EXPERIMENTAL AND CALCULATED (PPP) ELECTRONIC SPECTRA OF FLAVONOID, STILBENE AND COUMARONE STRUCTURES*

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Electronic spectra of seven hydroxy and methoxy substituted flavones as well as nine hydroxy and methoxy substituted flavonoles have been studied experimentally and theoretically with the use of the semiempirical SCF LCI PPP method. The same method has been applied to electronic spectra of some model compounds of lignin of stilbene and coumarone type. The calculated excitation energies agree well with the observed ones. Results of our experimental and theoretical studies of electronic spectra of basic chromophoric structural units of lignin are summarized from the viewpoint of their contribution to colour of lignin.

Several years ago a method was developed[1] enabling determination of UV and visible spectra of lignin in situ and, hence, study of chromophoric properties of lignin in wood fibrous materials. Lingin absorption spectra characterize a complex macromolecule which represents a mosaic composed of many monomeric structural units absorbing in UV and visible region. Therefore it is important to know spectral properties of individual basic structural units of lignin.

Our previous communications[2-5] dealt with basic structural units of lignin *viz.* chromophoric systems of hydroxybenzaldehyde, quinoid, quinonemethide and cinnamaldehyde types with the use of the semiempirical CNDO/S method modified by Del Bene–Jaffé. The present communication deals with experimental and theoretical (PPP) studies of electronic spectra of structural units of flavonoid (Table I), stilbene and coumarone types (Scheme 1).

Flavones and flavonoles are intensively coloured chromogenes naturally occurring first of all in plants[6,7]. In wood flavonoid structures occur frequently as components of wood extractives. As colour of wood is not markedly changed by extraction with solvents, it is presumed that these compounds might be bound by covalent bonds with lignin or wood polysaccharides[8]. Besides that they can easily polymerize with one another and, hence, cannot be completely removed from wood by simple extraction.

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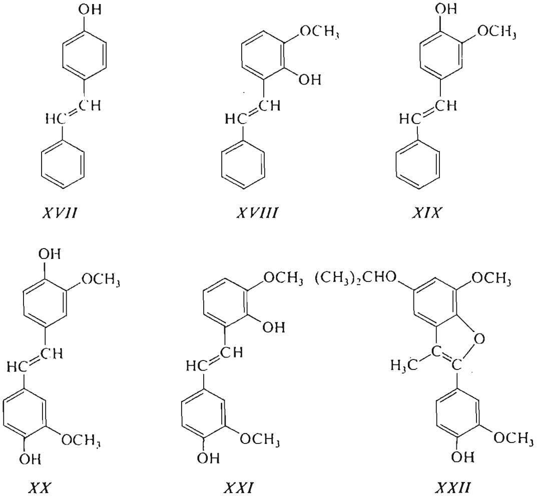
The lignin model substances of stilbene type are not considered to be primary structural units of protolignin, they are, however, known to be formed on heating of some model substances of lignin in alkaline medium[9], and differential UV spectra, $\Delta\varepsilon$, detected their presence in lignin after alkali or sulphate delignification of wood, dissolved in black liquor as well as in residual lignin of sulphate celluloses. It was found that stilbene structures tend to be formed in lignin under very mild conditions, and with respect to their chromogene properties they probably lower the bleaching effect in lignified pulpwood produced in alkaline medium with *e.g.* $NaBH_4$ (ref.[10]).



SCHEME 1

Phenylcoumarone structures are mainly formed during delignification of wood in acid medium[11] and, hence, belong to important secondary chromophores of lignins from *e.g.* sulphite pulping.

CALCULATIONS AND EXPERIMENTAL

Calculations of electronic spectra and electronic structure of the studied molecules were carried out with the use of the standard PPP method[12,13] with the Pople parametrization[14]. The bicentric repulsion integrals were calculated according to the Mataga–Nishimoto approximation[15]. The calculations started from experimental geometries[16,17]. The calculations were carried out with a Siemens 4004/150 computer in the Computer Centre, Comenius University.

TABLE I
The Flavones Studied

Compound	Position					
	3	5	7	3′	4′	5′
I	H	H	H	H	H	H
II	H	OH	H	H	H	H
III	H	H	OH	H	H	H
IV	H	OH	OH	H	H	H
V	H	H	H	H	OCH_3	H
VI	H	H	OH	H	OH	H
VII	H	OH	OH	H	OH	H
VIII	OH	H	H	H	H	H
IX	OH	H	H	H	OCH_3	H
X	OH	H	OH	H	OH	H
XI	OH	OH	OH	H	H	H
XII	OH	H	H	OH	OH	H
XIII	OH	OH	OH	H	OH	H
XIV	OH	H	OH	OH	OH	H
XV	OH	OH	OH	OH	OH	H
XVI	OH	H	OH	OH	OH	OH

The experimental spectra of the studied sixteen compounds of flavonoid type (Table I) were measured in spectroscopically pure ethanol (96%) using a Beckman DBG recording spectrophotometer. The substances measured were either commercial samples or were synthetized by known methods[18,19]. Our measured spectra (Figs 1 and 2) agree in the main with the data given in ref.[20] for positions of the absorption bands measured in methanol.

The spectra of the stilbene structures *XIX*—*XXI* were taken from ref.[23], and that of the coumarone structure *I* was taken from ref.[22].

RESULTS AND DISCUSSION

Electronic Spectra of Flavonoid Structures

The calculated excitation energies and oscillator strenghts are given in Figs 1 and 2 along with the experimental spectra of the studied flavones. The calculated energies agree well with the experimental ones and correspond to $\pi \rightarrow \pi^*$ transitions.

The experimental spectrum of the non-substituted flavone *I* (Fig. 1) consists of three intensive bands corresponding to $\pi \rightarrow \pi^*$ transitions and occuring at 33 890, 39 640 and 47 162 cm^{-1}. The long-wave $\pi \rightarrow \pi^*$ transition at 32 050 cm^{-1} is observed as an inflection. Hydroxy substitution at 5, 7 or 5 and 7 positions (compounds *II*, *III*, *IV*) shifts this transition bathochromically. Light absorption in visible region is further increased by OCH_3 or OH substitution in the side aromatic ring B (compounds *V*, *VI*, *VII*).

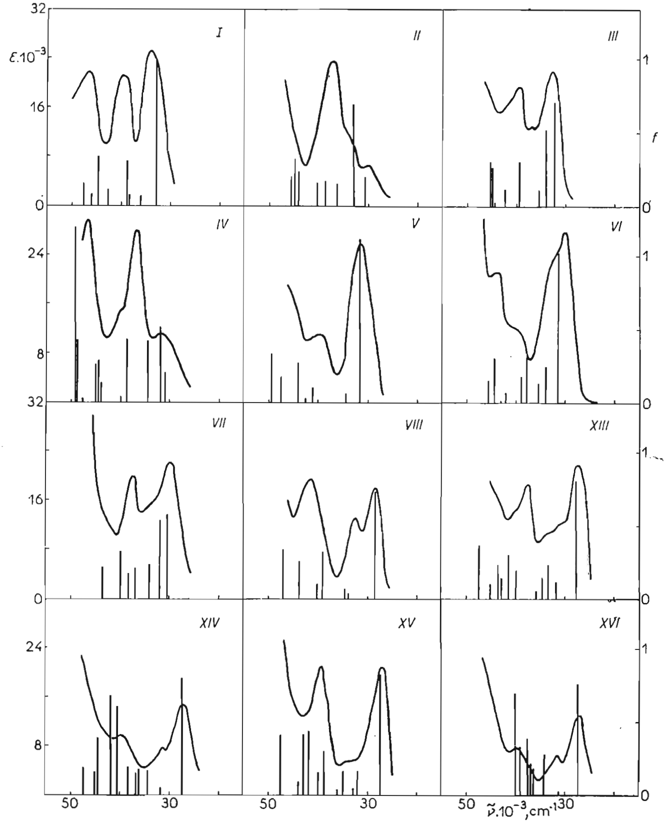


FIG. 1

Experimental (ε is molar linear absorption coefficient) and Calculated (PPP method) Electronic Spectra of Flavones *I—VII* and *XIII—XVI*

The experimental spectrum of 3-hydroxyflavone measured in ethanol consists of three bands at 28650, 32750 and 41660 cm^{-1}. The $\pi \rightarrow \pi^*$ transition at 41150 cm^{-1} is observed as an inflection. 3-Hydroxy substitution shifts the first $\pi \rightarrow \pi^*$ transition considerably bathochromically as compared with that of the non-substituted flavone. The bathochromic shift is still more pronounced by substitution in the rings A and B, which is also accompanied by strong intensity increase of this $\pi \rightarrow \pi^*$ transition (Figs 1 and 2) and, hence, intensification of colour of the compounds *IX*–*XVI*.

From analysis of charge distribution of the ground state and several lower singlet excited states of flavone and 3-hydroxyflavone it follows that, in the case of the non-substituted flavone, the first (long-wave) $\pi \rightarrow \pi^*$ transition is accompanied by charge transfer in direction to the aromatic ring B. The second $\pi \rightarrow \pi^*$. transition (36380 cm^{-1}) is mainly accompanied by charge transfers in the rings A and C. The other two $\pi \rightarrow \pi^*$ transitions (at 38800 and 47670 cm^{-1}) are accompanied by charge transfer from the region of the aromatic ring A through C to the aromatic ring B.

In case of 3-hydroxyflavone the first $\pi \rightarrow \pi^*$ transition (28710 cm^{-1}) is accompanied by charge transfer from the aromatic ring B and hydroxyl oxygen to the aromatic ring A. A similar charge transfer also accompanies the $\pi \rightarrow \pi^*$ transition at 40330 cm^{-1}. The transition at 34360 cm^{-1} is accompanied by charge transfer from the

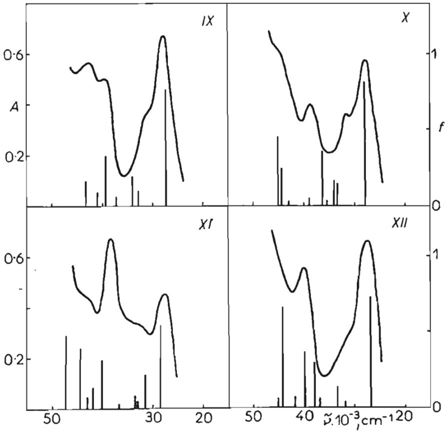


FIG. 2

Experimental (*A* is absorbance) and Calculated (PPP method) Electronic Spectra of Flavones *IX*—*XII* region of the ring C to the aromatic rings A and B. On the contrary, the $\pi\rightarrow\pi^*$ transition at 39280 cm^{-1} is accompanied by the charge transfer from the ring A to B.

As it follows from our experimental and theoretical studies on electronic spectra of the flavonoid-type model substances of lignin the structures studied are strongly coloured chromophores, the colour of which is due especially to the long-wave $\pi\rightarrow\pi^*$ transitions, occurring in the region 27000 to 32000 cm^{-1}. Light absorption of these substances in visible region increases in the series: unsubstituted flavone, hydroxy-substituted flavone (in the rings A, B), flavonol, hydroxy-substituted flavonol.

Electronic Spectra of the Stilbene and Coumarone Structures

The experimental and calculated (PPP) energies and oscillator strenghts are given in Table II along with the dominant mono-excited configurations of the studied compounds *XVII*–*XXII*. The calculated excitation energies agree well with the experimental ones and correspond to the $\pi\rightarrow\pi^*$ transitions.

Generally the experimental electronic spectra of the studied hydroxy and methoxy substituted derivatives of trans-stilbene consist of three bands A, B, C at about 29000, 42000, 50000 cm^{-1} as it is the case in the electronic spectrum of the non-substituted *trans*-stilbene, too[21]. The first two (long-wave) bands are composed of several sub-bands and are shifted to longer wavelengths (as compared with those of *trans*-stilbene) due to auxochromic effects of hydroxy and methoxy substituents. As compared with 4-hydroxy-*trans*-stilbene *XVII*, both experimental and calculated spectra of disubstituted *trans*-stilbenes *XVIII* and *XIX* show further sub-bands in the bands B and C (Table II). Hydroxy or methoxy substitution in the second benzene ring shifts both the experimental and theoretical transitions of the B and C bands towards higher energies.

Stilbene-type conjugation occuring in phenylcoumarones causes their strong UV absorption in long-wave spectral region. Adler and coworkers[22] found for the phenylcoumarone structure* *XXII* (which is formed *e.g.* during heating of lignins in acid medium) intensive absorption bands at 32200 and 30300 cm^{-1} measured in neutral and alkaline solutions, respectively. Theoretical calculations gave the value 30080 cm^{-1} for the first $\pi\rightarrow\pi^*$ transition (Table II).

From Table II it can be seen that the first long-wave $\pi\rightarrow\pi^*$ transition of all the studied compounds is accompanied by the mono-excited configuration $1\rightarrow1'$ due to electronic transition from the highest occuppied to the lowest unoccupied molecular orbital. The other calculated $\pi\rightarrow\pi^*$ transitions are accompanied by various dominant mono-excited configurations (Table II).

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* There is an error in Scheme 1: Insert HOH_6C_3 instead of $(CH_3)_2$ CHO into the corresponding formula.

TABLE II

Singlet-Singlet Transitions in the Compounds Studied

Compound	Energy, 10^3 cm^{-1}		i—j′[d]	Weight[e] %	Oscillator strengths	
	obs.	calc.			obs.	calc.
XVII	29·05[a]	29·92	1—1′	96	0·705	1·441
	32·36	33·80	1—3′	62	0·237	0·040
		35·73	1—2′, 3—1′	42, 33		0
	42·27	42·10	2—1′	86	0·253	0·012
		44·36	1—4′	82		0·021
		44·69	4—1′	51		0·022
		45·25	5—1′, 1—2′	44, 34		0·785
	49·26	51·14	2—3′	65	0·099	0·245
XVIII	29·41[a]	28·15	1—1′	84	0·326	0·592
	32·15	31·29	2—1′	83	0·870	0·751
		35·33	1—2′, 4—1′	35, 25		0·001
	33·55	40·65	1—3′, 2—4′	36, 32	0·350	0·345
		41·62	1—4′	53		0·142
		43·96	4—1′, 3—1′	31, 30		0·249
		44·69	1—2′, 3—1′	40, 27		0·406
		45·73	2—3′, 3—1′	33, 15		0·285
		48·56	2—2′, 1—2′	63, 16		0·001
		48·80	2—4′, 2—3′	40, 26		0·521
		52·59	4—2′, 3—2′	62, 21		0·319
XIX	30·80[b]	29·52	1—1′	94	0·44	1·075
	34·41	32·18	2—1′, 1—3′	46, 33	0·21	0·085
		35·89	1—2′, 4—1′	42, 34		0·0001
	37·63	37·91	2—1′, 1—3′	39, 25	0·08	0·230
	41·9	42·91	3—1′, 1—3′	64, 21	0·21	0·294
	44·2	44·12	1—4′, 2—3′	63, 14	0·099	0·009
		45·17	4—1′, 1—2′	51, 39		0·528
	47·4	47·67	2—3′, 1—4′	67, 16	0·28	0·605
	49·4	51·06	2—4′, 4—2′	36, 31	0·14	0·226
XX	29·7[b]	28·55	1—1′	94	0·44	1·411
	31·5	31·62	2—1′, 1—2′	40, 26	0·11	0·004
	34·0	32·59	3—1′, 1—3′	41, 30	0·22	0·049
	36·9	37·18	2—1′, 1—2′	51, 17	0·06	0·313
		40·09	3—1′, 1—3′	50, 32		0·169
	41·3	42·75	1—4′, 1—2′	38, 22	0·23	0·118
		43·96	4—1′, 1—4′	56, 31		0·541
	44·4	45·33	3—3′, 2—2′	36, 30	0·20	0·572
	46·9	47·59	2—3′, 1—4′	38, 25	0·25	0·037
XXI	29·9[b]	28·07	1—1′	84	0·35	1·035
	32·3	30·89	2—1′	67	0·17	0·255

TABLE II
(*Continued*)

Compound	Energy, 10^3 cm^{-1}		i—j'[d]	Weight[e] %	Oscillator strenghts	
	obs.	calc.			obs.	calc.
	34·5	32·26	3—1', 1—2'	39, 31	0·18	0·168
	37·1	37·91	3—1', 1—2'	49, 22	0·051	0·116
		40·81	2—3', 1—3'	46, 24		0·459
	41·7	41·54	1—3', 1—4'	36, 21	0·26	0·229
		43·23	4—1', 1—2'	67, 16		0·207
		44·12	1—4', 2—3'	30, 27		0·379
	46·0	47·19	3—2', 1—4'	44, 19	0·51	0·124
		48·56	2—4'	72		0·376
		50·41	2—2', 4—2'	33, 26		0·105
	51·0	51·79	3—4', 2—2'	64, 16	1·7	0·107
XXII	32·25[c]	30·08	1—1'	88	strong	1·120
		32·59	1—2', 2—1'	35, 25		0·198
		33·15	3—1', 2—1'	32, 30		0·004
		38·80	2—1', 3—1'	27, 20		0·207
		41·86	1—3', 3—1'	30, 25		0·740
		43·64	1—4', 1—3'	42, 12		0·018
		44·75	4—1', 1—4'	57, 23		0·076
		45·82	2—3', 3—2'	28, 19		0·506
		48·15	2—2', 1—4'	23, 22		0·078

[a] Ref.[24]; [b] ref.[23]; [c] ref.[22]. [d] The dominant transitions from the i-th occupied MO to the j-th unoccupied MO; 1, 2, 3, *etc* occupied (starting from the highest), 1',2',3', *etc.* unoccupied (starting from the lowest). [e] Per cent proportion to the respective transition.

CONCLUSIONS

Our studies of electronic spectra of basic chromophoric structural units of lignin[2–5] allow to draw the following conclusions with respect to their absorption in visible spectral region: *a*) Simple structures of oxybenzaldehyde type are colourless compounds[2] not absorbing in visible region of spectrum. *b*) Cinnamaldehyde structural units of lignin[4] in which there is conjugation of carbonyl group and benzene ring through C=C bond show absorption in visible region. Colour of these compounds is due especially to $n \rightarrow \pi^*$ transitions within 27000–29000 cm^{-1}. *c*) Simple quinone and quinonemethide structures[3] are moderately coloured chromogenes. Their colour is due to $n \rightarrow \pi^*$ and long-wave $\pi \rightarrow \pi^*$ transitions within 17000–28000 cm^{-1}. Their colour is considerably increased by their combination with other oxyaromatic units[5]. *d*) Structures of flavone or flavonol type show strong absorption in the region

$27000-32000\,cm^{-1}$ corresponding to the first $\pi \rightarrow \pi^*$ transition which is (together with the long-wave $n \rightarrow \pi^*$ transition) responsible for colour of these compounds. *e*) The stilbene- and coumarone-type model substances of lignin have no structural chromogene of $n \rightarrow \pi^*$ type, but the presence of auxochromic hydroxy and methoxy groups shifts the first (long-wave) $\pi \rightarrow \pi^*$ transition towards lower energies (both observed and calculated within $27000-32000\,cm^{-1}$) reaching the visible spectral absorption region.

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