275 (2 630) 281 (2 190)s	212 (6 030) 246 (355)	^a	^a
1,2-(CH ₂ O ₂)	233 (4 200) 283 (3 100)	253 (500)	232 (4 790) 282 (3 160)	217 (3 630) 256 (890)	^a	^a
1,3-(CH ₃ O) ₂	222 (6 460) 267 (1 410)s 275 (2 190) 281 (1 910)	244 (160) 279 (1 780)	221 (6 760) 268 (1 660)s 275 (2 190) 281 (1 910)	216 (6 610) 244 (282) 279 (1 820)	^a	^a
1,4-(CH ₃ O) ₂	228 (8 800) 292 (3 160) 300 (2 340)s	249 (200)	226 (9 340) 290 (3 020) 300 (2 000)s	209 (4 900) 249 (250)	^a	^a
1,2,3-(CH ₃ O) ₃	225 (7 420)s 268 (850) 277 (600)s	250 (500)	210 (16 600) 223 (8 130)s 268 (890) 276 (660)s	249 (430)	^a	^a
1,2,4-(CH ₃ O) ₃	227 (7 150)s 231 (7 300) 288 (3 800)	218 (6 460) 254 (400)	226 (7 080) 287 (3 600)	218 (6 460) 254 (355)	^a	^a
1,3,5-(CH ₃ O) ₃	225 (9 120)s 267 (630)	250 (310)	211 (18 000) 225 (7 950)s 266 (620)	250 (320)	^a	^a

^aIn ethanolic NaOH no change in the spectra of methyl ethers.

compared to those of the acids display a small red shift. On the other hand, the secondary and the first primary band of the ionized forms of the methyl esters of hydroxy benzoic acids shift to the red. Obviously, ionization of the hydroxy and the carboxyl group leads to summation of the shift of the secondary and the first primary band in the ultraviolet spectrum (Table II).

TABLE II

Ultraviolet Data of Substituted Benzoic Acids and Their Methyl Esters

Substituent ^a	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
Acids						
Unsubstituted	228 (11 400)	253 (780)	228 (11 400)	208 (4 080)	223 (9 550)	260 (870)
	267 (935) _s	277 (830)	269 (910) _s	256 (780)	262 (890)	265 (760)
	273 (1 150)		272 (1 000)	277 (795)	269 (780)	274 (600)
	280 (955)		280 (815)		276 (660)	
2-(HO)	237 (8 320)	221 (5 250)	212 (13 800)	221 (5 900)	223 (7 420) _s	258 (760)
	307 (4 370)	263 (500)	234 (7 420)	261 (450)	228 (8 130)	
			302 (4 170)		297 (4 170)	
3-(OH)	215 (14 800)	224 (6 300)	213 (17 400)	225 (6 600)	242 (7 770) _s	272 (690)
	236 (7 590)	261 (580)	234 (6 900)	261 (620)	314 (2 800)	
	296 (3 160)		296 (2 760)			
4-(HO)	252 (15 900)	222 (2 190)	212 (10 700)	224 (2 400)	279 (17 600)	237 (2 090)
	273 (4 100) _s		254 (14 100)			
	283 (1 070) _s		274 (5 900) _s			
			283 (2 000) _s			
2,3-(HO) ₂	219 (17 800)	234 (4 800)	216 (19 800)	235 (5 500)	229 (22 100)	279 (1 200)
	250 (8 200)	273 (380)	246 (6 400)	269 (315)	250 (7 100) _s	
	323 (3 500)		314 (3 200)		329 (4 170)	
2,4-(HO) ₂	215 (17 000)	235 (3 600)	212 (19 700)	234 (4 400)	220 (13 300)	225 (12 300)
	221 (13 800) _s	275 (2 200)	218 (14 500) _s	275 (2 800)	232 (13 000)	249 (6 400)
	258 (14 300)		255 (11 800)		272 (15 900)	286 (11 200)
	297 (5 900)		295 (5 500)		299 (13 200)	
2,5-(HO) ₂	219 (18 600)	232 (6 300)	215 (19 000)	269 (280)	223 (16 600)	278 (2 950)
	238 (6 700)	272 (200)	234 (6 500) _s		236 (9 340) _s	
	340 (4 800)		332 (4 200)		320 (3 550)	
2,6-(HO) ₂	222 (15 500)	236 (5 020)	217 (18 400)	239 (5 500)	216 (19 100)	240 (5 890)
	254 (10 000)	276 (660)	249 (6 760)	274 (1 000)	235 (6 460) _s	266 (2 240)
	310 (2 950) _s		304 (3 630)		246 (6 170)	279 (2 290)
	323 (3 160)				273 (2 340)	
					303 (4 370)	
3,4-(HO) ₂	219 (16 000)	233 (2 500)	211 (17 200)	234 (3 800)	222 (13 500)	250 (5 800)
	257 (9 550)	276 (2 600)	254 (7 800)	277 (3 000)	273 (7 100)	290 (6 170)
	291 (4 400)		293 (4 300)		296 (6 200)	370 (1 600)
				424 (2 140)		

TABLE II
(Continued)

Substituent ^a	Dioxane		Ethanol		Ethanol-NaOH	
	$\lambda_{\max} (\epsilon)$	$\lambda_{\min} (\epsilon)$	$\lambda_{\max} (\epsilon)$	$\lambda_{\min} (\epsilon)$	$\lambda_{\max} (\epsilon)$	$\lambda_{\min} (\epsilon)$
3,5-(HO) ₂	250 (6 760) 307 (3 310)	235 (4 200) 275 (1 000)	215 (18 200) 251 (5 890) 310 (2 690)	236 (3 630) 277 (760)	223 (20 200) 265 (2 950) _s 320 (2 800)	289 (1 620)
2,4-(CH ₃ O) ₂	221 (15 900) 253 (13 500) 289 (5 250)	230 (5 250) 271 (3 240)	214 (19 700) 221 (17 200) _s 254 (13 200) 290 (5 370)	232 (4 370) 273 (3 240)	245 (8 710) 282 (3 630) 287 (3 550) _s	229 (6 310) 266 (2 190)
2,6-(CH ₃ O) ₂	219 (8 920) 238 (2 630) _s 280 (2 500)	258 (1 260)	210 (16 600) 241 (2 400) _s 280 (2 190)	260 (1 120)	227 (6 460) _s 275 (1 410) _s 277 (1 430)	258 (725)
3,5-(CH ₃ O) ₂	216 (17 200) 250 (5 400) 304 (2 950)	236 (3 550) 276 (890)	213 (19 700) 249 (5 500) 301 (2 800)	236 (4 200) 275 (1 070)	243 (4 370) 294 (2 200)	237 (4 170) 270 (690)
2-(HO), 3-(CH ₃ O)	221 (19 100) 249 (6 300) 321 (3 800)	239 (5 370) 273 (500)	242 (5 400) _s 311 (3 550)	266 (400)	221 (17 000) 230 (10 300) _s 304 (5 500)	266 (3 000)
2-(HO), 4-(CH ₃ O)	222 (14 100) _s 259 (16 200) 297 (6 920)	234 (3 980) 275 (3 160)	211 (30 200) 224 (11 500) _s 253 (12 000) 294 (5 630)	233 (5 000) 273 (2 400)	218 (16 600) 248 (11 200) 293 (5 130)	231 (6 030) 267 (1 550)
2-(HO), 5-(CH ₃ O)	221 (15 500) 238 (7 420) 335 (5 130)	231 (7 080) 272 (500)	214 (25 700) 236 (7 250) 331 (4 570)	229 (6 920) 270 (265)	230 (7 950) _s 320 (4 800)	266 (380)
2-(HO), 6-(CH ₃ O)	217 (15 100) 252 (7 400) 315 (3 800)	234 (3 800) 277 (660)	213 (17 800) 251 (7 350) 311 (3 500)	234 (4 200) 275 (955)	220 (16 200) 246 (9 120) 300 (5 130)	239 (8 920) 272 (3 400)
3-(HO), 4-(CH ₃ O)	223 (14 800) 257 (10 700) 294 (5 500)	233 (3 020) 274 (2 630)	219 (21 900) 258 (10 400) 295 (5 630)	234 (3 630) 277 (3 240)	227 (22 900) 259 (6 500) 311 (5 020)	250 (6 200) 282 (1 970)
3-(HO), 5-(CH ₃ O)	216 (16 200) 251 (5 630) 306 (2 900)	236 (3 630) 276 (780)	213 (18 800) 245 (4 800) 298 (2 300)	236 (4 400) 272 (830)	227 (20 200) 245 (8 700) _s 315 (3 800)	282 (2 290)

TABLE II
(Continued)

Substituent ^a	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
4-(HO), 3-(CH ₃ O)	221 (18 200)	233 (2 900)	218 (18 200)	234 (3 200)	224 (15 900)	247 (5 000)
	259 (12 300)	278 (4 170)	260 (10 500)	280 (4 700)	286 (15 300) _s	
	289 (5 400)		291 (5 500)		297 (15 900)	
	295 (5 100) _s					
2,4,6-(HO) ₃	223 (25 700)	237 (2 510)	220 (27 600)	237 (3 890)	222 (15 300)	249 (3 630)
	266 (16 200)	286 (2 240)	261 (12 000)	285 (2 400)	228 (13 500) _s	
	305 (3 020)		295 (2 570)		277 (15 900)	
3,4,5-(HO) ₃	221 (20 900)	238 (2 100)	216 (25 700)	239 (2 190)	—	—
	269 (9 340)		271 (8 320)			
2,4,5-(CH ₃ O) ₃	227 (17 400)	237 (5 500)	221 (21 900)	238 (6 030)	218 (16 200)	233 (7 250)
	255 (11 200)	275 (1 590)	255 (10 000)	275 (1 780)	246 (8 710)	268 (1 320)
	308 (7 080)		307 (6 610)		297 (5 500)	
2,4,6-(CH ₃ O) ₃	221 (12 300)		214 (20 400)		218 (14 800)	
	250 (4 900) _s		250 (4 680) _s		238 (6 310) _s	
					273 (1 000) _s	
3,4,5-(CH ₃ O) ₃	217 (29 500)	237 (2 630)	214 (32 400)	235 (2 630)	219 (16 800)	238 (9 780)
	266 (9 780)		262 (8 920)		251 (10 500)	280 (5 370)
	290 (4 370) _s		295 (3 090) _s		291 (5 370)	
2-(HO), 4,5-(CH ₃ O) ₂ ¹⁸	—	—	222 (19 800)	240 (4 000)	—	—
			256 (10 600)	276 (730)		
			318 (7 400)			
2-(HO), 4,6-(CH ₃ O) ₂	224 (16 000)	235 (2 630)	219 (30 900)	235 (3 390)	218 (33 900)	237 (5 890)
	264 (16 200)	285 (3 160)	263 (14 300)	285 (3 090)	256 (11 800)	278 (2 290)
	297 (3 550)		295 (3 310)		292 (2 890)	
4-(HO), 3,5-(CH ₃) ₂	226 (16 200)	239 (1 680)	216 (26 900)	238 (2 240)	223 (15 300) _s	252 (2 190)
	275 (12 300)		271 (10 200)		227 (15 500)	
					301 (16 200)	
Methyl esters						
Unsubstituted	229 (12 600)	256 (890)	228 (12 900)	256 (708)	—	—
	273 (1 260)	277 (912)	273 (1 000)	277 (830)		
	280 (1 120)		280 (890)			
2-(OH)	238 (9 120)	222 (5 250)	210 (16 200)	220 (4 370)	222 (20 900)	237 (6 310)
	305 (4 700)	262 (500)	238 (8 800)	263 (450)	247 (7 420)	275 (360)
			305 (4 270)		339 (5 760)	

TABLE II

(Continued)

Substituent ^a	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
3-(OH)	235 (7 600) 295 (3 160)	262 (450)	213 (19 200) 237 (8 320) 298 (3 310)	225 (6 920) 262 (500)	227 (33 900) 248 (10 000) _s 333 (3 800)	278 (460)
2,6-(OH) ₂	223 (13 200) 254 (1 150) 300 (3 470) 323 (2 240) _s	235 (4 800) 275 (1 410)	212 (16 800) 219 (16 200) 255 (1 100) 300 (3 800) 323 (2 290) _s	236 (4 790) 277 (2 000)	215 (10 100) 235 (14 100) 277 (6 610) _s 306 (1 070) 352 (2 950)	222 (8 710) 256 (5 020) 333 (2 510)
2,4-(CH ₃ O) ₂	217 (19 100) 252 (13 200) 289 (5 370)	231 (5 630) 270 (2 800)	215 (18 800) 255 (13 300) 291 (5 760)	233 (4 170) 273 (3 160)	—	—
2,5-(CH ₃ O) ₂	216 (16 200) 234 (7 720) 316 (3 630)	229 (7 590) 267 (500)	215 (18 600) 235 (7 420) 320 (3 890)	229 (7 250) 266 (380)	—	—
2,6-(CH ₃ O) ₂	222 (7 250) _s 273 (2 190) _s 281 (2 500)	257 (1 100)	209 (15 100) 246 (2 500) _s 281 (2 630)	262 (1 570)	—	—

^aFor the spectra of 2-, 3-, 4-methoxy-, 2,3-, 3,4-dimethoxy-, 2,3-, 3,4-methylenedioxybenzoic acids, and their methyl esters see ref.². 4-(OH) methyl ester in ethanol λ_{\max} 198 nm (ϵ 20 000), 208 (14 800), 255 (17 000), λ_{\min} 225 (1 500), ref.¹⁹.

Plant material often shows the presence of derivatives of benzoic acid substituted by one hydroxyl and one methoxyl group. Their spectra resemble those of the corresponding dihydroxy acids, however, in contrast to them, they display a blue shift of the secondary and the first primary band. An exception is the secondary and the first primary band of 2-hydroxy-6-methoxy and 3-hydroxy-4-methoxybenzoic acid and the first primary band of 4-hydroxy-3-methoxybenzoic acid which shift to the red. In ethanolic-alkaline medium, the secondary and the first primary band of compounds with a hydroxyl group in position 2 undergo a blue shift which is similar to that of the bands of salicylic acid. The bands of acids having a hydroxyl group in the positions 3 and 4 shift to the red.

The spectra of trihydroxybenzoic acids (Table II) differ from those of dihydroxybenzoic acids. In the spectrum of 2,4,6-trihydroxybenzoic acid, the band at 295 nm bears analogy to that of 2,6-disubstituted acid. The observed increase in the intensity of the band at 261 nm is caused by the presence of the substituent in position 4. Remarkable is the low intensity of the longer wavelength band (295 nm) which, in all probability, is due to the limited rotation of the carbonyl group, which is similar to that of 2,6-dihydroxybenzoic acid. 3,4,5-Trihydroxybenzoic acid exhibits a secondary plus first primary band at c. 270 nm which corresponds to the hydroxyl group in position 4. In ethanol, the spectra of acids with one hydroxyl and two methoxyl groups are practically identical with those of trihydroxy acids. The spectra of 2,4,5- and 3,4,5-trimethoxybenzoic acids resemble those of 3,4-dimethoxybenzoic acid except that the secondary band of these acids is shifted to the red. The bands of the ionized forms are shifted similarly to those of dimethoxy substituted acids. The spectrum of 2,4,6-trimethoxybenzoic acid is not comparable with that of any of the so far mentioned acids. It is characterized by a high-intensity absorption band at 214 nm which shows a red displacement on ionization.

Derivatives of benzaldehyde: The spectra of hydroxy and methoxybenzaldehydes (Table III) show analogy with those of similarly substituted derivatives of benzoic acid except that their secondary and first primary bands display a red shift by c. 25 nm. Even here, the largest distance is observed between the secondary and the first primary band of 2,5-dihydroxy or 2,5-dimethoxybenzaldehyde. In ethanolic-alkaline medium, the bands of hydroxybenzaldehydes exhibit a larger red shift than those of the derivatives of benzoic acid. The smaller displacement of the bands of hydroxybenzoic acids is the result of the simultaneous ionization of the carbonyl and the hydroxyl group. The largest red shift is shown by the ionized forms of 2-hydroxy-, a smaller one by the 4-hydroxy- and the smallest by 3-hydroxy derivatives. Such shifts, though smaller in extent, are also displayed by the bands of compounds having two hydroxyl groups or of compounds where at least one electron donating substituent is a hydroxyl group. The individual bands of trihydroxy and trimethoxybenzaldehydes undergo a red shift compared to those of disubstituted compounds. The bands of the partially etherified trihydroxy derivatives are located in almost the same position as those of the non-etherified derivatives.

Derivatives of acetophenone and propiophenone: The pattern of the spectra of mono-, di- and trihydroxy(methoxy)acetophenones and of propiophenones (Table IV) is in all the three solvents identical with those of the spectra of the corresponding derivatives of benzaldehyde and of benzoic acid; the displacements of the bands are similar to those described by Conover¹⁰. The bands of the derivatives of acetophenone (propiophenone) are located between the bands of the derivatives of benzoic acid and that of benzaldehyde. Ionization causes a red shift of the secondary band of these compounds in the order 4-OH > 3-OH > 2-OH. The spectra of trisubstituted derivatives of acetophenone are similar to those of trisubstituted benzaldehydes except that the secondary and the first primary band shift toward the blue. The spectra of acetophenones, substituted at the same time by hydroxyl and methoxyl groups, are also similar to those of the corresponding derivatives of benzaldehyde.

Indanone derivatives: In compounds monosubstituted in the positions 4, 6 and 7 (Table V), the distance between the secondary and the first primary band is considerable. These two bands of 5-hydroxy(methoxy)-1-indanone (in ethanol) are separated, the distance between them is, however, only small. The spectra of 4,5-dimethoxy and 4,5-methylenedioxy-1-indanone resemble those of 4,5-disubstituted phthalides² and of 3,4-disubstituted oxy derivatives of benzene. The position of the first primary and the secondary band of 5-substituted 1-indanone is similar to that of the 4-substituted phthalide. Consequently, even in these compounds, a marked effect of the interaction of the electron donating and the electron accepting substituent in *para*-position to each

TABLE III
 Ultraviolet Data of Substituted Benzaldehydes

Substituent ^a	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
Unsubstituted	244 (12 900)	217 (3 090)	246 (12 300)	217 (1 820)	—	—
	280 (1 410)	267 (1 120)	281 (1 260)	272 (1 150)		
	286 (1 200) _s		287 (1 120) _s			
2-(HO)	218 (16 600)	233 (2 950)	215 (17 000)	232 (2 510)	230 (17 200)	252 (5 600)
	254 (11 000)	276 (450)	255 (11 600)	278 (450)	266 (7 250)	301 (295)
	324 (3 630)		327 (3 980)		382 (6 760)	
3-(HO)	219 (17 600)	233 (4 170)	221 (18 800)	236 (4 200)	241 (25 700)	303 (457)
	251 (9 550)	273 (480)	255 (9 200)	278 (630)	267 (6 030) _s	
	313 (3 280)		317 (2 950)		365 (2 690)	
4-(HO)	219 (14 800)	235 (1 740)	222 (12 400)	239 (1 120)	241 (7 590)	221 (3 550)
	270 (17 800)		286 (16 400)		296 (5 200) _s	265 (1 320)
	283 (14 100) _s		291 (15 500) _s		336 (30 200)	
		330 (320) _s				
2,4-(HO) ₂	218 (15 900)	224 (10 500)	213 (14 500)	224 (7 500)	220 (12 600)	245 (7 650)
	231 (12 300)	247 (2 090)	216 (14 100) _s	248 (1 450)	230 (11 900) _s	271 (980)
	277 (17 400)	296 (5 760)	233 (9 780)	304 (7 420)	250 (7 800)	
	313 (7 000)		281 (15 700)		336 (20 900)	
			314 (7 590)			
2,5-(HO) ₂	231 (15 900)	248 (5 020)	210 (10 300)	215 (10 000)	223 (13 800)	330 (660)
	258 (6 460)	293 (280)	231 (15 900)	248 (5 760)	240 (11 500) _s	
	365 (3 720)		259 (7 590)	294 (330)	268 (6 920) _s	
			367 (4 080)		417 (4 270)	
3,4-(HO) ₂	229 (15 000)	245 (2 000)	209 (14 700)	220 (7 950)	253 (9 120)	234 (4 680)
	272 (11 200)	291 (6 030)	234 (14 100)	252 (2 690)	275 (3 800) _s	286 (3 020)
	307 (8 320)		281 (10 300)	298 (7 590)	297 (3 630) _s	
			315 (9 340)		353 (21 400)	
			360 (1 120) _s		400 (1 230) _s	
2,4-(CH ₃ O) ₂	232 (15 700)	242 (1 820)	209 (12 700)	219 (8 130)	—	—
	271 (14 100)	288 (4 470)	232 (14 500)	244 (1 590)		
	309 (9 120)		274 (13 800)	294 (6 310)		
			314 (10 000)			
2,5-(CH ₃ O) ₂	225 (17 400)	241 (6 030)	225 (18 600)	242 (5 800)	—	—
	254 (8 920)	281 (400)	257 (9 550)	284 (410)		
	350 (5 250)		355 (5 250)			
3,5-(CH ₃ O) ₂	221 (16 400)	241 (1 780)	215 (25 700)	241 (1 740)	217 (22 900)	241 (1 780)
	267 (7 250)	294 (1 230)	269 (7 420)	299 (1 580)	269 (7 420)	299 (1 660)
	322 (2 820)		325 (2 760)		325 (2 760)	

TABLE III
(Continued)

Substituent ^a	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
2-(HO), 3-(CH ₃ O)	225 (17 400)	242 (3 160)	221 (18 400)	241 (3 090)	238 (19 100)	260 (3 160)
	264 (10 300)	290 (760)	267 (11 000)	294 (1 000)	282 (6 460)	312 (480)
	341 (2 890)		344 (3 390)		396 (6 760)	
3-(HO), 4-(CH ₃ O)	230 (18 800)	245 (2 400)	208 (13 800)	218 (8 520)	252 (24 000)	228 (7 080)
	272 (11 800)	290 (5 250)	232 (17 000)	248 (2 510)	292 (7 950)	272 (4 570)
	308 (8 320)		276 (11 000)	296 (6 310)	365 (5 890)	319 (2 040)
		314 (8 520)				
4-(HO), 3-(CH ₃ O)	229 (16 600)	216 (10 300)	208 (13 800)	217 (7 770)	252 (9 550)	228 (3 890)
	274 (12 300)	243 (2 700)	232 (15 900)	249 (1 820)	294 (2 890)	272 (1 660)
	303 (9 550)	289 (7 590)	280 (10 800)	294 (9 120)	354 (30 200)	
		309 (11 000)				
2,4,5-(CH ₃ O) ₃	235 (18 200)	250 (3 310)	237 (16 400)	220 (7 590)	237 (16 600)	220 (8 130)
	273 (12 600)	292 (1 260)	275 (11 800)	252 (2 510)	277 (11 800)	252 (2 760)
	336 (9 120)		344 (9 120)	300 (2 000)	345 (9 340)	300 (2 040)
2,4,6-(CH ₃ O) ₃	229 (17 000)	243 (1 070)	211 (15 500)	220 (14 500)	227 (16 200)	245 (760)
	280 (18 000)		227 (16 600)	245 (660)	289 (20 400)	
	311 (3 550) _s		288 (20 400)			
3,4,5-(CH ₃ O) ₃	226 (15 900)	244 (1 000)	218 (24 000)	244 (1 260)	222 (20 400)	244 (1 150)
	288 (10 500)		288 (10 300)		289 (10 300)	
	315 (4 570) _s					
3-(CH ₃ O), 4,5-(HO) ₂	231 (16 600)	248 (890)	219 (18 200)	251 (1 410)	219 (14 100)	238 (6 610)
	295 (13 200)		229 (15 500) _s		252 (8 710)	283 (2 000)
			309 (12 600)		364 (15 100)	
		368 (1 480) _s				
3,5-(HO) ₂ , 4-(CH ₃ O)	226 (16 200)	244 (1 550)	220 (22 400)	245 (1 230)	238 (21 400)	275 (1 230)
	280 (10 500)		285 (10 000)		334 (6 760)	
	320 (2 950) _s		325 (3 550) _s			
2-(HO), 4,6-(CH ₃ O) ₂	226 (12 400)	245 (315)	212 (16 600)	244 (400)	219 (19 500)	228 (17 000)
	292 (20 900)		224 (11 800) _s		235 (17 600)	257 (1 450)
	331 (3 160) _s		294 (20 900)		293 (19 100)	319 (3 310)
		335 (3 160) _s		359 (7 590)		
3,5-(CH ₃ O) ₂ , 4-(HO)	233 (17 400)	249 (630)	217 (17 400)	226 (15 300)	218 (12 000)	234 (4 080)
	303 (13 800)		232 (16 200)	251 (1 000)	254 (10 700)	278 (450)
			310 (13 200)		294 (710) _s	
		368 (795) _s		370 (25 700)		

^aFor the spectra of 2-, 3-, 4-methoxy, 2,3-, 3,4-dimethoxy-, and 2,3-, 3,4-methylenedioxybenzaldehydes see ref.², 3,5-(OH)₂ in ethanol λ_{\max} 220 nm (ϵ 15 100), 255 (10 000), 334 (3 470), ref.²⁰; 2,3,5-(HO)₃ 276 (10 000), 332 (2 000), ref.²¹; 2,4,6-(HO)₃ 293 (25 100), 340 (2 510) s, ref.²².

TABLE IV
 Ultraviolet Data of Substituted Acetophenones and Propiophenones

Substituent ^a	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
Acetophenones						
Unsubstituted	241 (11 800)	263 (690)	242 (12 600)	217 (2 140)	244 (12 600)	269 (725)
	279 (1 070)		280 (1 190)	269 (1 000)	281 (940)	
	288 (794) _s					
3-(HO)	220 (14 500)	232 (5 130)	219 (19 100)	234 (2 570)	238 (23 400)	293 (615)
	247 (8 710)	269 (7 250)	251 (8 710)	277 (830)	263 (6 310) _s	
	306 (3 020)		311 (2 760)		357 (2 510)	
2,4-(HO) ₂	217 (15 900)	225 (9 340)	213 (16 200)	225 (7 590)	217 (11 500)	230 (2 340)
	229 (10 100)	245 (2 090)	216 (15 900) _s	247 (1 780)	251 (6 170)	270 (1 500)
	273 (14 300)	292 (4 400)	231 (8 920)	302 (6 760)	335 (29 500)	
	312 (6 460)		277 (14 300)			
			315 (7 250)			
2,5-(HO) ₂	226 (16 000)	243 (5 760)	227 (15 500)	246 (5 630)	243 (15 500)	347 (1 030)
	255 (7 080)	279 (316)	257 (6 920)	287 (302)	273 (4 680) _s	
	361 (4 470)		367 (4 000)		297 (2 760) _s	
					407 (1 800)	
2,6-(HO) ₂	223 (13 800)	241 (3 090)	223 (12 300)	241 (2 400)	216 (10 400)	224 (7 770)
	267 (11 500)	294 (1 340)	270 (11 000)	303 (1 260)	241 (13 400)	262 (3 630)
	338 (3 470)		344 (3 310)		286 (9 120)	322 (935)
					392 (5 630)	
2,3-(CH ₃ O) ₂	220 (17 000)	238 (4 900)	218 (18 200)	238 (4 680)	—	—
	248 (5 760)	269 (560)	251 (6 170)	275 (890)		
	303 (2 140)		306 (2 140)			
2,4-(CH ₃ O) ₂	224 (15 300)	227 (15 000)	212 (14 300)	219 (11 800)	—	—
	229 (15 100)	238 (3 160)	227 (14 500)	241 (2 820)		
	263 (13 200)	280 (4 270)	267 (12 600)	286 (5 800)		
	298 (7 080)		303 (8 320)			
2,6-(CH ₃ O) ₂	220 (7 100)	267 (1 590)	213 (12 000) _s	238 (2 040)	—	—
	244 (2 430) _s		259 (2 760)			
	279 (1 880)		270 (2 510) _s			
2-(OH), 4-(CH ₃ O)	229 (14 500)	223 (1 180)	213 (14 800)	222 (9 890)	227 (14 600)	234 (12 800)
	270 (17 000)	246 (1 000)	229 (1 230)	245 (1 550)	243 (16 600)	258 (3 090)
	313 (8 320)	294 (6 380)	277 (17 500)	299 (6 610)	282 (1 150)	313 (1 320)
			314 (7 590)		368 (9 120)	

TABLE IV
(Continued)

Substituent ^a	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
2-(OH), 5-(CH ₃ O)	230 (24 600)	245 (6 610)	229 (16 100)	245 (5 190)	224 (16 200)	312 (316)
	257 (8 710)	299 (200)	257 (7 420)	284 (316)	263 (7 335) _s	
	362 (5 250)		360 (4 170)		414 (7 000)	
2-(HO), 6-(CH ₃ O)	221 (12 300)	239 (1 590)	207 (12 300)	211 (12 000)	227 (10 000)	223 (9 780)
	272 (10 800)	299 (1 480)	217 (12 300)	238 (1 120)	275 (5 500)	255 (3 630)
	335 (3 470)		272 (11 000)	302 (1 410)	340 (2 630)	306 (1 740)
			340 (3 310)			
3-(CH ₃ O), 4-(HO)	228 (16 000)	241 (1 660)	207 (12 600)	216 (7 770)	250 (9 120)	227 (2 820)
	271 (12 300)	288 (6 460)	230 (15 100)	246 (1 860)	295 (3 980) _s	270 (1 350)
	298 (7 650)		278 (10 500)	292 (8 320)	348 (24 600)	
			305 (9 120)			
2,4,6-(HO) ₃	229 (15 100)	244 (1 200)	211 (11 000)	216 (10 400)	228 (13 600)	269 (1 000)
	282 (16 400)		227 (12 600)	245 (630)	240 (10 500) _s	
	320 (2 820) _s		288 (16 200)		319 (24 600)	
			325 (2 950) _s		370 (3 160) _s	
2,4,5-(CH ₃ O) ₃	231 (16 800)	246 (3 720)	233 (16 200)	218 (9 600)	233 (16 600)	249 (3 550)
	266 (9 780)	284 (1 590)	269 (9 780)	249 (3 550)	270 (10 000)	291 (2 400)
	323 (7 080)		329 (8 200)	290 (2 240)	329 (8 520)	
2,4,6-(CH ₃ O) ₄	225 (12 300)	243 (3 160)	223 (11 500)	216 (11 000)	223 (11 200)	247 (2 290)
	262 (4 790)		274 (5 630)	246 (2 290)	276 (5 890)	
Propiophenones						
2-(HO)	220 (11 000)	233 (2 890)	213 (18 200)	232 (3 020)	230 (18 600)	297 (970)
	251 (7 950)	279 (580)	251 (8 800)	280 (795)	256 (6 310)	
	326 (3 160)		325 (3 310)		365 (5 250)	
4-(HO)	219 (11 200)	232 (1 590)	220 (11 200)	209 (7 950)	237 (6 610)	220 (3 980)
	265 (16 200)		277 (15 100)	235 (1 590)	329 (24 600)	261 (1 120)
	276 (12 000) _s					

^aFor the data of the other substances see ref.^{2,23}.

TABLE V
 Ultraviolet Data of Substituted 1-Indanones and 1,2-Indandiones

Substituent ^a	Dioxane		Ethanol	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
1-Indanones				
6-(CH ₃ O)	222 (14 100)	233 (6 800)	219 (19 700)	234 (5 630)
	235 (7 080) _s	265 (160)	248 (8 920)	272 (280)
	243 (8 920)		320 (4 080)	
	247 (8 400) _s			
	316 (4 470)			
6-(CH ₃ O), 7-(C ₂ H ₅ O)	226 (16 000)	242 (6 760)	219 (22 900)	241 (6 030)
	253 (8 710)	274 (630)	255 (9 550)	281 (630)
	320 (3 550)		325 (3 550)	
2-(HO), 5,6-(CH ₂ O ₂)	232 (17 800)	249 (2 460)	233 (16 600)	217 (8 800)
	267 (8 000)	282 (1 700)	270 (7 590)	248 (2 510)
	319 (10 150)		322 (10 300)	286 (2 460)
1,2-Indandiones				
4,5-(CH ₃ O) ₂	249 (10 400)	225 (4 470)	233 (15 300)	217 (7 800)
	324 (11 650)	271 (2 240)	289 (12 800)	251 (3 630)
			340 (2 460) _s	
4,5-(CH ₂ O ₂)	256 (12 100)	227 (4 270)	208 (15 500)	217 (7 080)
	335 (6 030) _s	279 (1 860)	239 (20 900)	255 (3 980)
	345 (6 170)		265 (4 270) _s	
			293 (8 320)	
			312 (7 250) _s	
		380 (1 450) _s		
5,6-(CH ₂ O ₂)	233 (10 300)	245 (6 760)	234 (14 900)	217 (7 250)
	239 (7 250) _s	269 (3 020)	272 (6 760)	250 (3 160)
	250 (6 800)	318 (2 760)	326 (9 120)	289 (2 760)
	293 (5 630)		373 (1 910) _s	
	363 (7 250)			
6,7-(CH ₂ O ₂)	238 (12 700)	265 (7 590)	233 (19 100)	248 (8 920)
	251 (10 700) _s	336 (955)	260 (11 900)	281 (1 350)
	286 (13 200)		295 (1 590)	314 (1 260)
	390 (2 570)		353 (3 020)	

^aFor the spectra of 4,5- and 5,6-dimethoxy-, 4,5-, 5,6- and 6,7-methylenedioxy-1-indanones see ref.². 1-Indanone in ethanol λ_{\max} 244 nm (14 500), 286 (3 020), 291 (3 090), ref.²⁴; 4-(OH) 225 (25 100), 257 (87 100), 312 (26 900), ref.²⁵; 5-(OH) 270 (7 950), 292 (7 950), ref.²⁶; 7-(OH) 255 (10 000), 315 (3 160), ref.²⁷; 7-(OH) in ethanol-NaOH 238 (20 000), 262 (7 950), 368 (6 310), ref.²⁷; 4,7-(OH)₂ in ethanol 220 (17 400), 230 (17 000), 278 (17 400), ref.²⁵; 5-(CH₃O) no solvent specified 266 (2 140), 287 (1 550), ref.²⁸; 7-(CH₃O) in ethanol 240 (6 310), 295 (2 000), ref.²⁹.

other is observed. Contrary to the bands of the corresponding phthalides, the bands of 5,6- and 6,7-methylenedioxy-(dimethoxy)-1-indanone display a slight red shift. The secondary band of all the 1-indanone derivatives having a methylenedioxy group is shifted to the red contrary to that of the corresponding dimethoxy derivatives. However, the intensity of the secondary band of compounds with a methylenedioxy group does not exceed that of the same band of compounds having a pair of *ortho*-methoxyl groups.

The spectra of 1,2-indanedione derivatives (Table V) are similar to those of 1-indanones except that the 4,5- and 5,6-substituted 1,2-indanediones display a further band in form of a shoulder. The spectrum of the 6,7-substituted compound shows a further band at c. 300 nm; the other bands of 1,2-indanedione are shifted toward the red by c. 5 nm in contrast to the band of 1-indanone.

TABLE VI
Ultraviolet Data of Substituted 1-Propenylbenzenes

Substituent	Dioxane		Ethanol	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
4-(CH ₃ O)	214 (12 300)	230 (5 500)	210 (16 000)	226 (3 700)
	261 (14 700)		259 (18 800)	
	270 (12 400)s		289 (2 600)s	
	286 (3 300)s		305 (1 400)s	
	309 (900)s			
3,4-(CH ₃ O) ₂ ¹³	—	—	260 (16 600)	240 (8 100)
			293 (5 250)s	
3,4-(CH ₂ O ₂)	226 (11 000)	241 (5 760)	216 (18 000)	240 (5 500)
	261 (12 750)		284 (4 470)	
	266 (12 150)s		264 (12 000)s	
	303 (5 630)		304 (5 370)	
	320 (2 760)s		320 (2 400)s	
3-(CH ₃ O), 4-(HO) ^a	226 (11 200)	241 (6 310)	215 (17 600)	240 (6 460)
	261 (13 200)		260 (12 600)	
	265 (12 900)s		265 (12 300)s	
	302 (4 270)s		292 (4 470)s	
	315 (2 140)s		313 (2 190)s	
3-(CH ₃ O), 4,5-(CH ₂ O ₂)	231 (16 800)	246 (3 630)	220 (28 900)	245 (4 000)
	275 (12 000)		273 (12 300)	
	298 (5 130)s		294 (5 400)s	
	309 (2 630)s		304 (3 000)s	

^aIn ethanol-NaOH λ_{\max} 220 (15 900), 286 (14 830), 308 (10 000) s, 360 (1 100) s, λ_{\min} 250 (4 790).

TABLE VII
Ultraviolet Data of Substituted Cinnamic Acids

Substituent ^a configuration	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
Unsubstituted ³⁰ <i>cis</i>	—	—	257 (12 900)	—	254 (12 000)	—
Unsubstituted <i>trans</i>	218 (12 300)	221 (11 800)	211 (13 400)s	220 (13 200)	217 (14 700)	219 (14 500)
	222 (11 900)	232 (2 460)	216 (15 900)	231 (2 500)	221 (15 900)	229 (5 370)
	274 (20 500)		222 (13 800)		267 (20 400)	295 (4 790)
			274 (21 400)		296 (4 800)	
			296 (9 120)s			
2-(HO) <i>trans</i>	218 (12 900)	244 (4 220)	216 (14 500)	245 (4 570)	232 (14 100)	262 (9 550)
	224 (12 100)s	299 (5 130)	226 (12 100)s	301 (5 500)	274 (10 500)	307 (2 760)
	274 (16 600)		274 (16 600)		365 (7 250)	
	324 (9 120)		326 (9 120)			
3-(HO) <i>trans</i>	219 (12 600)	226 (11 500)	216 (15 900)	227 (12 100)	214 (15 900)	225 (15 000)
	233 (12 000)	249 (6 100)	234 (12 900)	250 (7 250)	230 (15 100)	236 (14 800)
	277 (17 600)	307 (4 680)	277 (19 100)		252 (20 000)	269 (14 800)
	315 (4 790)		313 (5 130)s		277 (15 100)	
					330 (2 500)s	
4-(HO) <i>trans</i>	227 (12 900)	247 (1 450)	211 (11 200)	216 (10 300)	313 (16 600)s	256 (2 760)
	294 (20 900)	296 (20 600)	226 (12 000)	248 (1 780)	336 (20 200)	
	299 (20 900)	305 (20 600)	292 (19 500)s			
	311 (20 900)		300 (20 400)s			
			311 (21 400)			
4-(HO)-methyl ester <i>trans</i>	—	—	211 (10 300)	217 (8 900)	244 (7 500)	273 (630)
			229 (12 000)	250 (1 350)	300 (4 700)s	316 (6 610)
			298 (20 400)s		312 (6 920)	
			314 (24 000)		368 (29 500)	
			390 (320)s			
2,3-(HO) ₂ <i>trans</i>	224 (15 900)	247 (3 390)	224 (15 900)	249 (3 470)	235 (12 500)	227 (12 100)
	285 (18 800)		288 (18 600)		287 (9 120)	263 (7 770)
	330 (4 570)s		335 (3 350)s		442 (2 460)	412 (2 300)
2,5-(OH) ₂ <i>trans</i>	216 (12 100)	235 (8 320)	215 (13 000)	235 (8 400)	216 (12 300)	256 (6 310)
	247 (9 600)	256 (9 120)	250 (9 780)	255 (9 600)	305 (7 590)	386 (2 290)
	275 (14 500)	311 (2 340)	278 (15 300)	313 (2 510)	427 (1 590)s	
	355 (6 760)		355 (6 610)			
3,4-(HO) ₂ <i>trans</i>	220 (14 100)	228 (10 700)	218 (16 600)	229 (11 100)	215 (18 000)	276 (7 080)
	236 (11 900)s	262 (4 170)	235 (11 600)	238 (11 500)	245 (11 600)s	311 (8 320)
	241 (12 000)	304 (14 100)	243 (11 600)	264 (5 500)	302 (9 120)	
	296 (14 800)		299 (14 800)	303 (14 700)	348 (15 900)	
	324 (17 800)		326 (17 800)		394 (6 170)s	

TABLE VII

(Continued)

Substituent ^a configuration	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (e)	λ_{\min} (e)	λ_{\max} (e)	λ_{\min} (e)	λ_{\max} (e)	λ_{\min} (e)
2-(CH ₃ O) ^{16b} <i>cis</i>	—	—	225 (12 600) 265 (6 310) 308 (5 020) _s	243 (4 370)	254 (7 950) 295 (4 170)	240 (6 310) 282 (3 630)
2-(CH ₃ O) ^{16b} <i>trans</i>	—	—	223 (12 600) 275 (15 900) 320 (8 100)	244 (3 980) 300 (5 760)	269 (14 300) 312 (6 760)	240 (5 020) 297 (6 170)
3-(CH ₃ O) <i>trans</i>	218 (16 600) 232 (16 000) 276 (18 200) 312 (5 000)	228 (15 900) 249 (7 800) 306 (4 900)	217 (15 500) 228 (14 100) _s 276 (17 800) 309 (4 800) _s	249 (7 100)	222 (19 500) 270 (17 600) 305 (4 790) _s	245 (8 320)
4-(CH ₃ O) <i>trans</i>	226 (12 300) 291 (21 400) 299 (21 400) 308 (21 400)	246 (1 260) 295 (21 200) 303 (21 200)	211 (11 200) 225 (12 300) 293 (20 900) _s 299 (21 400) 308 (21 400)	215 (16 600) 245 (20 000) 303 (20 900)	220 (14 800) 284 (22 400) 300 (16 200) _s	239 (2 890)
2,3-(CH ₃ O) ₂ <i>cis</i>	221 (17 600) 270 (9 200)	245 (6 460)	220 (17 600) 264 (8 620)	244 (6 310)	222 (19 100) 259 (10 300) 300 (1 600) _s	241 (6 760)
2,3-(CH ₃ O) ₂ <i>trans</i>	228 (18 600) 280 (19 300) 330 (2 240) _s	248 (5 370)	226 (19 500) 279 (19 500) 325 (2 600) _s	247 (5 700)	226 (22 400) 273 (17 800) 311 (2 140) _s	244 (6 920)
2,3-(CH ₂ O) ₂ <i>trans</i>	235 (13 200) 278 (20 900) 336 (3 500)	249 (5 900) 311 (2 500)	232 (15 300) 275 (19 000) 329 (3 300)	213 (9 300) 248 (6 600) 313 (2 900)	—	—
2,4-(CH ₃ O) ₂ <i>cis</i>	215 (12 000) 238 (10 700) 282 (9 780) _s 293 (10 300) 322 (12 900)	226 (9 340) 255 (3 630) 301 (9 400)	210 (13 500) 230 (10 000) _s 275 (7 950) 315 (9 550)	254 (5 130) 289 (7 800)	220 (14 800) 267 (12 000) 303 (8 130)	245 (6 460) 292 (7 420)
2,4-(CH ₃ O) ₂ <i>trans</i>	237 (12 500) 285 (14 100) _s 291 (15 000) 324 (17 000)	226 (9 120) 255 (2 890) 302 (11 000)	216 (11 700) 237 (11 200) 290 (13 500) 324 (15 500)	226 (9 120) 255 (3 390) 302 (11 200)	220 (12 300) 273 (11 800) 285 (10 000) _s 309 (9 400)	248 (5 370) 294 (8 130)
2,5-(CH ₃ O) ₂ <i>cis</i>	221 (12 900) 238 (9 780) _s 275 (10 000) 345 (5 370)	256 (7 250) 307 (2 630)	218 (13 200) 237 (9 550) _s 272 (8 520) 335 (4 570)	257 (7 500) 303 (3 160)	261 (9 300) 323 (4 850)	249 (8 520) 294 (2 630)

TABLE VII
(Continued)

Substituent ^a configuration	Dioxane		Ethanol		Ethanol-NaOH	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
2,5-(CH ₃ O) ₂ <i>trans</i>	221 (13 500)	237 (11 000)	218 (13 500)	254 (9 120)	219 (13 800)	248 (8 710)
	228 (12 600) _s	255 (8 920)	240 (10 700) _s	307 (2 570)	235 (10 500) _s	296 (2 290)
	241 (11 200)	308 (2 140)	275 (14 500)		265 (10 700)	
	275 (15 900)		346 (6 310)		328 (5 250)	
	351 (7 250)					
2,6-(CH ₃ O) ₂ <i>cis</i>	217 (18 200)	248 (4 570)	211 (17 000)	245 (2 630)	221 (17 000)	242 (2 950)
	284 (8 520)		285 (8 000)		273 (8 130)	
3,4-(CH ₃ O) ₂ <i>trans</i>	235 (12 000)	225 (9 340)	208 (13 000)	224 (9 800)	219 (12 000)	223 (11 800)
	289 (8 800)	260 (3 020)	218 (10 800) _s	257 (3 390)	230 (12 500)	252 (3 800)
	323 (10 000)	302 (7 590)	233 (10 700)	300 (7 590)	283 (10 300)	295 (7 770)
			287 (8 600)		309 (8 400)	
			318 (8 900)			
3,4-(CH ₂ O) ₂ <i>trans</i>	218 (13 200)	225 (9 780)	215 (15 500)	225 (10 500)	218 (16 200)	254 (6 170)
	235 (11 900)	261 (4 470)	234 (12 000)	260 (5 020)	229 (14 500) _s	295 (9 550)
	240 (11 300) _s	300 (9 120)	238 (11 500) _s	300 (9 550)	279 (13 200) _s	
	290 (12 400)		289 (11 800)		282 (13 400)	
	324 (16 800)		324 (15 300)		314 (13 400)	
2-(HO), 4-(CH ₃ O) <i>trans</i>	218 (12 900)	228 (10 000)	219 (12 900)	230 (9 550)	228 (14 500)	269 (7 250)
	238 (11 900)	255 (3 310)	239 (10 300)	257 (3 630)	250 (9 550) _s	306 (4 170)
	285 (15 100) _s	302 (11 500)	292 (13 200)	304 (10 300)	279 (7 800)	
	291 (16 200)		328 (14 800)		345 (7 420)	
	324 (17 800)					
2-(HO), 5-(CH ₃ O) <i>trans</i>	218 (13 200)	236 (9 400)	218 (13 400)	236 (9 120)	231 (13 800)	314 (1 150)
	246 (10 100)	256 (9 340)	246 (10 500)	255 (9 780)	275 (9 120) _s	
	275 (14 100)	307 (2 290)	276 (14 900)	309 (2 190)	385 (6 610)	
	351 (7 080)		354 (7 080)			
2-(HO), 6-(CH ₃ O) <i>trans</i>	223 (16 400)	246 (2 200)	220 (15 100)	245 (1 900)	236 (13 200)	226 (12 300)
	293 (20 400)		297 (18 600)		295 (10 400)	262 (3 890)
				354 (5 630)	328 (4 270)	
4-(HO), 3-(CH ₃ O) <i>trans</i>	219 (11 200)	225 (9 780)	218 (14 000)	226 (11 100)	218 (13 800)	271 (3 240)
	235 (12 000)	261 (3 310)	235 (12 600)	261 (4 200)	238 (10 500) _s	310 (11 000)
	296 (13 500)	301 (13 200)	296 (14 500) _s		306 (11 200)	
	322 (18 200)		323 (19 100)		348 (22 400)	
3-(HO), 4-(CH ₃ O) <i>trans</i>	220 (14 100)	227 (10 500)	218 (15 100)	228 (10 600)	216 (16 000)	242 (12 300)
	235 (11 600) _s	260 (4 900)	235 (11 200) _s	262 (5 370)	230 (14 100) _s	278 (12 500)
	241 (12 900)	304 (13 500)	242 (11 800)	305 (13 700)	260 (16 600)	
	293 (15 500)		292 (14 500)		289 (13 500)	
	320 (16 200)		322 (15 300)		346 (5 630) _s	

Aromatic Compounds With a Double Bond in the Side Chain

Compounds with a vinyl or propenyl group: The effect of hydroxyl, methoxyl or methylenedioxy groups on the spectrum is also observed in aromatic compounds having an α,β -double bond in the side chain (Table VI). In the literature, a great number of aromatic substances of the vinyl or propenyl type with methoxyl or methylenedioxy groups in the positions 3,4 have been reported. The spectra show that, contrary to the methoxyl groups, the presence of a methylenedioxy group causes a hyperchromic and a red shift of the longest wavelength band. The spectra of 3,4-methylenedioxy and 3,4-dimethoxypropenylbenzene and of the corresponding epoxides have been described earlier by Hillmer and coworkers^{13,14}. The spectra of epoxides resemble those of compounds with double bonds. However, those authors did not describe the effect of the methoxyl and methylenedioxy groups on the ultraviolet spectra. A shift of these bands due to the effect of the pair of *ortho*-methoxyl groups against that of the methylenedioxy group can also be observed in tetrahydroberberinmethine if compared with tetrahydropseudoeberberinmethine¹⁵.

Derivatives of cinnamic acid:* The spectra of mono- and disubstituted *cis*- and *trans*-hydroxy, methoxy, and methylenedioxy cinnamic acids resemble those of similar benzoic acids (Table VII, Fig. 2). The secondary bands of 2- and 3-hydroxy-*trans*-cinnamic acids are shifted by c. 20 nm and the first primary bands by c. 40 nm to the red compared to the bands of the corresponding derivatives of benzoic acid. The band in the 300 nm region of 4-hydroxy cinnamic acid corresponds to the sum of the secondary and the first primary band similarly to that of 4-hydroxybenzoic acid; it is also shifted to the red. Similar displacements are observed in the spectra of dihydroxy, methoxy, and dimethoxy acids if compared with those of the corresponding benzoic acids. In all the hydroxy acids, ionization of the carboxyl and hydroxyl groups in alkaline medium results in a marked red shift of the secondary band; the pattern of the first primary band does not change. The largest displacement is observed in 2,3-dihydroxy-*trans*-cinnamic acid. Ionization of the carboxyl group causes a blue shift of the secondary and the first primary band of all the methoxy acids. The spectra of cinnamic acids (in ethanol) substituted simultaneously by a methoxyl and a hydroxyl group are similar to those of the corresponding derivatives of benzoic acid; however, all their bands display a large red shift. An exception is 2-hydroxy-6-methoxy-*trans*-cinnamic acid whose absorption bands are shifted to the blue against the band of the equally substituted benzoic acid. The secondary band of acids simultaneously substituted by a methoxyl and a hydroxyl group undergo a red shift in ethanolic-alkaline medium and the first primary band a blue shift compared to that of the non-ionized form. An exception is the first primary band of 4-hydroxy-3-methoxy-*trans*-cinnamic acid which is also shifted to the red. The band of the non-ionized 2-hydroxy-6-methoxy-*trans*-cinnamic acid at 297 nm (in ethanol) probably consists of a secondary and a first primary band because on ionization of the compound this band is split.

* Many *cis*- and *trans*-substituted cinnamic acids have been studied earlier by Böhme and coworkers¹⁶ (Marburg, G.F.R.) whom we wish to thank for many of the derivatives studied in this paper.

Explanation to Table VII: ^a*cis*-2-(HO)Na₂ salt in methanol λ_{\max} 228 (12 900), 254 (7 950)s, 330 (5 890), λ_{\min} 290 (1 740), ref.¹⁶; *trans*-2,4-(HO)₂ in methanol λ_{\max} 217 (12 600), 244 (6 310)s, 286 (10 000), 324 (12 600), λ_{\min} 260 (3 000), 301 (7 800), ref.¹⁶; *cis*-4-(CH₃O) in methanol λ_{\max} 272 (10 500), λ_{\min} 242 (4 000), ref.³¹; *trans*-2-(HO), 3-(CH₃O) in methanol λ_{\max} 227 (20 000), 278 (20 000), 325 (5 020)s, λ_{\min} 250 (5 020), ref.¹⁶. ^bSpectra of acids and their sodium salts in methanol.

The intensity of the secondary and the first primary band of *cis*-derivatives is lower than that of the bands of the corresponding *trans*-derivatives (Fig. 2). The secondary band of dimethoxy-*cis*-cinnamic acids is shifted to the blue by c. 10 nm and the first primary band by c. 15 nm contrary to that of the *trans*-derivatives (except for the 2,5-dimethoxy-*cis*-cinnamic acid whose first primary band shifts only by 3 nm). The secondary band of 2,5-dihydroxy, 2,5-dimethoxy and 2-hydroxy-5-methoxy-*cis* and *trans*-cinnamic acids (in ethanol) shows an unusual red shift (in the region of 350 nm) whereas the position of the first primary band is similar to that of other cinnamic acids. The red shift location of the secondary band of 2,5-disubstituted derivatives of cinnamic acid corresponds to that observed in 2,5-dihydroxy, 2,5-dimethoxy and 2-hydroxy-5-methoxy derivatives of benzaldehyde, benzoic acid and acetophenone (Tables II, III, IV).

Only the secondary band of 2,3-methylenedioxy-*trans*-cinnamic acid is shifted to the red contrary to that of the corresponding dimethoxy derivative. The absorption bands of 3,4-methylenedioxy-*trans*-cinnamic acid undergo a red shift compared to those of the dimethoxy derivatives. The relative intensity of the secondary bands of these two compounds with methylenedioxy groups is higher compared to that of the bands of compounds with a pair of methoxyl groups. The intensity of the first primary bands of compounds having a methylenedioxy group and of those of compounds with a pair of methoxyl groups in the positions 2,3 is the same. The intensity of the first primary band of 3,4-methylenedioxy-*trans*-cinnamic acid is higher than that of the band of the derivative having a pair of methoxyl groups in the same position, however, lower than the intensity of the secondary band.

Oximes of Methoxy and Methylenedioxy Derivatives of Aromatic Compounds

Benzaldehyde and acetophenone derivatives: The difference between the spectra of hydrazones and those of the oximes of various aliphatic and aromatic oxo compounds has been studied

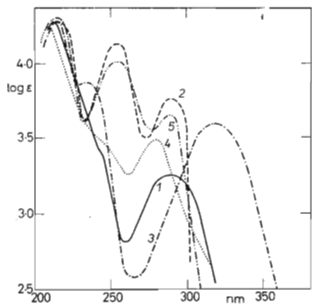


Fig. 1

UV Spectra of 1 2,3-, 2 2,4-, 3 2,5-, 4 2,6- and 5 3,4-Dimethoxybenzoic Acids (in ethanol)

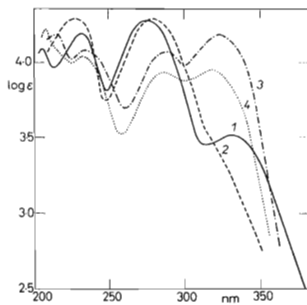


Fig. 2

Spectra of 1 2,3-Methylenedioxy-*trans*-, 2 2,3-Dimethoxy-*trans*-, 3 3,4-Methylenedioxy-*trans*-, 4 3,4-Dimethoxy-*trans*-cinnamic Acids (in ethanol)

TABLE VIII

Ultraviolet Data of Oximes of Substituted Benzaldehydes, Acetophenones, 1-Indanones, and 1,2-Indandiones

Substituent	Dioxane		Ethanol	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
Benzaldoximes				
Unsubstituted	215 (11 700)	224 (5 020)	210 (15 100)	222 (4 470)
	253 (14 600)	290 (1 000)	214 (11 900) _s	289 (1 000)
	283 (2 090) _s		252 (14 800)	
	293 (1 290)		282 (2 090) _s	
			292 (1 180)	
3-(CH ₃ O)	227 (13 200)	239 (8 710)	217 (19 500)	239 (8 400)
	256 (12 000)	283 (2 290)	256 (12 100)	284 (2 460)
	299 (3 240)		299 (3 300)	
	308 (2 340) _s			
4-(CH ₃ O)	263 (19 700)	228 (3 160)	212 (15 300)	231 (3 000)
	284 (4 680) _s		265 (19 100)	
	293 (1 700) _s		293 (4 470) _s	
			302 (2 300) _s	
2,3-(CH ₃ O) ₂	230 (16 600)	241 (7 300)	222 (26 900)	241 (7 800)
	262 (12 100)	288 (1 950)	260 (12 900)	290 (2 240)
	300 (2 190)		301 (2 400)	
3,4-(CH ₃ O) ₂	228 (13 800)	244 (6 460)	215 (18 400)	243 (6 170)
	267 (14 800)	286 (7 420)	222 (16 400) _s	288 (7 250)
	291 (7 590) _s		266 (14 900)	
	297 (7 770) _s		299 (7 800)	
	301 (7 950)		310 (5 630) _s	
	312 (5 130) _s			
3,4-(CH ₃ O) ₂	227 (11 900)	245 (5 370)	212 (18 400)	244 (5 250)
	267 (11 600)	283 (5 130)	222 (14 100) _s	285 (5 130)
	306 (7 700)		267 (11 900)	
	317 (5 250) _s		306 (7 950)	
			310 (5 630) _s	
Oximes of acetophenones				
2,4-(HO) ₂	222 (14 100)	245 (5 020)	218 (20 000)	245 (5 370)
	227 (13 200) _s	285 (4 680)	228 (13 200) _s	286 (5 370)
	236 (10 300) _s		266 (12 900)	
	266 (12 600)		299 (7 250)	
	272 (11 500) _s			
	300 (7 080)			
	305 (6 920) _s			

TABLE VIII
 (Continued)

Substituent	Dioxane		Ethanol	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
Oximes of acetophenones				
2,4-(CH ₃ O) ₂	220 (11 500)	231 (7 950)	215 (18 200)	232 (7 250)
	247 (11 500)	272 (3 160)	249 (10 700)	273 (3 310)
	285 (3 800)		285 (3 800)	
4-(HO), 3-(CH ₃ O)	222 (12 600)	239 (5 760)	216 (18 200)	239 (5 890)
	263 (13 200)	286 (5 500)	263 (12 900)	287 (5 890)
	294 (5 630)		293 (5 950)	
2,4,5-(CH ₃ O) ₃	222 (12 600)	238 (7 770)	215 (18 000)	239 (7 250)
	252 (9 340)	275 (2 290)	253 (8 710)	275 (2 460)
	299 (5 760)		298 (5 630)	
2-(HO) (propiofenone)	224 (14 100)	238 (6 460)	217 (19 500)	237 (6 170)
	256 (9 780)	276 (1 380)	255 (9 340)	276 (1 320)
	263 (7 250)s		263 (6 610)s	
	307 (4 570)		304 (4 080)	
Oximes of 1-indanones				
5,6-(CH ₃ O) ₂	224 (14 500)	239 (6 610)	216 (18 200)	240 (6 610)
	260 (16 000)	279 (2 570)	261 (15 100)	281 (2 760)
	296 (6 760)s	312 (9 550)	297 (7 080)s	317 (9 120)
	303 (8 920)s	317 (9 000)	308 (10 700)	
	308 (10 000)		314 (9 780)s	
	314 (9 780)		321 (9 780)	
	320 (10 000)			
5,6-(CH ₂ O) ₂	221 (13 200)	235 (5 370)	212 (27 600)	240 (5 250)
	260 (12 000)	282 (1 820)	225 (13 800)s	281 (2 000)
	316 (10 500)		262 (12 300)	
	321 (10 000)s		314 (11 000)	
			319 (10 500)s	
		326 (9 780)s		
6,7-(CH ₃ O) ₂ , 4-(Br)	224 (36 300)	251 (10 500)	224 (36 300)	246 (7 590)
	255 (11 200)s	289 (2 090)	264 (10 500)	289 (2 460)
	264 (12 000)		273 (8 420)s	
	272 (9 500)s		309 (3 850)	
	309 (3 980)		321 (3 160)s	
	320 (3 470)s			
6,7-(CH ₂ O) ₂ , 4-(Br)	230 (32 400)	257 (15 900)	230 (24 600)	255 (11 100)
	264 (17 400)	291 (1 590)	265 (12 400)	291 (1 260)
	270 (13 800)s		272 (10 000)s	
	321 (5 020)		324 (3 670)	

TABLE VIII
(Continued)

Substituent	Dioxane		Ethanol	
	λ_{\max} (ϵ)	λ_{\min} (ϵ)	λ_{\max} (ϵ)	λ_{\min} (ϵ)
Oximes of 1,2-indandiones				
4,5-(CH ₃ O) ₂	246 (17 400)	221 (5 890)	248 (15 900)	223 (5 500)
	312 (16 000)	272 (5 130)	319 (16 000)	277 (6 170)
4,5-(CH ₂ O) ₂	251 (19 700)	222 (5 400)	254 (19 500)	225 (4 570)
	313 (7 590) _s	281 (3 470)	321 (7 600) _s	286 (3 800)
	332 (8 710)		341 (8 900)	
5,6-(CH ₂ O) ₂	233 (9 780) _s	269 (6 610)	240 (9 550) _s	213 (5 900)
	248 (12 700)	304 (3 020)	251 (10 900)	270 (6 900)
	285 (8 920)		290 (9 300)	312 (3 500)
	347 (10 500)		352 (10 700)	
6,7-(CH ₂ O) ₂	242 (14 000)	259 (11 600)	240 (11 900)	214 (5 130)
	248 (13 200) _s	318 (630)	282 (18 000)	258 (10 500)
	277 (17 000)		379 (2 570)	324 (500)
	369 (2 950)			

earlier^{11,12}. However, so far, no attention has been paid to the effect of the methoxyl and methylenedioxy groups on the spectra of the oximes of aromatic oxo compounds. A comparison of the spectra of the compounds listed in Table VIII with those of the initial benzaldehydes (Table III) shows that the secondary and the first primary band of the oximes of 3-methoxybenzaldehyde are shifted to the blue. The absorption band of 4-methoxy derivative (which in the initial compound corresponds to the secondary and to the first primary band) broadens. This is probably due to the fact that the first primary and the secondary band are shifted in opposite direction. A similar phenomenon is also observed in the bands of the oximes of acetophenones. The secondary bands of oximes of 2,3-disubstituted derivatives of benzaldehyde are shifted by 22 nm to the blue whereas the pattern of the first primary band remains unchanged. The two bands of 3,4-dimethoxy and 3,4-methylenedioxy derivatives are shifted to the blue by less than 10 nm (Tables I, II and Fig. 3, ref.²). The pattern of the spectra of oximes of benzaldehydes monosubstituted and disubstituted in the positions 2,3 and 3,4 does not change, which is similar to the finding made in the initial compounds. Consequently, the effect of the pair of *ortho*-methoxyl groups on the wavelength and intensity of the longer wavelength absorption bands against the methylenedioxy group can also be observed in the spectra of the oximes of benzaldehyde.

Oximes of 1-indanones and of 1,2-indanediones: A comparison was carried out between the spectra of oximes of 5,6-dimethoxy and 5,6-methylenedioxy-1-indanone (Table VIII) and those of the initial substances (Table III, ref.²). Whilst the secondary band of the two oximes is split into two bands and is shifted to the red, the first primary band remains uniform and shifts to the blue. The difference in the spectra caused by various electron donating substituents of the two

oximes is similar to that observed in the spectra of the initial compounds. The longer wavelength band of the oxime of 4-bromo-6,7-methylenedioxy-1-indanone is shifted as expected to the red (without change in intensity) compared to that of the dimethoxy derivative. The shorter wavelength band does not differ at all; this finding might be accounted for by the presence of the electro-negative bromine atom in the vicinity of electron donating groups. The spectra of 4,5-, 5,6-methylenedioxy and 4,5-dimethoxy-1,2-indanedione-2-oximes (for the position of the oximino group see ref.^{17,18}) do not reveal the presence of a longer wavelength shoulder, which is contrary to the finding made in the initial diones. The other bands are shifted to the red compared to those of the initial compounds. A similar red shift is also observed in the spectrum of 6,7-methylenedioxy-1,2-indanedione-2-oxime. However, there disappears the band of low intensity at 300 nm which is present in the spectrum of the corresponding dione. All the bands of 4,5-methylenedioxy-1,2-indanedione-2-oxime shift to the red against those of the dimethoxy derivatives similarly to the bands of the initial 1,2-diones. The intensity of the bands of these four compounds changes in the opposite direction to that observed in other compounds with methylenedioxy and methoxyl groups.

DISCUSSION

The results obtained show *a*) the effect of various positions of hydroxyl and methoxyl groups of simple aromatic compounds (benzene, benzoic acid, benzaldehyde, acetophenone, and propiophenone) upon the ultraviolet spectra; *b*) a comparison of the effect of the pair of *ortho*-methoxyl groups and the methylenedioxy group on the spectra of these compounds. It may be concluded that in unpolar and in polar media the hydroxy/methoxy substituted acids, aldehydes, acetophenones, and propiophenones behave in a similar manner. However, the secondary and the first primary bands of aldehydes undergo a larger shift to the red than the bands of the acids. These compounds show a different behaviour in ethanolic-alkaline medium. The bands of 2-hydroxy acids are shifted to the blue and those of 3- and 4-hydroxy acids to the red compared to the bands of non-ionized compounds. In the spectra of aldehydes and ketones, the largest red shift is displayed by the bands of 2-hydroxy derivatives, a smaller one by those of 3-hydroxyderivatives and the smallest by the bands of 4-hydroxy derivatives. Ionization of all these compounds results in the formation of another pair of unbonded electrons which may enter into interaction with the π -electrons of the aromatic nucleus. This manifests itself by a red shift and an increase in the intensity of the bands. This interaction is limited when the ionized hydroxyl group is in the *ortho*-position to the ionized carboxyl group and it manifests itself by a blue shift of the secondary and the first primary band of 2-hydroxybenzoic acid. This phenomenon can also be observed in the bands of ionized disubstituted derivatives, except in those of cinnamic acids (*vide infra*). The pattern of the spectra of disubstituted derivatives indicates the position of the substituents; the greatest difference in wavelengths of the secondary and the first primary band show 2,5-dihydroxy or methoxy derivatives (acids, aldehydes and ketones). This finding can be accounted for by the presence of electron donating substituents in *para*-position to each other and by the asymmetric location of the electron accepting group. Doub

and Vandenberg⁸ found that the spectra of disubstituted derivatives consist of the spectra of the corresponding monosubstituted compounds. The additivity of the intensities holds good for all the bands, however, substitution by electron donating and electron accepting groups in some positions causes either a blue or a red shift of the bands of these compounds (see 2,3-, 2,5- and 2,6-disubstituted compounds). On ionization of the hydroxyl group, the bands are shifted to the red against those of compounds with non-ionized groups, whereas when the carboxyl group is ionized, the bands are shifted to the blue (Tables II, VII). The position of the secondary and the first primary band of the salts of hydroxy acids (ionized hydroxyl and carboxyl groups) results from these two shifts.

A similar effect of the electron donating groups (hydroxyl, methoxyl, and methylenedioxy groups) on the position and intensity of the individual bands of the ultraviolet spectra in dioxane, ethanol, and in ethanolic hydroxide can also be observed with compounds whose carboxyl group is substituted by the vinyl, propenyl of the *cis*- and *trans*- $\text{CH}=\text{CH}-\text{COOH}$ group. The pattern of the spectra of compounds with a five-membered side ring carrying a carbonyl group in the α -position to the aromatic nucleus (1-indanone) shows to be affected by the position of the electron donating substituent (substituents). The largest red shift (in dioxane or ethanol) of the secondary band is observed in the spectra of compounds whose hydroxyl, methoxyl or methylenedioxy group is located in the vicinity of the carbonyl group.

Furthermore, we have studied the effect of the formation of oximes of the above-mentioned oxo compounds on the pattern of the ultraviolet spectra. The secondary band of oximes of benzaldehydes and acetophenones substituted with a hydroxyl group in the position 2 undergoes a blue shift and the two primary bands a red shift compared to the bands of the initial carbonyl compounds. All three bands of the other mono- and disubstituted oximino derivatives (except those of compounds with substituents in position 2) display a blue shift. The difference between the pattern of the spectra of *ortho*-dimethoxy substituted and that of methylenedioxy substituted oximes of benzaldehydes and of 1-indanone and 1,2-indanedione is analogous to that observed in similarly substituted simple aromatic oxo compounds². Consequently, the effect of these substituents is quite regular and holds true in the ultraviolet spectra of simple aromatic compounds having an electron accepting group.

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