# Spectrographic Contributions to Lignin Chemistry

IX.* Absorption Properties of Some 4-Hydroxyphenyl, Guaiacyl, and 4-Hydroxy-3,5-dimethoxyphenyl Type Model Compounds for Hardwood Lignins

GUNHILD AULIN-ERDTMAN and ROLAND SANDÉN

Wood Chemistry Laboratory, Royal Institute of Technology, Stockholm, Sweden

About forty *p*-substituted phenols, some of them carrying one or two *o*-methoxyl groups, have been investigated as regards their UV absorption in non-ionized and in ionized forms. A series of regular absorption differences are found on comparison of 4-hydroxyphenyl, 4-hydroxy-3-methoxyphenyl, and 4-hydroxy-3,5-dimethoxyphenyl derivatives with identical *p*-side-chains. A marked effect of *o*-methoxyl groups on the planarity of 2,2'-dihydroxybiphenyls and an easy light induced *cis-trans*-rearrangement of di-ionized *p*-coumaric acids are reported.

Lignins contain aromatic units of three types: (1) 4-hydroxyphenyl, (2) guaiacyl, and (3) 4-hydroxy-3,5-dimethoxyphenyl. These units carry
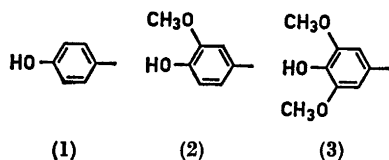
straight three-carbon side-chains *para* to the hydroxyl group and the phenylpropane units are linked to each other by ether bridges or carbon-carbon bonds.

In softwood lignins most aromatic elements are of the guaiacyl type, carrying different *p*-substituents. The so-called $\Delta\varepsilon$-method,[1,2] which is based on UV absorption measurements, was developed in the 1950:s as a means of distinguishing between different types of *p*-substituted guaiacyl elements

---

* Part VIII: *Svensk Papperstid.* **61** (1958) 187.

in softwood lignins. The method permits the study of special types of chromo-
phores in spite of the presence of other chromophores, but it requires an
extensive knowledge of the spectral properties of model compounds, partic-
ularly of the change in absorption occurring on reactions such as hydrogena-
tion and ionization. Since 1953 a considerable number of "$\Delta\varepsilon$-curves", illustrat-
ing such absorption changes for model compounds mainly of the guaiacyl
type have been published in this series of papers and elsewhere. Those curves
form a rather satisfactory basis for $\Delta\varepsilon$-studies on softwood lignins.

   Hardwood lignins are more complicated. Apart from guaiacyl units (type 2)
with different side-chains they also contain a large proportion of syringyl
elements (type 3), again with different side-chains. It was of interest to
investigate to what extent the $\Delta\varepsilon$-method can be used to distinguish between
the many types of phenylpropane units which are present in those lignins.
For this purpose we have studied the UV absorption properties of a series
of model compounds of types 1—3 carrying different p-substituents, some of
the compounds being of the biphenyl type. Their UV absorption characteristics
in different solvents will be discussed in this paper, particularly from the
following points of view, which seem to be of general spectrochemical interest:
comparison of compounds of types 1, 2, and 3 with identical side-chains,
as regards position and strength of various types of absorption bands; the
hydrogen bonding patterns and planarity of o,o'-diguaiacyl derivatives; cis-
trans-rearrangements in fully ionized p-hydroxycinnamic acids. We intend to
publish the $\Delta\varepsilon$-curves for ionization, hydrogenation, etc., which can be derived
from the present experimental results, in a subsequent paper.

EXPERIMENTAL

   The compounds investigated are listed in Tables 1—3 together with some data on
their preparation, purification, and physical properties. Sulphonations were carried out
in sealed glass tubes, about twice the volume of the solution. The ionization constants
given were determined by potentiometric titration in aqueous solution. The melting
points for trans-p-coumaric acid (12), cis-p-coumaric acid (13), trans-2,6-dimethoxy-4-
propenylphenol (37) (not previously obtained crystalline), and trans-sinapic acid (40)
as well as the refractive index for 37 were higher than the values reported by earlier
investigators. Compound 27, 3,2',3'-trimethoxy-5,5'-dipropylbiphenyl-2-ol is new.
   Preparation of cis-p-coumaric acid. A 25-ml glass-stoppered flask containing trans-p-
coumaric acid (1.65 g) and NaOH (0.8—0.9 g) was filled completely with water to exclude
the air and give a solution with pH 12—13. The solution was irradiated at 30—40° in a
Rayonet Srinivasan-Griffin Photochemical Chamber Reactor Model RPR 100, using
3500 Å lamps. (The intensity of radiation in the 3500 Å range is stated to be approximately
8000 microwatts/cm² at the centre of the reactor.) The UV absorption curve of the solution
was determined from time to time on small samples. After 24 h the reaction was slow.
The irradiation was then interrupted, conc. H_2SO_4 was added to pH 2, precipitated trans-
acid (0.26 g) was removed by filtration and crude cis-p-coumaric acid (1.30 g) was ex-
tracted from the filtrate with ether. Recrystallisation from water and from benzene gave
fine needles, m.p. 134—5° (decomp.).
   As a rule, a Zeiss PMQ II spectrophotometer was used for measuring UV absorptions.
In only a few cases were Beckman DU and Beckman DK-2 instruments employed. Cali-
brated 1 cm cells were used throughout. Readings were taken at intervals of 5 nm or,
when desirable, 1—2 nm, and the concentrations were chosen so as to give $0.1 < \log(I_0/I)$
<1.5. Some of the compounds (see below and the notes in the tables) were unstable in
certain solvents (cis-trans-rearrangements, oxidations, etc.). Those complications were

Table 1. 4-Hydroxyphenyl derivatives.

Compound	Solvent	Fig. No.	UV absorption maxima				*Cf.* Ref.
			nm	log ε	nm	log ε	
1. 4-Propylphenol,[a] $n_D^{23} = 1.5218$	water (pH *ca.* 5)		221	3.83	277	3.21	3
	N NaOH		237	3.95	294—5	3.39	3
	95 % EtOH	2	224	3.88	279	3.27	
	0.1 N KOH in 95 % EtOH	7	242	4.01	297—8	3.41	
2. 4-Hydroxybenzyl alcohol, recryst. from water to constant UV abs.	0.1 N HCl		223	3.91	273	3.15	4
	N NaOH		243	4.10	291	3.40	4
	0.1 N HCl in 95 % EtOH	2	226	3.94	277	3.22	
	0.1 N KOH in 95 % EtOH	7	247	4.13	295	3.43	
3. 4-Hydroxybenzyl sulphonic acid (?), obtained by sulphonation of *2.* (52 mg of *2* were heated with 3.0 ml cooking acid /5.5 % SO₂, 5.8% NaOH, pH 6—7/ from 20° to 85° over 10 h, at 100° for 6 h.) Product not isolated	0.04 N HCl in dilute sulphite liquor (SO₂ removed by bubbling N₂)	2	226 280	4.01 3.00	274	3.08	
	0.9 N NaOH in sulph. liq. as above	7	246	4.15	290—1	3.37	
4. 1-(4-Hydroxyphenyl)-propane-1-sulphonic acid (?), obtained by sulphonation of *9.* (48 mg of *9*, 3.0 ml cooking acid /5.5 % SO₂, 5.8 % NaOH, pH 6—7/; 20°→85°: 10 h; 100°: 79 h; 135°: 48 h.) Prod. not isol.	0.5 N HCl in sulph. liq. as above		226 280	4.00 3.02	274	3.08	
	0.7 N NaOH in sulph. liq.		245 336—7	4.14 2.13 [b]	291	3.36	
5. 4-Hydroxybenzaldehyde, dist. *in vacuo,* recryst. from water, m.p. 117—118°	0.01 N HCl		221	4.05	283—4	4.19	5
	0.1 N NaOH		238	3.84	330	4.40	5, 6
	0.01 N HCl in 95 % EtOH	5	222—3	4.09	285—6	4.21	7
	0.1 N KOH in 95 % EtOH	9	241	3.87	336—7	4.48	8
6. 4′-Hydroxypropiophenone, recryst. from water, m.p. 152—153°	0.1 N HCl in 95 % EtOH	5	220	4.01	276—8	4.17	8
	0.1 N KOH in 95 % EtOH	9	237—8	3.80	327	4.39	8
7. Hydroxybenzoic acid, m.p. 214.5—215°	0.1 N HCl in 95 % EtOH		255—6	4.18			9, 8
	N KOH in 94 % EtOH		277	4.25			8
8. Ethyl 4-hydroxybenzoate, m.p. 115—116.5°	0.01 N HCl		256	4.20			10
	0.1 N NaOH		295—6	4.37			10
	0.1 N HCl in 95 % EtOH		258—9	4.23			11, 12
	0.1 N KOH in 95 % EtOH		300—1	4.43			12
9. *trans*-4-Propenylphenol (*p*-anol), recryst. from water and light petroleum, m.p. 92.5—93°	0.01 N HCl		257	4.30	*285—90*	*3.34* [c]	13
	N NaOH		278	4.34			13
	0.01 N HCl in 95 % EtOH	4	259	4.32	291	3.39	14
	0.1 N KOH in 95 % EtOH	8	284	4.35			
10. *trans*-*p*-Coumaryl alcohol,[a] m.p. 118—124°	water (pH *ca.* 5)		259	4.29			
	N NaOH		284	4.33			
	0.1 N HCl in 95 % EtOH	4	263	4.29			15
	0.1 N KOH in 95 % EtOH	8	290	4.35			

Table 1. Continued.

11. *trans-p-*Coumaralde-hyde,[a] recryst. from benzene, m.p. 139.5–140.5°, pK = 8.2–8.3	0.01 N HCl	6	234	4.02	323–4	4.44	
	N NaOH	11	249	3.89	312	3.62	
			383	4.56			
	0.01 N HCl in 95 % EtOH		236	4.03	327–8	4.45	
	0.1 N KOH in 95 % EtOH		255	3.88	303	3.38	
			314	3.50	398	4.59	
12. *trans-p-*Coumaric acid, recryst. from water, dried, m.p. 226–227° (decomp.)	0.1 N HCl		226	4.03	308–9	4.31	
	pH 6.8 phosphate buffer soln.	12	286	4.32			
	N NaOH[d]	12	333	4.38			
	0.1 N HCl in 95 % EtOH	6	227–8	4.07	311	4.35	16
	0.1 N KOH in 95 % EtOH[d]		336–7	4.40			
13. *cis-p-*Coumaric acid,[a] recryst. from water and benzene, m.p. 134–134.5° (decomp.) (subl. from 124°)	0.1 N HCl[d]		293–4	3.98			
	pH 7.1 phosphate buffer soln.		265–6	4.12			
	0.1 N NaOH[d]	13	290	4.18			17
	0.1 N HCl in 95 % EtOH[d]		306	4.12			
	0.1 N KOH in 95 % EtOH[d]		297	4.19			
14. 5,5'-Dipropylbiphenyl-2,2'-diol (tetrahydromag-nolol),[a] recryst. from heptane and 70 % EtOH, m.p. 142.5–144.5°	pH 11.2 phosphate buffer soln.		*250*	*4.01*	317	3.92	
	0.1 N HCl in 95 % EtOH	3	243–4	4.00	292–3	3.87	
	0.1 N KOH in 95 % EtOH	10	*251*	*4.03*	321	3.93	
	dioxan (dist. over Na)	1	*243*	*3.94*	291	3.88	
	hexane	1	*242*	*3.73*	288	3.82	

[a] Compounds *1*, *10* and *11* supplied by I.A. Pearl, *13* by A. J. Merritt, *14* by H. Erdtman.
[b] Due to by-product.
[c] Numbers printed in Italics denote points of inflexion.
[d] Solution protected from light.

eliminated by working in the dark, using a nitrogen atmosphere or measuring the absorption within a few minutes after preparing the solutions. When necessary, corrections were made by extrapolating to "time zero" from consecutive readings.

The solvents were so chosen that the dissolved compound would, whenever possible, occur in a practically monotypic state (99 % or more of the neutral molecule or the desired ion). Whenever possible the reference solutions had the same composition as the sample solution except for the compound to be investigated. Reference solutions for the measurements on the sulphonated materials were prepared from sulphonation "blanks", run on the "sulphite cooking acid" alone.

A Perkin-Elmer 421 instrument was used for the IR investigations reported in Table 4.

The absorption maxima are listed in Tables 1—3. Absorption data for many of the compounds — in one or more solvents — have already been reported in the literature. In the tables references are given to the earliest results found, which coincide with ours.

Some of the absorption curves are reproduced in Figs. 1—13. Previously published curves of some related compounds have been included in the diagrams to enable direct comparison of the absorption properties of 4-hydroxy-phenyl, guaiacyl, and 4-hydroxy-3,5-dimethoxyphenyl derivatives (the types 1—3).

Table 2. Guaiacyl derivatives.

Compound	Solvent	Fig. No.	UV absorption maxima				*Cf.* Ref.
			nm	log ε	nm	log ε	
15. 4-Propylguaiacol, b.p. 125—126°/14 mm, $n_D^{23} = 1.5210$	water (pH *ca.* 5)		279—80	3.45			
	N KOH in 95 % EtOH	7	245	3.96	296—7	3.61	18
16. Vanillyl alcohol, m.p. 113—114°	N KOH in 95 % EtOH	7	250	4.03	294	3.63	8
	0.1 N HCl in 50 % dioxan		229—30	3.82	280	3.45	
	0.1 N KOH in 50 % dioxan		251	4.01	295	3.63	
17. Vanillic acid, m.p. 209—210°	0.1 N HCl	5	218	4.29	261	4.03	5
			292—3	3.74			
	pH 7.0 phosphate buffer soln.	10	251	3.97	285—6	3.61	19, 5
	N NaOH	10	298	4.17			5
	0.1 N HCl in 95 % EtOH		219	4.30	261	4.06	20
			291—2	3.77			
	0.1 N KOH in 95 % EtOH		298	4.17			8
18. 2,4′-Dihydroxy-3′-methoxypropiophenone,[a] m.p. 102.5—103° (dimorphous; after recryst. from AcOH: 115—116°)	0.01 N HCl		229—30	4.13	277—8	3.98	21
			304—5	3.91			
	N NaOH		247—8	3.93	345	4.31	
	0.1 N HCl in 95 % EtOH		231	4.16	278—9	4.00	22
			306	3.97			
	0.1 N KOH in 95 % EtOH		251	3.92	350	4.38	8
19. 4′-Hydroxy-3′-methoxy-2-(2-methoxyphenoxy)-propiophenone (α-guaiacoxypropioguaiacone),[23 a] m.p. 133—134°	0.01 N HCl in 95 % EtOH		230	4.26	280	4.04	
			310	3.99			
	0.1 N KOH in 95 % EtOH		254	3.93	276—7	3.54	
			355—6	4.39			
20. 4′-Hydroxy-3′-methoxy-2-oxopropiophenone (α-oxopropioguaiacone) (vanilloyl methyl ketone),[a] m.p. 69—70°	0.1 N HCl		234	3.89	319	3.90	21
	N NaOH (unstable)		251	3.84	357	4.23	
	0.1 N HCl in 95 % EtOH		236	3.92	320	3.96	24
	0.1 N KOH in 95 % EtOH		260	3.80	369	4.30	8
21. trans-Isoeugenol,[a] m.p. 25—26°, b.p. 141.5°/12.5 mm, $n_D^{20} = 1.5790$	95 % EtOH	4	260	4.18			25, 18
	0.1 N KOH in 95 % EtOH	8	286—7	4.24			
22. cis-Isoeugenol,[a] freshly dist., $n_D^{20} = 1.5711$	95 % EtOH	4	258	4.14	291	3.59	25, 18
	0.1 N KOH in 95 % EtOH	8	285	4.24			18
23. Coniferyl aldehyde, m.p. 80—81° (*trans*)	water (pH *ca.* 5)	6	222	3.94	239	3.99	
			337—8	4.34			
	0.2 N NaOH in 95 % EtOH		260	3.87	312	3.33	
			414	4.55			
24. Ferulic acid, m.p. 172—174° (*trans*)	0.01 N HCl		218	4.09	234	4.05	
			320	4.24			
	pH 7.2 phosphate buffer soln.	12	216	4.24	287	4.19	
			310—1	4.19			
	N NaOH [b]	12	239—40	3.99	305	3.99	
			346	4.38			
	0.1 N HCl in 95 % EtOH	6	235—6	4.09	299	4.15	26
			323—4	4.30			
	0.1 N KOH in 95 % EtOH [b]		306	3.99	348	4.40	
25. 6-Methoxy-*o*-cresol, m.p. 41—42°	95 % EtOH		274—5	3.30			
	0.1 N KOH in 95 % EtOH		245	3.92	290	3.59	

Table 2. Continued.

Compound	Solution						Ref.
26. 3,3'-Dimethoxy-5,5'-dipropylbiphenyl-2,2'-diol (4,4'-dipropyl-6,6'-diguaiacol), m.p. 149.5—151.5°	0.1 N HCl in 95 % EtOH	3	251	4.02	292	3.78	22, 27
	N KOH in 95 % EtOH	10	*261*[c]	*3.99*	*313*	*3.87*	
	0.1 N HCl in 99 % Bu^{t}OH		*251—2*	*4.04*	*292*	*3.78*	
	0.04 N HCl in 40 % dioxan		*251*	*3.91*	*289*	*3.75*	
	dioxan (dist. over Na)	1	*251*	*3.95*	*289*	*3.83*	
	0.1 N HCl in 99 % dioxan		*251*	*3.95*	*289*	*3.82*	
	0.1 N KOH in 40 % dioxan		*260*	*4.03*	*315*	*3.90*	
	hexane	1	*248—9*	*3.99*	*289—90*	*3.80*	
27. 3,2',3'-Trimethoxy-5,5'-dipropylbiphenyl-2-ol, prep. from 26 with CH$_2$N$_2$ in moist ether, dist., recryst. from EtOH and heptane, m.p. 47—49°. (Found: OCH$_3$ 26.7. Calc. for C$_{18}$H$_{19}$O(OCH$_3$)$_3$: 27.0)	0.1 N HCl in 95 % EtOH		*251*	*3.84*	*285*	*3.66*	
	0.12 N KOH in 95 % EtOH		*260*	*3.83*	*311*	*3.58*	
	0.1 N HCl in 99 % dioxan	1	*252*	*3.79*	*286*	*3.69*	
	0.01 N HCl in 45 % dioxan		*252—3*	*3.76*	*285*	*3.66*	
	pH 9.0 glycine buffer soln/dioxan (55:45)		284	3.67			
	0.1 N KOH in 30 % dioxan		*280*	*3.54*	*306—7*	*3.65*	
	hexane	1	*250*	*3.93*	*286—7*	*3.66*	
28. 6,6'-Dihydroxy-5,5'-dimethoxybiphenyl-3,3'-dimethanol (dehydrodivanillyl alcohol),[a] m.p. 187—90°, pK$_1$ = 7.0, pK$_2$ ≥ 11.3	0.1 N HCl		252	3.72	285	3.69	
	pH 9.2 glycine buffer soln.		261	4.01	308—9	3.84	
	2 N NaOH		255	4.16	302	3.85	
	0.1 N HCl in 95 % EtOH		252	3.97	289	3.73	28
	N KOH in 91 % EtOH		257	4.12	305—6	3.85	
	0.1 N HCl in 99 % Bu^{t}OH		251	4.08	291	3.75	
	0.1 N HCl in 40 % dioxan		253	3.83	287	3.74	
	pH 9.1 glycine buffer soln/dioxan (65:35)		232	4.56	311	3.85	
	0.1 N KOH in 30 % dioxan		232—3	4.57	310—1	3.88	
	0.1 N KOH in 40 % dioxan		232—3	4.59	312—3	3.87	
29. 6,6'-Dihydroxy-5,5'-dimethoxy-3,3'-dimethylbiphenyl-ω,ω'-disulphonic acid (?), obtained by sulphonation of 28. (101 mg of 28 were heated with 2.4 ml cooking acid /5.5 % SO$_2$, 1.56 % NaOH, pH 2/ from 20° to 130° over 3 h, at 130° for 3 h.) Product not isolated	0.01 N HCl in dilute sulphite liquor (SO$_2$ removed by bubbling N$_2$)		286	3.66			
	pH 8.0 phosphate buffered dil. sulph. liq. (SO$_2$ removed)		231	4.53	292—3	3.64	
			304—5	3.64			
	pH 9.1 glycine buff. sulph. liq. as above		232	4.56	307	3.71	
	pH 10.5 carbonate buff. sulph. liq. as above		232—3	4.56	308	3.76	
	pH 11.0 phosphate buff. sulph. liq. as above		232—3	4.56	308	3.77	
	pH 11.5 phosph. buff. sulph. liq. as above		232—3	4.56	308	3.78	
	N NaOH in sulph. liq. as above		301	3.84			
	5 N NaOH in sulph. liq. as above		298	3.90			
30. 6,6'-Dihydroxy-5,5'-dimethoxybiphenyl-3,3'-dialdehyde (dehydrodivanillin),[a] recryst. from dioxan, m.p. >300° (decomp.), pK$_1$ ≤ 7.0, pK$_2$ ≥ 10.6	0.03 N HCl in 98 % dioxan		234	4.43	284	4.35	29
	pH 8.8 glycine buffer soln./dioxan (1:1)		234	4.16	280	4.38	
			318	4.37	336	4.35	
	pH 9.1 glycine buffer soln./dioxan (1:1)		233—4	4.16	280	4.37	
			318	4.36	334	4.35	
	0.1 N KOH in 50 % dioxan		261	4.15	299	3.99	
			361—2	4.68			
	0.3 N KOH in 50 % dioxan		260—1	4.16	300—1	3.98	
			361—2	4.69			
31. Dehydroguaiaretic acid,[a] m.p. 209—215°	95 % EtOH		236	4.81	286	3.98	30
			315—6	3.52	330	3.65	
	0.01 N KOH in 90 % EtOH		248	4.75	282	3.96	
			293	4.00	347	3.84	

[a] Compounds 18 and 19 supplied by E. Adler, 20, 28 and 30 by J. Gierer, 21 and 22 by Y. Tomita and 31 by B. Lindberg. [b] Solution protected from light. [c] Numbers printed in Italics denote points of inflexion.

NON-IONIZED STATE

Solvent effects. Hydrogen bonding and planarity of biphenyls

Those compounds and ions which were investigated both in aqueous and in ethanolic solution generally showed absorption bands of slightly longer wavelength and higher intensity in ethanol than in water.

In a previous investigation [34] UV spectrophotometry was used to study the influence of various solvents on the degree of molecular planarity of 2,2'-dihydroxybiphenyl and its methyl ethers. The effects found could be related to differences in the hydrogen bonding patterns of the phenols. Four new 2,2'-dihydroxybiphenyl derivatives, *14, 26, 27,* and *28,* have been included in the present investigation. In general their planarity, as judged by the intensity of the "conjugation band" at about 250 nm (sometimes appearing as a point of inflexion, *cf.* Tables 1 and 2), seemed to vary with the solvent in a manner known from our previous investigation.[34] Thus, the diphenol *14* (Fig. 1 a) showed a higher degree of coplanarity in dioxan, where hydrogen bonds exist between the phenolic groups and the solvent, than in hexane, where $O-H\cdots\pi$ bonds dominate. The mono-ol *27* (Fig. 1 c) showed a smaller interplanar angle in hexane, owing to the presence of a 7-membered $O-H\cdots OCH_3$ "ring", than in acidic dioxan solution, where $O-H\cdots$dioxan bonds dominate, *etc.* (Compare the chart in Ref. 34, p. 2001.)

However, the diguaiacol *26* (Fig. 1 b) differed from 2,2'-dihydroxybiphenyl [34] and tetrahydromagnolol (*14,* Fig. 1 a) — both of which lack methoxyl groups — in showing a higher degree of planarity in hexane than in dioxan
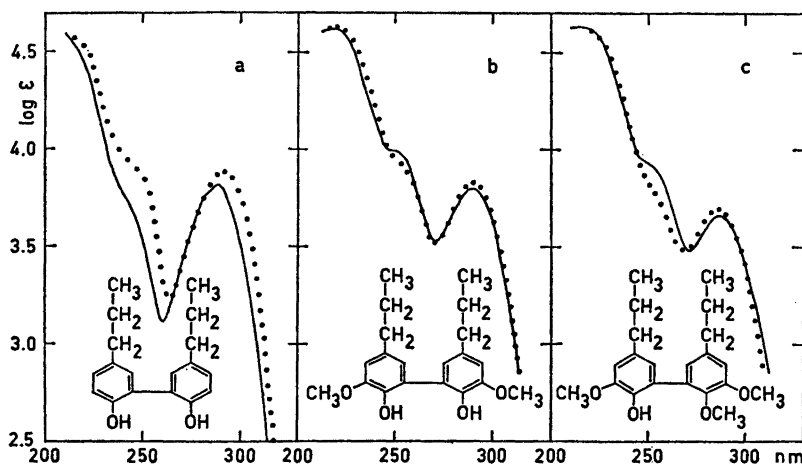
Fig. 1. a. Tetrahydromagnolol (*14*) in dioxan (....) and in hexane (———). b. 3,3'-Dimethoxy-5,5'-dipropylbiphenyl-2,2'-diol (*26*) in dioxan (....) and in hexane (———). c. 3,2',3'-Trimethoxy-5,5'-dipropylbiphenyl-2-ol (*27*) in 99 % dioxan, 0.1 N in HCl (....) and in hexane (———).

Table 3. 4-Hydroxy-3,5-dimethoxyphenyl derivatives.

Compound	Solvent	Fig. No.	UV absorption maxima				Cf. Ref.
			nm	log ε	nm	log ε	
32. 2,6-Dimethoxyphenol, m.p. 54.5—55.5°	0.1 N HCl		267—8	2.97			
	0.1 N NaOH		245—6	3.90	283	3.55	
	95 % EtOH	2	269	3.03			8
	0.1 N KOH in 95 % EtOH	7	249—50	3.92	285—6	3.57	
33. 3-(4-Hydroxy-3,5-dimethoxyphenyl)-propionic acid, m.p. 100.5—101.5°	0.1 N HCl		271	3.05			
	0.1 N NaOH		249	3.93	287	3.58	
	0.1 N HCl in 95 % EtOH		273	3.11			20
	0.1 N KOH in 85 % EtOH		252—3	3.96	289	3.58	
34. 4-Hydroxy-3,5-dimethoxybenzyl sulphonic acid (?), obtained by sulphonation of syringyl alcohol. (34 mg of syringyl alcohol were heated with 0.70 ml cooking acid /5.5 % SO₂, 5.8 % NaOH, pH 6—7/ from 20° to 100° over 6 h, at 100° for 13 h.) Prod. not isol.	0.05 N HCl in dilute sulphite liquor (SO₂ removed by bubbling N₂)	2	236	3.87	271	3.02	
	0.11 N NaOH in sulph. liq. as above	7	258	4.03			
35. 1-(4-Hydroxy-3,5-dimethoxyphenyl)-propane-1,3-disulphonic acid (?), obtained by sulphonation of *38.* (50 mg of *38*, 2.0 ml cooking acid /5.5 % SO₂, 5.8 % NaOH, pH 6—7/; 20°→100°: 2 h; 100°, 33 h.) Prod. not isol.	0.5 N HCl in sulph. liq. as above		236—7	3.86	271	3.03	
	0.7 N NaOH in sulph. liq. as above		258	4.01 [a]			
36. 4′-Hydroxy-3′,5′-dimethoxypropiophenone (propiosyringone),[b] recryst. from EtOH, m.p. 111.5—112.5°	0.1 N HCl in 95 % EtOH	5	215	4.21	229	4.17	31
			299	4.02			
	0.1 N KOH in 95 % EtOH	9	250—1	3.97	357—8	4.30	
37. 2,6-Dimethoxy-4-propenylphenol, m.p. *ca.* 25°, $n_D^{20.5}$=1.5820, n_D^{23}=1.5805, n_D^{28}=1.5786 (*trans:* IR 10.5 μ /s/)	0.09 N HCl in 10 % EtOH		220	4.47	268—9	4.16	
	0.09 N NaOH in 10 % EtOH		293—4	4.19 [a]			
	0.1 N HCl in 95 % EtOH	4	221—2	4.46	271—2	4.15	
	0.1 N KOH in 95 % EtOH	8	301	4.19 [a]			
38. *trans*-Sinapyl alcohol,[b] m.p. 65.5—66.5°	water (pH 5—6)		221	4.45	272	4.15	
	N NaOH		312	4.20			
	95 % EtOH	4	222	4.43	276	4.15	
	0.1 N KOH in 86 % EtOH	8	320	4.23			
39. *trans*-Sinapaldehyde,[b] m.p. 108.5—109.5°, pK = *ca.* 8.2	0.01 N HCl	6	242—3	4.21	341—2	4.34	
	N NaOH	11	263	4.11	421	4.49	
	0.1 N HCl in 95 % EtOH		246	4.26	348	4.38	
	0.1 N KOH in 95 % EtOH		268—9	4.07	436	4.56	

Table 3. Continued.

40. *trans*-Sinapic acid,[b] recryst. from EtOH, m.p. 200—202°, pK₁ ≤ 4.9 [Ref. 32, 4.5], pK₂ ≥ 9.2	pH 7.0 phosphate buffer soln.	12	229	4.30	305—6	4.23
	N NaOH [c]	12	248—9	4.11	355—6	4.36
	0.1 N HCl in 95 % EtOH	6	239	4.24	326	4.29
	0.1 N KOH in 85 % EtOH [c]		249	4.11	356—7	4.38
41. Syringaresinol,[b] m.p. 173—174°	0.01 N HCl in 95 % EtOH		238	4.17	271	3.42
	0.1 N KOH in 92 % EtOH		261—2	4.36		

[a] Value obtained by extrapolation to time zero.
[b] Compounds *36* and *40* supplied by I.A. Pearl, *38, 39* and *41* by K. Freudenberg.
[c] Solution protected from light.

solution. This fact indicates that in the diguaiacol *26* the conformation with a 7-membered O—H···O ring rather than that with O—H···π bonds predominates in hexane solution. This effect may be caused by one of the methoxyl

Table 4.

Compound	Solvent	O—H str. band, cm⁻¹, width	Assignment	Cf. Ref.
Guaiacol	hexane [a]	3560 (narrow)	O—H···OCH₃ (5-membered ring)	
	dioxan [a]	ca. 3340 (wide)	O—H···dioxan	(35)
2,2′-Dihydroxybiphenyl	heptane [a]	3550 (narrow) [34]	O—H···π	
	dioxan [a]	ca. 3320 (wide) [34]	O—H···dioxan	
2-Hydroxy-2′-methoxy-biphenyl	CCl₄	3560 (narrow) [36]	O—H···π	
	»	ca. 3450 (wide) [36]	O—H···OCH₃ (7-membered)	
	dioxan [a]	ca. 3340 (wide) [34]	O—H···dioxan	
Tetrahydromagnolol (*14*)	hexane [a]	3550 (narrow)	O—H···π	
	dioxan [a]	ca. 3330 (wide)	O—H···dioxan	
2,2′-Dihydroxy-3,3′-dimethoxy-5,5′-dipropyl-biphenyl (*26*)	hexane [a]	3550 (narrow)	O—H···π and/or O—H···OCH₃ (5-membered)	
	»	ca. 3300 (wide) [b]	O—H···OH (7-membered) ?	
	CCl₄ [c]	3540 (narrow)	O—H···π and/or O—H···OCH₃ (5-membered)	
	»	ca. 3340 (wide)	{one O—H···OH (7-membered) ?, one unknown	
	»	ca. 3250 (wide)		
	dioxan [a]	ca. 3360 (wide)	O—H···dioxan	
2-Hydroxy-3,2′,3′-tri-methoxy-5,5′-dipropyl-biphenyl (*27*)	hexane [a]	3550 (narrow)	O—H···π and/or O—H···OCH₃ (5-membered)	
	»	ca. 3360 (wide)	O—H···OCH₃ (7-membered)	
	»	ca. 3170 (wide)	?	
	dioxan [a]	ca. 3360 (wide)	O—H···dioxan	

[a] Distilled over Na.
[b] Due to low solubility, the presence of this band is doubtful.
[c] Dried over P₂O₅ and distilled.

groups through the formation of a 5-membered chelate ring, like the one occurring in guaiacol itself. This would increase the electronegativity of the phenolic oxygen involved and favour the formation of the 7-membered O—H···O ring.

Some IR investigations were undertaken as an attempt to check these interpretations, particularly as regards the diguaiacol *26*. The results (Table 4) were compatible with the interpretations of the UV data, but two factors made definite conclusions impossible, namely: the low solubility of the diguaiacol in hexane, and the similarity in O—H stretching frequency between the OH groups involved in the chelate ring of guaiacol and in the O—H···π bond of 2,2'-dihydroxybiphenyl in hexane or heptane solution.

Effects of methoxylation

Certain regular differences were observed when the absorption bands of the non-methoxylated phenols (type 1, *cf.* Introduction) were compared with those of analogous compounds possessing one or two methoxyl groups next to the phenolic hydroxyl group (types 2 and 3, respectively). As expected, the character of the changes that occur in each absorption band upon methoxylation seems to be dependent on the type of the electron excitation giving
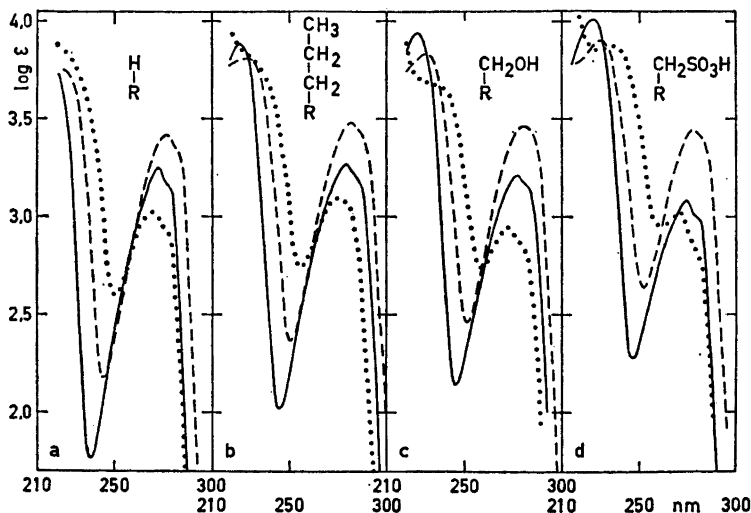
Fig. 2. UV absorption curves for 4-hydroxyphenyl (———), guaiacyl (— — —), and 4-hydroxy-3,5-dimethoxyphenyl (....) derivatives in acidic-neutral solutions: a. ——— Phenol in 95 % EtOH.[33] a. — — — Guaiacol in 95 % EtOH.[33] a. .... 2,6-Dimethoxyphenol (*32*) in 95 % EtOH. b. ——— 4-Propylphenol (*1*) in 95 % EtOH. b. — — — 4-Propylguaiacol in abs. EtOH.[27] b. .... 2,6-Dimethoxy-4-propylphenol in 95 % EtOH.[33] c. ——— 4-Hydroxybenzyl alcohol (*2*) in 95 % EtOH, 0.1 N in HCl. c. — — — Vanillyl alcohol in abs. EtOH.[27] c. .... Syringyl alcohol in 95 % EtOH.[33] d. ——— Sulphonated 4-hydroxybenzyl alcohol (*3*) in 0.04 N HCl. d. — — — Sulphonated vanillyl alcohol in water (pH *ca.* 5).[27] d. .... Sulphonated syringyl alcohol (*34*) in 0.05 N HCl.

rise to the band concerned. Such changes may, therefore, be useful for the interpretation of certain absorption bands.

The absorption bands given by the compounds investigated are of four types:

(1) *Long-wave benzenoid* $\pi{\rightarrow}\pi^*$ *bands* (= L.E. bands of the $^1A_{1g}{\rightarrow}^1B_{2u}$ type [37]). The bands occurring at about 270—280 nm in the absorption curves of phenol and of non-methoxylated p-alkylphenols (Fig. 2 a—d, solid lines) are of this type. With analogous compounds of the guaiacyl type, these bands are shifted to longer wavelengths and their intensities are increased (Fig. 2 a—d, broken lines). When passing to the syringyl type of compounds (Fig. 2 a—d, dotted lines), however, even stronger shifts occur in the opposite directions, so that the maximum of the dimethoxy derivative is the weakest of the three in each group of compounds and occurs at the shortest wavelength. The similarity between a hydroxyl group and a methoxyl group as regards auxochromic properties is thus great enough to make each group of substances of types 1, 2, and 3 (see each section of Fig. 2) analogous to, *e.g.*, the group phenol-catechol-pyrogallol, in which pyrogallol, due to its symmetry, shows the lowest λ_{max} and ε_{max} values, followed by phenol. The absorption properties of 1,2,3-homotrisubstituted benzene derivatives have been treated theoretically by Sklar,[38] Förster,[39] Murrell and McEwen,[40] Petruska,[41] and others.

The long-wave band of o-cresol [33] (273—274 nm, log ε 3.28 in EtOH) is also of the benzenoid $\pi{\rightarrow}\pi^*$ type, and so is probably the long-wave band of the biphenyl derivative tetrahydromagnolol *(14)*.[42] However, the long-wave o-cresol band is hardly altered upon 6-methoxylation, to compound *25* (Table 2); the tetrahydromagnolol band is lowered but not displaced on passing to the o,o'-dimethoxy derivative *26* (Fig. 3). It is evident that phenols containing
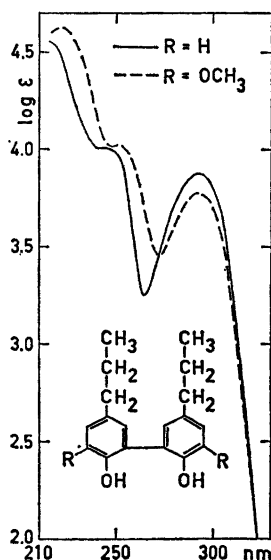
Fig. 3. ——— Tetrahydromagnolol *(14)* in 95 % EtOH, 0.1 N in HCl. — — — 4,4'-Dipropyl-6,6'-diguaiacol *(26)* in 95 % EtOH, 0.1 N in HCl.

a substituent other than methoxyl (or hydroxyl) next to the hydroxyl group may differ widely both from phenol and from guaiacol as regards the effect of o-methoxylation on their long-wave band. With the biphenyl *14*, the effect of methoxylation to *26* may partly be due to changes in hydrogen bonding (*cf.* above).

The absorption bands or shoulders found at about 290 nm for solutions of *trans-p*-propenylphenol (*p*-anol, *9*) and *trans-p*-coumaryl alcohol (*10*) (Fig.4)
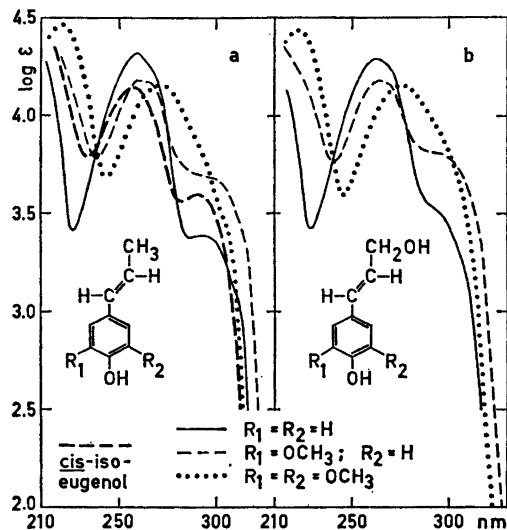

Fig. 4. a. ———— *trans*-4-Propenylphenol (*9*) in 95 % EtOH, 0.01 N in HCl. a. — — — *trans*-Isoeugenol (*21*) in 95 % EtOH. a. . . . . . *trans*-2,6-Dimethoxy-4-propenylphenol (*37*) in 95 % EtOH, 0.1 N in HCl. a. — — — — *cis*-Isoeugenol (*22*) in 95 % EtOH. b. ———— *trans-p*-Coumaryl alcohol (*10*) in 95 % EtOH, 0.1 N in HCl. b. — — — *trans*-Coniferyl alcohol in 95 % EtOH.[33] b. . . . . . *trans*-Sinapyl alcohol (*38*) in 95 % EtOH.

are also due to transitions of the local excitation type, occurring in the benzene nucleus. When methoxyl groups are introduced next to the phenolic hydroxyl group, these bands appear to be influenced (Fig. 4) in essentially the same way as the analogous bands of the non-conjugated phenols first discussed (Fig. 2). However, the presence of stronger obscuring bands makes it difficult to locate and estimate the intensity of the L.E. bands in the curves of the methoxylated derivatives of the conjugated phenols, particularly in those of the dimethoxy compounds. *cis*-Isoeugenol shows this band more clearly than *trans*-isoeugenol (Fig. 4).

The absorption bands given by p-substituted benzaldehydes, aceto-phenones, and benzoic acids have been interpreted in different ways.[43] The band assignments for substituted cinnamaldehydes and cinnamic acids are also uncertain. Figs. 5 and 6 show the absorption curves for compounds of these five types. A recurring feature in each of these groups of curves is the
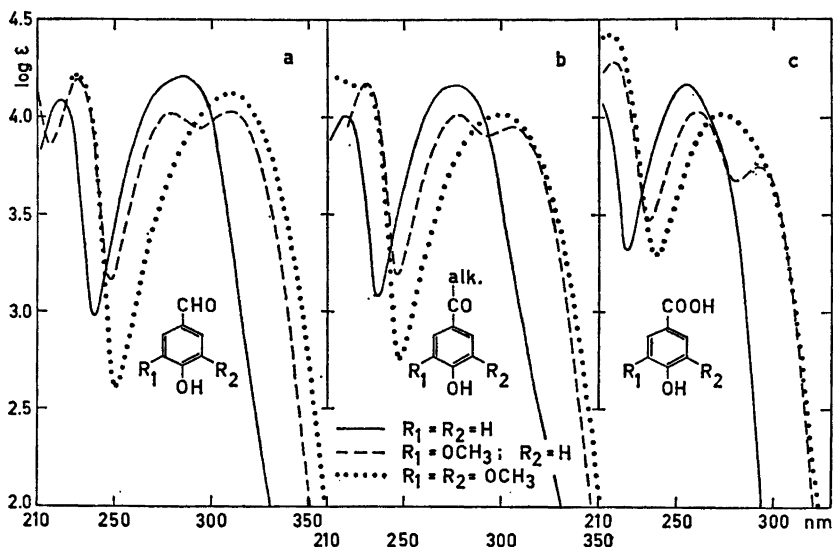
Fig. 5. a. ———— 4-Hydroxybenzaldehyde (*5*) in 95 % EtOH, 0.01 N in HCl. a. — — — Vanillin in 95 % EtOH, 0.01 N in HCl.[33]. a. . . . . Syringaldehyde in 95 % EtOH, 0.01 N in HCl.[33] b. ———— 4'-Hydroxypropiophenone (*6*) in 95 % EtOH, 0.1 N in HCl. b. —·— — Acetovanillone in 95 % EtOH, 0.01 N in HCl.[33] b. . . . . Propiosyringone (*36*) in 95 % EtOH, 0.1 N in HCl. c. ———— 4-Hydroxybenzoic acid in 0.1 N HCl.[33] c. — — — Vanillic acid (*17*) in 0.1 N HCl. c. . . . . Syringic acid in 0.01 N HCl.[33]
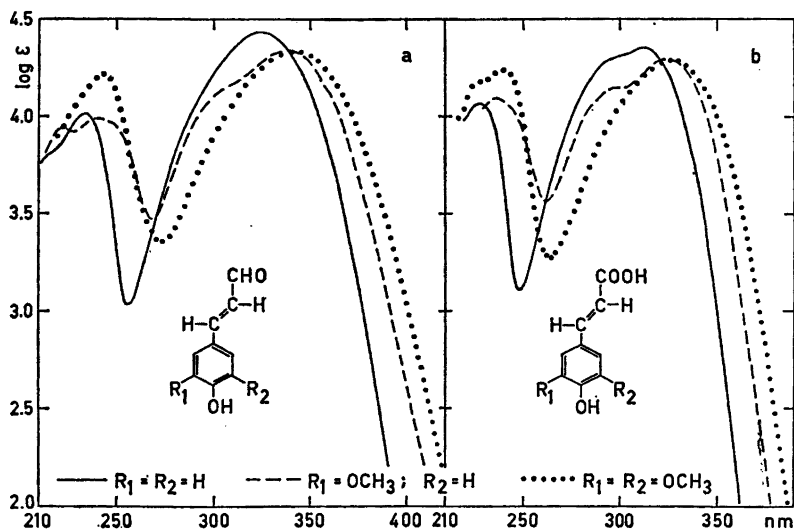

Fig. 6. a. ———— *trans-p*-Coumaraldehyde (*11*) in 0.01 N HCl. a. — — — *trans*-Coniferyl aldehyde (*23*) in water (pH *ca.* 5). a. . . . . *trans*-Sinapaldehyde (*39*) in 0.01 N HCl. b. ———— *trans-p*-Coumaric acid (*12*) in 95 % EtOH, 0.1 N in HCl. b. — — — *trans*-Ferulic acid (*24*) in 95 % EtOH, 0.1 N in HCl. b . . . . *trans*-Sinapic acid (*40*) in 95 % EtOH, 0.1 N in HCl.

strong long-wave band or shoulder that appears on passing from the non-methoxylated phenol (type 1) to the guaiacyl derivative (type 2) and disappears again on proceeding to the o,o'-dimethoxy derivative (type 3). Weaker analogous bands appear at shorter wavelengths in the absorption curves of two of the conjugated phenols of type 1, p-propenylphenol and p-coumaryl alcohol (Fig. 4). It seems very likely that corresponding bands are not totally missing in the absorption of the other conjugated phenols of type 1 and in those of type 3, but are weaker than the bands of the guaiacyl derivatives and occur at shorter wavelengths, so that they are submerged in the adjacent stronger absorption. If this interpretation is correct, the behaviour of all these bands is very similar to that of the long-wave bands of the simplest phenols (Fig. 2), which would suggest a similar origin, local excitations in the benzene ring.

(2) *Short-wave bands, with maxima up to approximately 250 nm.* These bands may be either displaced benzenoid primary L.E. bands ($^1A_{1g} \rightarrow {}^1B_{1u}$) or $p \rightarrow \pi^*$ bands resulting from the transfer of p-electrons from oxygen substituents (in OH or OCH_3) to the benzene ring, or combinations of those band types. With some compounds these short-wave bands, which are often called "first primary bands", partly overlap with stronger bands having maxima at shorter wavelengths, presumably "second primary bands" ($^1A_{1g} \rightarrow {}^1E_{2u}$).

Examples of "first primary bands" are those at about 210—230 nm exhibited by the phenols without a p-side-chain or with saturated p-substituents (Fig. 2). [In the curves of some of the syringyl derivatives (dotted lines) these bands are reduced to shoulders, due to interaction from stronger bands in the far ultraviolet.] These bands undergo a stepwise weakening and bathochromic displacement upon introduction of the two o-methoxyl groups (Fig. 2).

The interpretation of the absorption bands of biphenyls is still uncertain. The two short-wave bands exhibited by tetrahydromagnolol (*14*, Fig. 3) — the one at about 210 nm possibly a "second primary band", the one at about 250 nm often called the "conjugation band" indicating an E.T. origin — are shifted towards red upon methoxylation to the corresponding diguaiacyl derivative *26*, but their intensities are not decreased in ethanolic solution. The great difference in intensity of the "conjugation bands" of the two compounds in hexane solution (Tables 1 and 2) is not a direct effect of the change in structure but very probably attributable to differences in the hydrogen bonding patterns of the two solutes (see above).

As regards p-propenylphenol and its o-methoxy derivatives, and the corresponding group of p-coumaralcohols (Fig. 4), each methoxylation seems to cause a red-shift of the short-wave band. The intensities of the maxima, however, cannot be compared without extending the range of the absorption measurements.

The first o-methoxylation of p-hydroxybenzaldehyde and of p-hydroxyphenyl ketones (Fig. 5) causes an increase in wavelength as well as intensity of the short-wave absorption band, but the second o-methoxylation has very little influence.

The short-wave bands given by the p-coumaraldehydes and the p-coumaric acids (Fig. 6) and possibly also those given by the p-hydroxybenzoic acids

(Fig. 5) show still another type of change upon *o*-methoxylation: the first step brings mainly a bathochromic shift, the second one essentially an intensity increase.

In contrast to the influence on the long-wave benzenoid bands discussed above, the influence of the *o*-methoxylation on the short-wave bands is evidently strongly dependent on the type of the substituent *para* to the hydroxyl group. This fact supports the impression from theoretical investigations that the short-wave bands of the various compounds are not all of the L.E. type but originate in different electronic transitions, possibly of two or more types in combination. A band assignment on the basis of the effects discussed appears to be feasible but cannot be included here.

(3) *E.T. bands (K-bands), largely originating in electron transfers from a π orbital of one unsaturated group to a π* orbital of a conjugated unsaturated group*. The strong bands at about 260—275 nm exhibited by the *p*-propenylphenols and the *p*-coumaryl alcohols (Fig. 4) are of this type. The first *o*-methoxyl group causes a decrease in the intensity of this band and the second one a red-shift.

The "conjugation band" of the biphenyls, discussed under point (2), is perhaps another example of an E.T. band, although an L.E. origin has also been suggested. See also point (4).

(4) *Complex long-wave bands*. The broad long-wave bands of the *p*-hydroxyaldehydes, -ketones, and -acids (Figs. 5 and 6) are all more or less unsym-
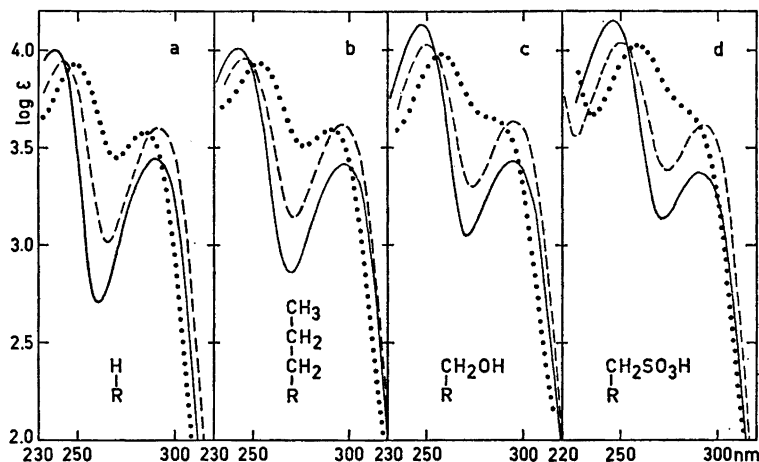
Fig. 7. a. ——— Phenol in 95 % EtOH, N in KOH.[33] a. — — — Guaiacol in 95 % EtOH, N in KOH.[33] a . . . . 2,6-Dimethoxyphenol *(32)* in 95 % EtOH, 0.1 N in KOH. b. ——— 4-Propylphenol *(1)* in 95 % EtOH, 0.1 N in KOH. b. — — — 4-Propylguaiacol *(15)* in 95 % EtOH, N in KOH. b. . . . . 2,6-Dimethoxy-4-propylphenol in 95 % EtOH, N in KOH.[33] c. ——— 4-Hydroxybenzyl alcohol *(2)* in 95 % EtOH, 0.1 N in KOH. c. — — — Vanillyl alcohol *(16)* in 95 % EtOH, N in KOH. c. . . . . Syringyl alcohol in 95 % EtOH, N in KOH.[33] d. ——— Sulphonated 4-hydroxybenzyl alcohol *(3)* in 0.9 N NaOH. d. — — — Sulphonated vanillyl alcohol in 0.1 N NaOH.[27] d. . . . . Sulphonated syringyl alcohol *(34)* in 0.11 N NaOH.

metrical, which indicates contributions from more than one kind of electron excitation. The probable contribution of benzenoid L.E. absorption to the long-wave portion of these band systems has already been discussed under point (1). The rest of the long-wave band system, for which E.T. type excitations are likely to be responsible, shows the following features: the first *o*-methoxylation causes little change; the second *o*-methoxylation causes a red-shift and with the *p*-coumaraldehydes and the *p*-coumaric acids also an intensity increase. This behaviour is not identical with any of the methoxylation effects discussed above, but it resembles the behaviour of the E.T. bands of the *p*-propenylphenols and the *p*-coumaryl alcohols.

ABSORPTION CHANGES CAUSED BY IONIZATION

The absorption changes caused by ionization of the phenols and phenolic carboxylic acids discussed in this paper are evident from the tables and figures but warrant a few comments. As a rule, the dissociation of carboxyl groups belonging to a conjugated system causes the expected violet-shift of the absorption range and decreases the intensity of the distinguishable long-wave bands, whereas the dissociation of phenolic hydroxyl groups has the reverse effects. The absorption curves of the *p*-hydroxybenzoic and -coumaric acids (Figs. 5 and 6) undergo less drastic changes on carboxylate ion than on phenolate ion formation (Figs. 10 and 12).

When the non-conjugated phenols are ionized, the increase in intensity of the long-wave benzenoid $\pi{\rightarrow}\pi^*$ band is much greater for the compounds
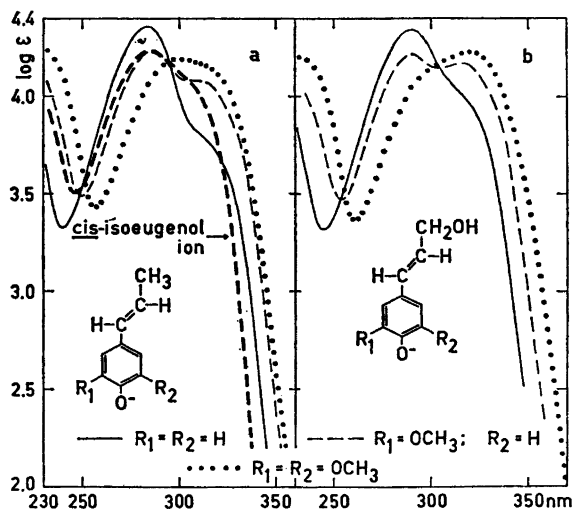
Fig. 8. a. ——— *trans*-4-Propenylphenol (*9*) in 95 % EtOH, 0.1 N in KOH. a. — — — *trans*-Isoeugenol (*21*) in 95 % EtOH, 0.1 N in KOH. a. .... *trans*-2,6-Dimethoxy-4-propenylphenol (*37*) in 95 % EtOH, 0.1 N in KOH. a. — — — *cis*-Isoeugenol (*22*) in 95 % EtOH, 0.1 N in KOH. b. ——— *trans*-*p*-Coumaryl alcohol (*10*) in 95 % EtOH, 0.1 N in KOH. b. — — — *trans*-Coniferyl alcohol in 95 % EtOH, N in KOH.[33] b. .... *trans*-Sinapyl alcohol (*38*) in 86 % EtOH, 0.1 N in KOH.

of type 3 — the 2.6-dimethoxyphenols — than for the ones of types 1 and 2 (Figs. 2 and 7). This is evidently due to the fact that the similarity to 1,2,3-homotrisubstituted compounds is lost when the phenolic group is dissociated. A similar effect on those, partly submerged, bands of the p-propenylphenols and the p-coumaryl alcohols which are likely to be of the benzenoid $\pi \rightarrow \pi^*$ type, may be observed by comparing Figs. 4 and 8 and would be expected for larger chromophores.

As regards the large chromophores, however, one must be cautious in comparing absorption bands of ions and non-ionized molecules. In these systems, ion formation may cause such different changes in the energies and probabilities of the various electron excitations that the individual absorption bands of the ions cannot always be related with certainty to individual bands given by the undissociated molecules. An example is provided by the short-wave portions of the complex long-wave band system given by the p-coumaric acids and their mono- and di-ions. As is seen by comparing Figs. 6 and 12, these curve portions — which are possibly not analogous in origin for the ionized and unionized compounds — exhibit anomalous intensity changes for the two ionization steps: increase on carboxylate ion formation, decrease on phenolate ion formation. Similar problems are encountered with the ions of each of the p-hydroxyaldehydes and -ketones (Figs. 9 and 11 as compared with Figs. 5 and 6, respectively).

The absorption curves for the biphenols 14 and 26 in ethanolic KOH solutions (Fig. 10) are so similar to the curves for the same compounds in aqueous solutions of pH 11.2 and 12 (Ref. 27), respectively, that the solutes
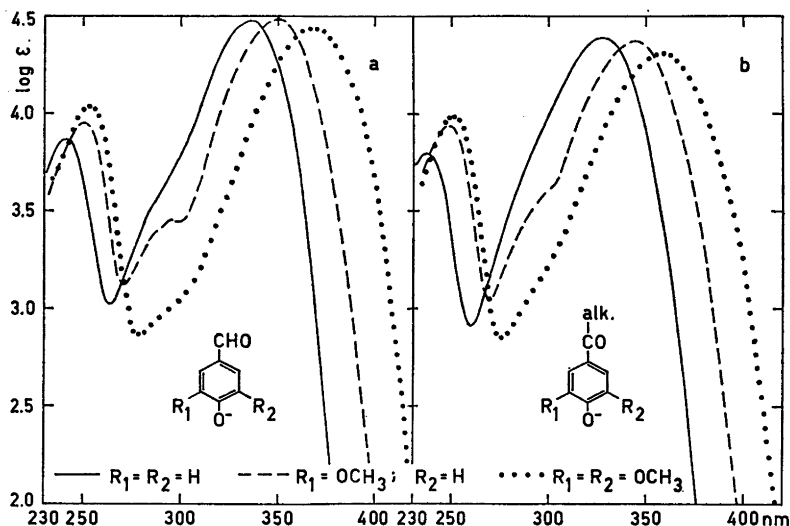

Fig. 9. a. ——— 4-Hydroxybenzaldehyde (5) in 95 % EtOH, 0.1 N in KOH. a. — — — Vanillin in 95 % EtOH, N in KOH.[33] a. . . . . . Syringaldehyde in 95 % EtOH, 0.1 N in KOH.[33] b. ——— 4'-Hydroxypropiophenone (6) in 95 % EtOH, 0.1 N in KOH. b. — — — Acetovanillone in 95 % EtOH, N in KOH.[33] b. . . . . Propiosyringone (36) in 95 % EtOH, 0.1 N in KOH.
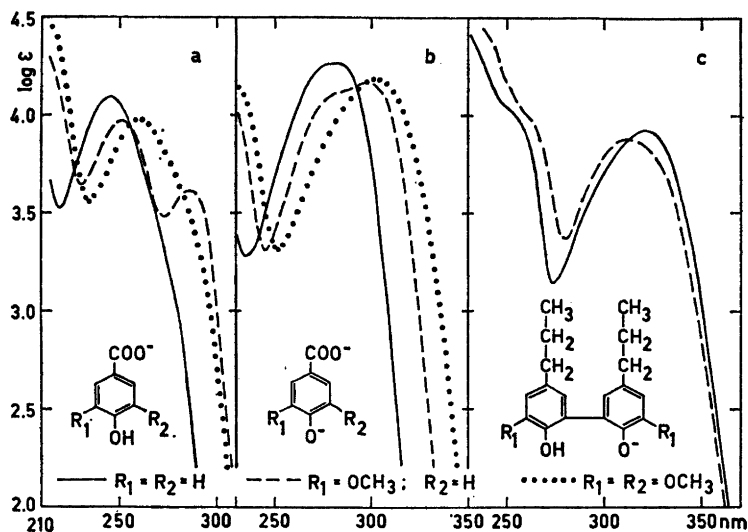
Fig. 10. a. ———— 4-Hydroxybenzoic acid in pH 7.0 phosphate buffer soln.[33] a. — — — Vanillic acid (*17*) in pH 7.0 phosphate buffer soln. a. . . . . Syringic acid in pH 6.5 phosphate buffer soln.[33] b. ———— 4-Hydroxybenzoic acid in N NaOH.[33] b. — — — Vanillic acid (*17*) in N NaOH. b. . . . . . Syringic acid in N NaOH.[33] c. ———— Tetrahydromagnolol (*14*) in 95 % EtOH, 0.1 N in KOH. c. — — — 4,4'-Dipropyl-6,6'-diguaiacol (*26*) in 95 % EtOH, N in KOH.

must be assumed to be present in practically purely mono-ionized form (see also Ref. 34). In that form they undoubtedly have a higher planarity than the molecular species present in acidic ethanol solution. In contrast, the long-wave band given by the monomethyl ether of the biphenol *26*, compound *27*, shows unchanged or decreased intensity after ionization, because the ion cannot form an intramolecular hydrogen bond that would increase the planarity.[34]

IONIZED STATE

Effects of methoxylation

From a spectrochemical point of view the dissociation of a phenolic hydroxyl group or of a carboxyl group attached to an unsaturated system constitutes a great change, influencing several of the factors determining the UV absorption: excitation energies, symmetry properties, hydrogen bonding, *etc.* Therefore, we cannot always expect to find the same influence of *o*-methoxylation on the absorption bands of the ions as on those of the undissociated molecules, even when we know which bands to compare for the two solute species. Band assignments still being uncertain for several of the ions investigated, we shall discuss the influences of the *o*-methoxyl groups on the absorption of the ions separately, comparing them with the influences on the absorption of the unionized molecules only when there is no doubt about the band correlations.
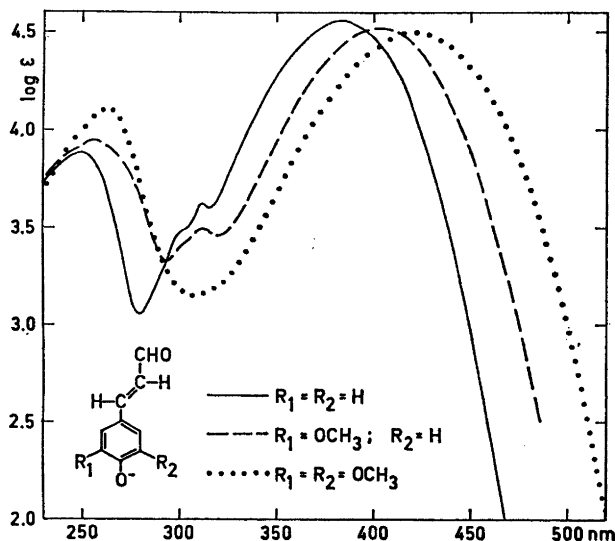
Fig. 11. ——— trans-p-Coumaraldehyde (11) in N NaOH. — — — trans-Coniferyl alde-
hyde in pH 12 phosphate buffer soln.[27] ..... trans-Sinapaldehyde (39) in N NaOH.

(1) *Long-wave benzenoid* $\pi{\to}\pi^*$ *bands*. For the phenolate ions containing
non-conjugated benzene rings (Fig. 7), the introduction of one o-methoxyl
group hardly affects the position of the long-wave maximum but increases
its intensity considerably. The introduction of the second o-methoxyl group
causes no further intensification but a blue-shift of about 5—10 nm. The
corresponding bands of the ions of the p-propenylphenols and the p-coumaryl
alcohols (Fig. 8) are also intensified by one o-methoxyl group. The effect of
the second one is hard to distinguish because of the interference from a neigh-
bouring band in the curves of the o,o'-dimethoxy derivatives. As far as this
comparison goes, then, the long-wave benzenoid $\pi{\to}\pi^*$ bands of the phenolate
ions differ considerably from those of the undissociated molecules as regards
the "methoxylation effect". Most probably this is a general rule (compare
"Absorption changes caused by ionization", above).

Carboxylate ions with an undissociated phenolic hydroxyl group, on the
other hand, are reminiscent of their parent molecules as regards the "meth-
oxylation effect" on the long-wave portion of their long-wave band system
(Figs. 10 and 12 as compared with Figs. 5 and 6, respectively). This behaviour
is expected, because in these ions the similarity with vicinally homo-substituted
compounds is remaining.

(2) "*First primary bands*". As far as the short-wave bands are included in
the range of our measurements on ions, they show "methoxylation effects"
which are very similar to those found for the corresponding bands of the undis-
sociated compounds. Examples are the unconjugated phenols (Fig. 7) and
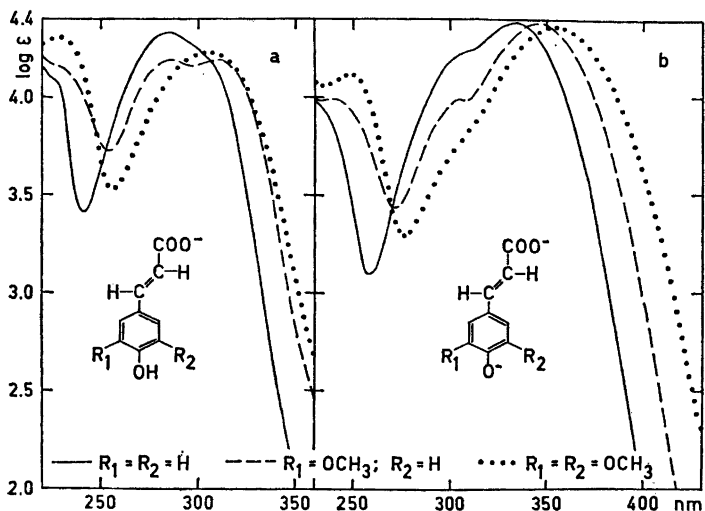the p-hydroxybenzaldehydes and -ketones (Fig. 9).

Fig. 12. a. ———— *trans-p*-Coumaric acid *(12)* in pH 6.8 phosphate buffer soln. a. — — — *trans*-Ferulic acid *(24)* in pH 7.2 phosphate buffer soln. a. . . . . *trans*-Sinapic acid *(40)* in pH 7.0 phosphate buffer soln. b. ———— *trans-p*-Coumaric acid *(12)* in N NaOH. b. — — — *trans*-Ferulic acid *(24)* in N NaOH. b. . . . . *trans*-Sinapic acid *(40)* in N NaOH.

(3) *"K-bands"*. The "methoxylation effects" on the strong bands at 280—300 nm given by the ions of the *p*-propenylphenols and the *p*-coumaryl alcohols (Fig. 8) are very similar to the "methoxylation effects" on the corresponding bands (at 260—275 nm) of the unionized molecules (Fig. 4). Thus, the first methoxyl group causes a decrease in the intensity of the band, and the second one a red-shift. With the ions, the second *o*-methoxyl group also causes a decrease in the intensity of the band, although such an effect is hardly noticeable for the unionized species.

(4) *Complex long-wave bands.* The complexity of the long-wave bands of the *p*-hydroxylated aldehydes and ketones (Figs. 5 and 6) is evident also after ionization (Figs. 9 and 11). The new shape in which these band systems appear after ionization indicates that the various partial bands have undergone different changes in position and intensity. The intensities of the long-wave maxima given by the ions are not much affected by the introduction of *o*-methoxyl groups, but their wavelengths increase by about 20—25 nm for each methoxyl group.

The long-wave bands of the di-ions of the *p*-hydroxybenzoic acids (Fig. 10) are not only shifted towards red upon increased "methoxylation", but they also change considerably in shape. The band given by the vanillic acid di-ion is clearly double. The flat top of the band shown by the *p*-hydroxybenzoic acid di-ion also indicates a complex character.

The fully ionized *p*-coumaric acids resemble the ionized aldehydes and ketones in that introduction of *o*-methoxyl groups causes a stepwise red-shift but hardly any intensity change of the long-wave maximum (Fig. 12).

c i s - t r a n s - R e a r r a n g e m e n t s

It is well-known that exposure to light may cause *cis-trans*-rearrangement in stilbenes, cinnamic acids, *etc.* A method for preparing *cis-p*-coumaric acid by intense illumination of the mono-ion of the *trans*-acid (using mainly 3000—3100 Å radiation) has been published some years ago.[17]

In our UV absorption work we found that even the most dilute solutions (0.00002—0.00003 M) of the *p*-propenylphenols, *p*-coumaryl alcohols, and *p*-coumaraldehydes in undissociated as well as in ionized form were relatively stable towards daylight (and normal artificial light). High stability was shown also by undissociated *trans*-cinnamic, -ferulic, and -sinapic acid as well as by the carboxylate ions of these acids and of *cis*- and *trans-p*-coumaric acid. However, undissociated *cis*- and *trans-p*-coumaric acid, di-ionized *trans*-ferulic, and -sinapic acid and, in particular, di-ionized *trans*- and *cis-p*-coumaric acid were highly sensitive to light in the visible and/or near ultraviolet range. Their absorption curves could be determined by preparing the solutions in a nearly dark room and protecting them against light before the measurement. (Some experiments confirmed that normal artificial lighting, being weaker than daylight, caused a slower rearrangement.)

As shown in Fig. 13, exposure to bright daylight (plus normal artificial lighting) for 5 min sufficed to give about 75 % rearrangement of *trans-p*-coumaric acid di-ion to the *cis*-form in dilute (0.00006 M) solution. With solutions of similar strength an equilibrium of approximately 80 % *cis*- and 20 % *trans*-di-ion was reached in about 10—15 min, from either the *cis*- or the *trans*-form. In 0.1 N HCl, however, an equilibrium of approximately 55 % *cis*- and 45 % *trans*-acid was reached in a couple of hours from the *cis*-form on similar light exposure.
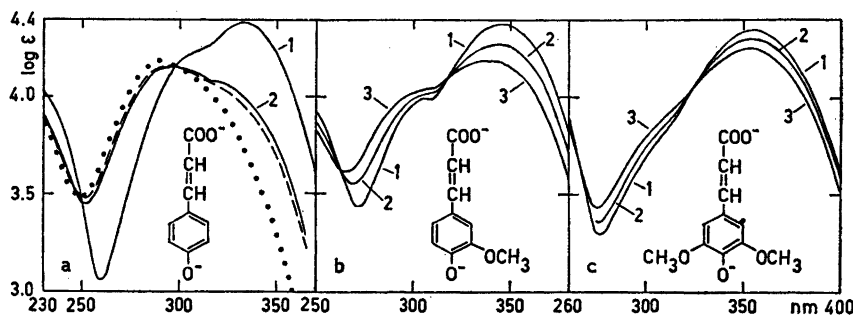

Fig. 13. a 1. *trans-p*-Coumaric acid *(12)* (0.00006 M) in 0.1 N NaOH, protected from light. a 2. Same soln. after exposure to daylight and normal artificial light for 5 min. a. .... *cis-p*-Coumaric acid *(13)* (0.00008 M) in 0.1 N NaOH, protected from light. a. — — — The soln. of *trans*-acid after 20 min or 15 h in light, = the *cis*-acid soln. after 10 min or longer in light. b 1. *trans*-Ferulic acid *(24)* (0.00006 M) in 0.1 N NaOH, protected from light. b 2. Same soln. after 5 min in light. b 3. Same soln. after 30 min or 17 h in light. c 1. *trans*-Sinapic acid *(40)* (0.00005 M) in 0.1 N NaOH, protected from light. c 2. Same soln. after 5 min in light. c 3. Same soln. after 80 min in light.

The ease, with which di-ionized *p*-coumaric acids undergo *cis-trans* rearrangement by the action of visible and/or long-wave ultraviolet light, and the high proportion of the *cis*-form at equilibrium may be explained as follows: The radiation causes an E.T. type excitation of the di-ion to a species of the type
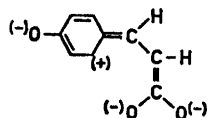
in which there is, in principle, free rotation around the central bond of the side-chain. However, the carboxylate group due to its strong negative charge is attracted by the positive charge on one of the *o*-carbon atoms (or the attached hydrogen atom). This favours the *cis*-conformation of the side-chain. When the excitation energy is lost and the double bond character of the central bond restored, the predominance of the *cis*-arrangement is preserved.

A preparative rearrangement of *trans-p*-coumaric acid to the *cis*-acid using the favourable photoisomerization properties of the di-ion, is described in the experimental part.

REFERENCES

1. Aulin-Erdtman, G. *Chem. Ind. (London)* **1955** 581.
2. Aulin-Erdtman, G. *Svensk Kem. Tidskr.* **70** (1958) 145.
3. Demerseman, P., Lechartier, J.-P., Reynaud, R., Cheutin, A., Royer, R., Rumpf, P. and Desvoye, M.-L. *Bull. Soc. Chim. France* **1963** II 2559.
4. Dodgson, K. S. and Spencer, B. *Biochem. J.* **53** (1953) 444.
5. Doub, L. and Vandenbelt, J. M. *J. Am. Chem. Soc.* **69** (1947) 2715.
6. Goldschmid, O. *J. Am. Chem. Soc.* **75** (1953) 3780.
7. Cohen, L. A. *J. Org. Chem.* **22** (1957) 1333.
8. Lemon, H. W. *J. Am. Chem. Soc.* **69** (1947) 2998.
9. Morton, R. A. and Stubbs, A. L. *J. Chem. Soc.* **1940** 1347.
10. Sager, E. E., Schooley, M. R., Carr, A. S. and Acree, S. F. *J. Res. Natl. Bur. Std.* **35** (1945) 521.
11. Kepianka, E. and Marchlewski, L. *Bull. Acad. Polon.* [A] **1926** 91; (*C.* **1926** II 335).
12. Lauerer, D., Coenen, M., Pestemer, M. and Scheibe, G. *Z. physik. Chem. (Frankfurt)* **10** (1957) 236.
13. Lindberg, J. J., Nordström, C.-G. and Laurén, R. *Suomen Kemistilehti* **B 35** (1962) 182.
14. Herzog, R. O. and Hillmer, A. *Ber.* **64** (1931) 1288.
15. Zioudrou, C. and Fruton, J. S. *J. Am. Chem. Soc.* **79** (1957) 5951.
16. Jurd, L. *Arch. Biochem. Biophys.* **66** (1957) 285.
17. Merritt, A. J. and Freedman, L. *U.S. Pat. 3 094 471* (1963).
18. Naves, Y.-R. and Grampoloff, A. V. *Bull. Soc. Chim. France* **1959** 1233.
19. Peniston, Q. P., Agar, H. D. and McCarthy, J. L. *Anal. Chem.* **23** (1951) 994.
20. Bhattacharya, A., Sondheimer, E. and Schuerch, C. *Tappi* **42** (1959) 446.

21. Töppel, O. *Holzforsch.* **14** (1960) 139.
22. Aulin-Erdtman, G. *Svensk Papperstid.* **47** (1944) 91.
23. Adler, E., Delin, S. and Miksche, G. *Acta Chem. Scand.* **20** (1966) 1035.
24. Kratzl, K. and Claus, P. *Monatsh.* **93** (1962) 219.
25. Uyeo, S., Miwa, T. and Nakanishi, M. *J. Chem. Soc. Japan* **64** (1943) 659.
26. Hergert, H. L. *Forest Prod. J.* **8** (1958) 335.
27. Aulin-Erdtman, G. *Svensk Papperstid.* **56** (1953) 91.
28. Pew, J. C. *J. Org. Chem.* **28** (1963) 1048.
29. Lindberg, J. J. and Enkvist, T. *Suomen Kemistilehti* **28** (1955) 23; (the value of log ε given in the table for the 297.5 nm maximum is not in accordance with the curve and probably erroneous).
30. Gilchrist, T., Hodges, R. and Porte, A. L. *J. Chem. Soc.* **1962** 1780.
31. Patterson, R. F. and Hibbert, H. *J. Am. Chem. Soc.* **65** (1943) 1862.
32. Kung, H. P. and Huang, W.-Y. *J. Am. Chem. Soc.* **71** (1949) 1836.
33. Aulin-Erdtman, G. and Hegbom, L. *Svensk Papperstid.* **60** (1957) 671.
34. Aulin-Erdtman, G. and Sandén, R. *Acta Chem. Scand.* **17** (1963) 1991.
35. Lindberg, J. J. *Paper and Timber* **37** (1955) 206.
36. Musso, H. and Matthies, H.-G. *Chem. Ber.* **94** (1961) 356.
37. Murrell, J. N. *The Theory of the Electronic Spectra of Organic Molecules,* Methuen, London, Wiley, New York 1963, p. 127.
38. Sklar, A. L. *J. Chem. Phys.* **10** (1942) 135; *Rev. Mod. Phys.* **14** (1942) 232.
39. Förster, Th. *Z. Naturforsch.* **2a** (1947) 149.
40. Murrell, J. N. and McEwen, K. L. *J. Chem. Phys.* **25** (1956) 1143.
41. Petruska, J. *J. Chem. Phys.* **34** (1961) 1120.
42. Pestemer, M. and Mayer-Pitsch, E. *Monatsh.* **70** (1937) 104.
43. See *e.g.* Jaffé, H. H. and Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy,* Wiley, New York 1962, p. 264.