

OPTICAL PROPERTIES OF NATURAL PHENOLS IN AQUEOUS MEDIA

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Abstract

Currently, the study of the photochemistry of natural phenols is relevant as it has a fundamental and a practical importance. The optical properties of natural phenols are studied: 3-methoxy-4-hydroxybenzaldehyde (vanillin) and 3-hydroxy-4-methoxybenzaldehyde (isovanillin), 4-hydroxy-3-methoxybenzoic acid (vanillic acid). The processes of proton transfer in the investigated molecules in ground and excited states under exposure to lamp and laser emissions are presented using the methods of electron spectroscopy and quantum chemistry. Vanillin, isovanillin, vanillic acid, fluorescence.

Introduction

Natural phenols, in particular vanillic acid, are considered to be promising compounds in production of polymers [1]: as catalysts in isomerization reactions, antimicrobial agents for building and textiles materials, agricultural products, in medicine as antiallergic medication, and as modifiers of dental cements [1 2]. This is due to the presence in the structure of three reactive oxygen groups: methoxy, hydroxy, and carboxy, and a manifestation in compounds of spectral and photophysical properties required for practical use. These groups determine the ion equilibrium of natural phenols of a vanillic series in aqueous solutions in ground and excited electronic states. [3] The impact of the medium (solvent) on the reactivity of intermediate compounds is an important area of modern chemical kinetics, and is the basis of fundamental research of mechanisms in many chemical processes. This is especially true in reactions under explosion to light, for which the polarity of the medium and the possibility of formation of hydrogen bonds between the substrate and the solvent are often the determining factors influencing the speed and the direction of photophysical and photochemical processes [4].

Research methods

Chemically pure (99%) objects of research made by the company “Acros organics” – 3-methoxy-4-hydroxybenzaldehyde (vanillin), 3-hydroxy-4-methoxybenzaldehyde (isovanillin), and 4-hydroxy-3-methoxybenzoic acid (vanillic) were used in the work.

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A pulse excilamp XeBr ($\lambda_{\text{rad}} \sim 283$ nm) [5] with the parameters: $\Delta\lambda = 5 \div 10$ nm, $W_{\text{peak}} = 18$ MW/cm², $f = 200$ kHz, the pulse duration 1 ms, was used as a UV radiation source. During the irradiation, the energy absorbed by the test solution was $E = 1 - 4.5$ J/cm³.

Moreover, an unfocused monochromatic pulsed radiation (6 ns, 15 Hz) of the 4th harmonic (266 nm, 20 mJ) of a solid-state laser Nd:YAG (LS-2132UTF, LOTIS TII) was used. The solutions were placed into a quartz cuvette and irradiated under various exposure times. An injected (absorbed by the sample) energy was evaluated as a difference between an incident and a transmitted through the cuvette, with the test sample of the radiation energy. The energy (average radiation power) before and after the cuvette with the sample was measured using a calorimeter head Ophir 12A-P with a display Nova II.

Phototransformations of irradiated samples were studied in regards to changes in absorption spectra in comparison with spectra of initial compounds on the spectrofluorimeter with a function of the spectrophotometer SM2203 (CJSC "SOLAR", Belarus).

Transient absorption spectra were studied using a pump-probe on the installation with a fluorescent probe [6] under the radiation excitation of the 4th harmonic of the same pulsed laser Nd:YAG. Probing was carried out both synchronously with pumping (variant 1) and with a delay of 30 ns (version 2). Such an experimental scheme allows, if necessary, to divide short-lived (singlet-singlet with lifetimes 10^{-8} sec or less) and long-lived (triplet-triplet, long-lived radicals of intermediate photoproducts, etc. with lifetimes more than 5×10^{-8} sec). The fluorescent probe of a mixture of well-emitting and photostable organic dyes provided a broadband spontaneous radiation in the spectral range of 370-800 nm (the analogue of a "white" light in pure solvents at picosecond and femtosecond pumping). When using the 4th harmonic of the laser Nd:YAG, a direct excitation of tested vanillines took place, explained in details in [7].

Results and discussion

For spectral and photochemical properties of a molecule, its structure is of fundamental importance. Investigation of dyes has showed that the color of the substance is caused by the presence of particular groups of chromophores, which usually consist of aromatic nuclei, multiple bonds, and a carbonyl group. Atomic groups enhancing and displacing the absorption band of a chromophore are called auxochromes. If the absorption shift under their influence goes into the red (long wavelength) region, it is called bathochromic; shift to the violet (short wavelength) region is called hypsochromic. Division of groups into chromophores and auxochromes is not strict. The latter class typically includes amino, hydroxyl, and mercapto groups, as well as halogens. The mutual influence of different chromophores and auxochromes in the molecule is so strong that it is impossible to easily and unambiguously identify in the oscillation spectra, caused by various transitions [8].

Parker S. [9] proposes to consider molecules that are in one of the excited states as a kind of a new compound, which is entirely different from a molecule in the ground state, i.e. as a "metastable isomer" of an unexcited molecule.

The paper presents a summary on the investigated molecules.

3-methoxy-4-hydroxybenzaldehyde (vanillin)

Vanillin in different pH ranges can be in three protolytic forms: anion, neutral form, and cation (Fig. 1). In an aqueous solution, together with the neutral form there is an anion. Spectrally it appears as a shoulder on the long-wavelength absorption edge. When adding alkali, this shoulder transforms into an anion absorption band with disappearance of the absorption of the neutral form. The neutral form of vanillin exists with small additions of sulfuric acid at pH=3-4. The spectrum consists of two distinct bands of an approximately equal intensity. In the ground state, the cation was obtained with very large additions of sulfuric acid ($\text{pK}_b = -1$); in the excited state, formation of the cation occurs much easier (with addition of acid $\sim 10^{-3}$ - 10^{-2} M). $\text{pK}_b^{*F-C} = 5.4$. $\text{pK}_a = 7.4$ [10].

The study of fluorescence characteristics have shown that vanillin spectra are of an anionic form, and the neutral two-band. The fluorescence of the anionic form is observed in the range of 405 nm, the neutral form at a wavelength of 30770 cm^{-1} (325 nm). The cation 23500 cm^{-1} (425 nm) (Fig. 2).

There are changes in the characteristics of absorption and fluorescence spectra of the neutral form of vanillin under exposure to various lamps. In fluorescence spectra, after irradiation with excilamps, there is an increase in the intensity in the region of 30770 cm^{-1} (325 nm) (corresponds to fluorescence H), and a decrease in the intensity in the region of $23,500\text{ cm}^{-1}$ (425 nm) (corresponds to emission K) with an isosbestic point.

Under exposure to the excilamp KrCl, the stability of protolytic forms of vanillin is distributed as follows: the most stable A, then A+H, and the lowest is H.

Under exposure to the lamp "Solar", the following changes are observed: at low radiation doses the most stable is H, and the less stable is A. An increase in the exposure time shows that the effectiveness of the neutral form remains unchanged, and solutions containing the anionic form (aqueous and with addition of alkali) become more stable.

3-hydroxy-4-methoxybenzaldehyde (isovanillin)

Spectral characteristics of isovanilline are heavily dependent on the pH of the medium. 3 protolytic forms are allocated (Fig. 3). In regards to absorption spectra, isovanillin and vanillin aqueous solutions differ only in the presence of a tail in the spectrum of isovanillin in the long-wave region. When comparing maxima of absorption bands (Table 1) it can be seen that anion and cation of isovanillin have higher long-wave values than similar forms of vanillin. Fluorescence spectra of isovanillin are more short-wave, unlike spectra of vanillin. This is due to the pK_a acidity of isovanillin 9.2 in the ground state and 0.64 in the excited Franck-Condon state. The cation in the ground state forms only at very large additions of acid (pK_b basicity = -1). In the excited $pK_a^{*F-C} = 3,7$ (with small additions of mineral acid). $pK_a = 8,9$ [11]. Isomers exhibit different solvatochromic properties: for example, during the transition from a water solution to an acetonitrile the direction of shifts of absorption bands changes. In acetonitrile, vanillin has a blue shift of the absorption spectrum; in isovanillin, on the contrary, it is red.

Vanillic acid

Vanillic acid is interesting because when forming an anionic form, as compared to benzaldehydes, there is a change in center of deprotonation. The anion is formed at deprotonation from a carboxyl group COOH in an aqueous solution (in the ground state), and with an increase in pH of the solution up to 10 or more, the deprotonation from a hydroxyl group occurs, and formation of a dianion takes place.

A comparative analysis of the fluorescence spectra of vanillic acid (Fig. 6) has shown that for cation the fluorescence maximum in the region of 24096 cm^{-1} (425nm) has the highest long-wave value and the widest band; it is shifted, as compared to the fluorescence maximum of the neutral form 29000 cm^{-1} (in the region of 350 nm) to the region of large wavelengths by about 75 nm. The neutral form is observed in a small range of pH [12]; with an increase in pH, there is a short-wave shift by 20 nm (anion), and the band maximum is observed in the region of 30303 cm^{-1} (330 nm), and then the long-wave shift by 30 nm (dianion) 28160 cm^{-1} (355nm). In regards to location of bands, the anionic form of vanillic acid has the most short-wave fluorescence. pK_a acidity of vanillic acid 4.5 (4.54) in the ground state $pK_a^{*F-C} = 5,57$, pK_a basicity₂=11. However, in the transition from the anion to the dianion in the excited state the acidity increases, $pK_a^{*F-C} = 5,43$. pK_b basicity -1; $pK_b^{*F-C} = 4,04$. $pK_{a1} = 4,51$ [1] $pK_{a2} = 9,39$ [10].

Conclusion

The pH of solution affects optical properties of natural phenols. We have allocated three protolytic forms for vanillin and isovanillin– neutral, cationic, and anionic. And four forms for vanillin acid – neutral form, cation, anion, and dianion. In benzaldehydes, formation of all forms takes place under the same scheme.

The study of fluorescence characteristics has shown that spectra of the studied isomers have a multiband glow. The studied compounds are characterized by individual fluorescence spectra, therefore, vanillin and isovanillin can be distinguished in the excited state, as the position of band maxima are different (Table 3). [3]

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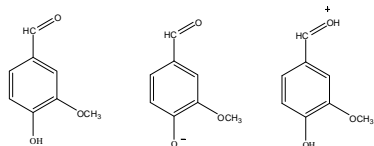


Figure 1 Protolytic forms of vanillin: the neutral (NF), the anion (A) and cation (K).

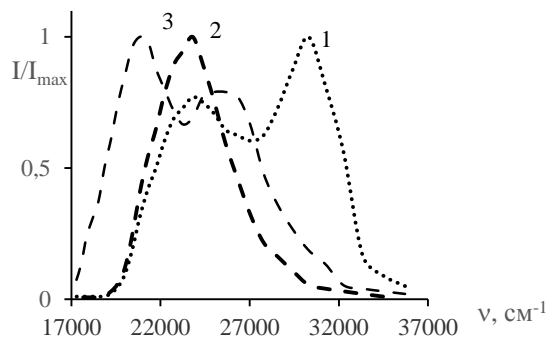


Figure 2 Fluorescence spectra of vanillin at $C = 5 \times 10^{-5}$ M: 1 - neutral form for $\lambda_{\text{exc}} = 290$ nm; 2 - cation for $\lambda_{\text{exc}} = 290$ nm; 3 - anion for $\lambda_{\text{exc}} = 290$ nm.

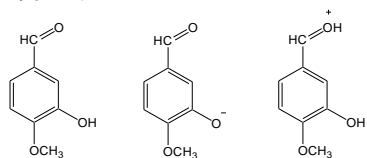


Figure 3 Protolytic forms of isovanillin: the neutral (NF), the anion (A) and cation (K).

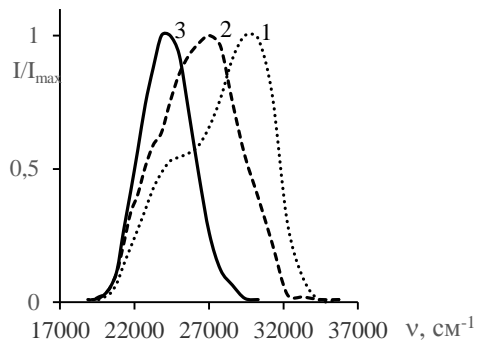


Figure 4 Fluorescence spectra of isovanillin at $C = 5 \times 10^{-5}$ M: 1 - neutral form for $\lambda_{\text{exc}} = 270$ nm; 2 - cation for $\lambda_{\text{exc}} = 270$ nm; 3 - anion for $\lambda_{\text{exc}} = 290$ nm.

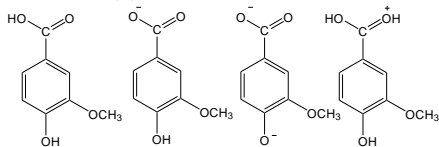


Figure 5 Protolytic forms of vanillic acid: the neutral (NF), the anion (A), the dianion (DA) and the cation (K).

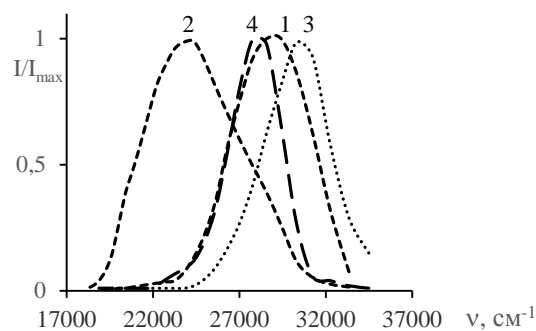


Figure 6 Fluorescence spectra of vanillic acid at $C = 5 \times 10^{-5}$ M: 1 - neutral form for $\lambda_{exc} = 290$ nm; 2 - cationic form for $\lambda_{exc} = 290$ nm; 3 – anionic form for $\lambda_{exc} = 290$ nm; 4 – dianionic form for $\lambda_{exc} = 290$ nm.

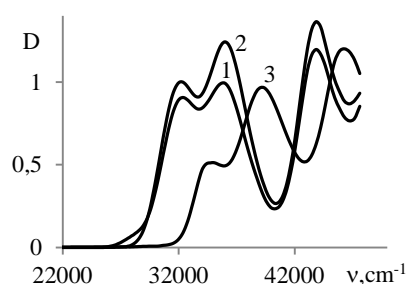


Figure 7 Absorption spectra of molecules at $C = 5 \times 10^{-5}$ M in water: 1 - vanillin, 2 - isovanillin, 3 - vanillic acid

Table 1. Spectral characteristics of the studied molecules

Compound		Neutral form	Anionic form	Cationic form	Dianionic form
Vanillin	Absorption, cm^{-1} (nm)	32600 (306) 35800 (279)	28800 (347)	30000(333)	-
	Fluorescence, cm^{-1} (nm)	30300 (330) 23530 (425)	25320 (395) 19230 (520)	22222 (450)	-
	pH (S_0)	-1 ÷ 7,2	>7,2	<-1	-
	pH (S_1)	-0,5 ÷ 5,4	>5,4	<-0,5	-
Vanillic acid	Absorption, cm^{-1} (nm)	34200(292) 38400 (260)	34700(288) 39800(251)	31050(322) 34400(290)	33500(298) 35250(283)
	Fluorescence, cm^{-1} (nm)	350	330	425	355
	pH (S_0)	6,7 ÷ 4,5	4,5 ÷ 11	<6,7	>11
	pH (S_1)	4,04 ÷ 5,57	5,57 ÷ 5,43	<4,04	>5,43
Isovanillin	Absorption, cm^{-1} (nm)	32600 (306) 35800 (279)	28000 (357)	30000 (333)	-
	Fluorescence, cm^{-1} (nm)	29850 (335) 24390 (410)	24100 (415)	24690 (405) 27030 (370)	-
	pH (S_0)	-1 ÷ 9,2	> 9,2	< -1	-
	pH (S_1)	0,64 ÷ 3,7	> 3,7	< 0,64	-

References

- [1] Belkov, M.V., Brinkevich, S.D., Samovich, S.N., Skornyakov, I.V., Tolstorozhev, G.B., Shadyro, O.I., "Infrared spectra and structure of molecular complexes of aromatic acids," *Journal of Applied Spectroscopy*, 78 (6) 851—858 (2011).
- [2] Merezhkin, A.V., Ivanov, V.A., Potekhin, V.M., Tyulmenkov, A.V., Deyneko, I.P., "A method for producing vanillin acid" Patent // Russia № 2109008 (1998).
- [3] Vusovich, O.V., Tchaikovskaya, O.N., Sokolova, I.V., Vasileva, N.Y., "Experimental and quantum-chemical study of electronically excited states of protolytic isovanillin species," *Russian Physics Journal*, 57(1) 86-94 (2014).
- [4] Sokolova, T. V., [Spectral-luminescent and photochemical properties of some METHYLPHENOL and dihydroquinoline in different environments]: dis. ... candidate. chem. Sciences, Tomsk, 160 (2006).
- [5] Svetlichnyi, V. A., "A setup for investigating the absorption spectra of dyes in excited states by the pump-probe method utilizing a fluorescence probe," *Instruments and Experimental Techniques*, Pleiades Publishing, Ltd., 53(4), 575-580 (2010).
- [6] Sokolova, T.V., Chaikovskaya, O.N., Sokolova, I.V., Sosnin, É.A., "Photoconversion of 2-methylphenol, 4-methylphenol, and 2-amino-4-methylphenol in water," *Journal of Applied Spectroscopy*, T. 73(5), 632-639 (2006).
- [7] Vusovich, O.V., Tchaikovskaya, O.N., Sul'timova, N.B., Lapin, I.N., Svetlichnyi, V.A., "Comparison of vanillin and isovanillin photolysis in aqueous solutions," *Russian Physics Journal*, 56(11), 1287-1291 (2014).
- [8] Zhdanov, Y.A., [Theory of structure of organic compounds], *Visshaya Shkola*, Moscow, 100-288 (1971).
- [9] Parker, C., [Photoluminescence of Solutions], Publishing house Mir, Moscow, 312-360 (1972).
- [10] Ragnar, M., Lindgren, C.T. and Nilvebrant, N.O. "pK_a-values of guaiacyl and syringyl phenols related to lignin," *J. Wood Chem. Technol*, 20 (3), 277-305 (2000).
- [11] Zinchenko, A.V., Simanova, S.A., "The dissociation constants of bases and acids" http://chemanalytica.com/book/novyy_spravochnik_khimika_i_tekhnologa/07_khimicheskoe_ravnovesie_svoystva_rastvorov/5018 (02.06.2015).
- [12] Vusovich, O.V., Tchaikovskaya, O.N., Sokolova, I.V., Vasil'eva, N.Y. "Protolytic equilibrium vanillic acid in ground and excited states," *Journal of Applied Spectroscopy*, in print (2015).