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Note

The UV and VIS Absorption Spectra of Jatrorubine

Š. Komorsky-Lovrić

OUR »Ljekarne«, Zagreb, Croatia, Yugoslavia,

and

Z. Gašparec

The Faculty of Pharmacy and Biochemistry University of Zagreb, Croatia, Yugoslavia

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The absorption spectra of water, methanolic, ethanolic and propanolic solutions of jatrorubine in the VIS and UV spectral range were recorded. The acidity and the alkalinity of the solutions were changed in the wide range from pH = 2 to pH = 13 by the addition of KOH and HCl in the solutions. From the influence of pH on the shapes of the absorption curves, it was concluded that jatrorubine exists as quaternary aminic cation in the acidic medium and as the resonance dipole molecula in the basic media, but no evidence for the existence of carbinolic form was found. The results were compared with the literature data.

Jatrorubine is a synthetic derivative of berberine (Figure 1.). It was synthesized for the first time by pyrolysis of jatrorhizine chloride in an atmosphere of CO_2 at a temperature of 190° for 3 hours[1].

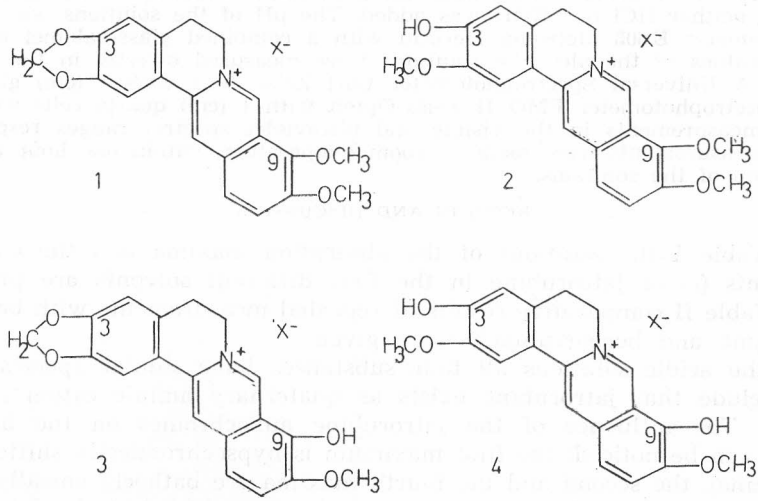

Figure 1. The alkaloids of the protoberberinic group: 1 — berberine, 2 — jatrorhizine, 3 — berberrubine, 4 — jatrorubine

In acidic media, berberine and its derivatives are cyclic, quaternary aminic cations[2-8]. In strongly alkaline solutions (pH $>$ 10)[3,4] berberine turns into a carbinolic (or a cyclic amino-aldehydic) form[2-4]. Although predicted[2], the carbonylic (or the open amino-aldehydic) form of berberine has not been found[3,4]. In slightly basic solutions, the phenolic group of jatrorhizine dissociates and the molecule becomes a dipole[3]. Higher concentrations of hydroxy ions stimulates its conversion into a sarbinolic form[3,4]. Berberrubine reacts similarly to jatrorhizine[5-8], but its dipole ionic state is so stable that no existence of the carbinolic form has been found[8]. This characteristic of berberrubine has made Frerichs believe that it possesses an oxygen bridge between carbon C9 and N atoms[9].

The spectral characteristics of jatrorubine have not yet been examined, although its structure is very interesting because it possesses both the jatrorhizinic and the berberrubinic phenolic groups. In order to analyze the changing of its molecular structure under the influence of different pH and solvent properties, we have undertaken measurements of the absorption spectra of jatrorubine in four different media (water, abs. methanol, abs. ethanol and abs. propanol) and in the wide pH-range between pH = 2 and pH = 13. The aim of this work is to present the results of htese measurements.

EXPERIMENTAL

For the preparation of solutions, the following chemicals were used: abs. methanol, abs. ethanol, abs. propanol, KOH and HCl (all p. a. »Merck«), distilled water and jatrorubine chloride synthesized by the Feist method

(*Anal.:* $C_{19}H_{18}NO_4Cl$ (359.80) calc'd: C 63.42%, H 5.04%, N 3.89%
found: C 63.28%, H 5.31%, N 3.67%).

The purity of jatrorubine was checked by thin-layer chromatography until only one spot was detected (stationary phase was Stahl's silica-gel and mobile phase was a 15% solution of NH_4OH in methanol). Stock solutions of jatrorubine, KOH and HCl in all four solvents were prepared. Four series (20 solutions each) of $5\ 10^{-5}$ (mol dm^{-3}) jatrorubine chloride were prepared. The concentrations of HCl and KOH added varied from $2.5\ 10^{-5}$ to 0.5 (mol dm^{-3}). In every series there was one solution in which neither HCl nor KOH was added. The pH of the solutions was detected by a pH-meter E 603 Metrohm Herisau with a combined glass-calomel electrode. The pH-values of the alcoholic solutions were measured directly in the absolute alcohols. A Universal Spectrophotometer Carl Zeiss Jena with 1 (cm) glass cells and a spectrophotometer PMQ II Zeiss-Opton with 1 (cm) quartz cells were used for the measurements in the visible and ultraviolet spectral ranges respectively. All the measurements were made at room temperature, within one hour after the preparation of the solutions.

RESULTS AND DISCUSSION

In Table I the positions of the absorption maxima and the extinction coefficients (ε) of jatrorubine in the four different solvents are presented.

In Table II comparative results of repeated measurements with berberine, jatrorhizine and berberrubine[3,4,8] are given.

In the acidic solutions all four substances have similar spectra, so we can conclude that jatrorubine exists as quaternary aminic cation in acidic medium. The influence of the jatrorubine auxochromes on the berberine maxima can be noticed: the first maximum is hypsochromically shifted (as in jatrorhizine), the second and the fourth maxima are bathochromically shifted (as in berberrubine), the third maximum is untouched, but the jatrorhizine maximum at 238—242 (nm) does not exist.

TABLE I

The Absorption Maxima of Jatrorubine

Solvent	λ_{max}/nm				(ε)				pH	addition	colour
water	226(19000)	274(14000)	—	348(11600)	—	445(2040)	—	—	3.13	HCl	lime-yellow
	226(18500)	276(13600)	—	350(7000)	—	—	480(1630)	—	5.03	—	yellow
	228(19200)	276(13000)	325(5600)	—	380(6700)	—	480(1700)	—	8.52	KOH	orange
	228(19500)	276(13400)	324(5600)	—	380(7600)	—	490(1840)	—	12.70	KOH	red
methanol	224(10300)	278(6700)	—	350(5600)	—	450(1670)	—	—	0.74	HCl	lime-yellow
	220(21500)	278(13300)	—	350(8000)	—	450(1500)	—	540(350)	5.96	—	brown-yellow
	220(21400)	278(14600)	325(7800)	—	390(9300)	—	505(1750)	550(550)	9.13	KOH	brown
	220(23000)	278(8500)	325(4500)	—	395(5200)	—	510(1750)	550(900)	13.51	KOH	violet
ethanol	226(12500)	278(11000)	—	350(10000)	—	448(1700)	—	—	0.95	HCl	lime-yellow
	220(19500)	285(8600)	—	350(6000)	—	—	505(1750)	—	5.85	—	green-yellow
	220(22500)	278(9800)	330(6400)	—	385(5500)	—	505(1750)	—	9.45	KOH	green
	220(23000)	278(15000)	324(9400)	—	395(11500)	—	505(2200)	—	13.63	KOH	violet
propanol	220(9000)	278(7100)	—	355(6500)	—	464(2380)	—	—	1.13	HCl	yellow
	236(5400)	276(7800)	320(3400)	—	400(3600)	—	490(1500)	—	6.21	—	rose
	226(11000)	278(8200)	326(3500)	—	400(4200)	—	—	540(1740)	7.83	KOH	rose
	220(24000)	276(22200)	320(8000)*	—	385(6700)	460(3200)	—	540(1910)	13.95	KOH	rose

* covered by 276 nm peak

TABLE II

The Absorption Maxima of Berberine[3,4], Jatrorhizine[3,4], and Berberrubine[8]

Solvent	λ_{max}/nm berberine				λ_{max}/nm jatrorhizine							λ_{max}/nm berberrubine							addition
water	227	262	346	422	224	—	274	340	—	425	—	235	268	—	348	—	441	—	HCl
	227	262	346	422	224	—	274	340	—	425	—	235	268	—	348	—	—	—	—
	227	262	346	422	227	238	262	348	372	—	457	235	269	330	—	380	—	490	KOH<0.05 M
	227	262	346	422	230	244	290	—	370	—	457	235	268	330	—	380	—	490	KOH>0.05 M
methanol	230	266	349	431	226	238	264	350	—	433	—	238	278	—	355	—	447	—	HCl
	230	266	349	431	226	240	265	350	—	433	—	238	278	328	—	392	447	513	—
	230	266	349	431	230	248	—	—	388	—	487	238	278	328	—	392	—	513	KOH<0.05 M
	—	(266)	(349)*	—	220	248	—	—	386	—	487	238	278	328	—	392	—	513	KOH>0.05 M
ethanol	236	266	351	431	228	242	264	348	—	436	—	240	276	—	356	—	450	—	HCl
	236	266	351	431	228	242	264	348	404	436	—	240	276	—	356	—	450	—	—
	236	266	351	431	230	248	—	—	398	—	500	240	276	329	—	396	—	516	KOH<0.05 M
	—	(266)	(351)	—	—	248	—	—	375	—	—	240	276	329	—	396	—	516	KOH>0.05 M
propanol	238	268	352	431	—	240	264	352	—	440	—	240	278	—	359	—	450	—	HCl
	238	268	352	431	—	242	266	354	417	—	—	240	278	332	—	399	—	516	—
	238	268	352	431	—	248	—	362	404	—	518	240	278	330	—	399	—	516	KOH<0.05 M
	—	(268)	(352)	—	—	—	260	—	400	—	—	240	278	330	—	399	—	516	KOH>0.05 M

* very small peaks

In basic solutions, jatrorubine exhibits five absorption maxima, similarly to berberrubine, which can be recognized as the result of the dissociation of one of the phenolic groups (Figures 2 and 3). The similarity between the spectra of berberrubine and jatrorubine and the large dissimilarity between the spectra of jatrorhizine and jatrorubine, made us believe that the phenolic group which dissociates in slightly basic solutions is that based on the C9 atom, i. e. the same one as in the berberrubine molecule. In this way, jatrorubine becomes a dipole molecule with similar stability as berberrubine dipole which can be a reason why the further addition of KOH (up to 0.5 mol dm^{-3}) does not provoke any spectral changes characteristica for the appearance of the carbinolic form of jatrorubine (vanishing of the absorption peaks in the visible spectral range and decreasing of the extinction coefficients of the peaks in the UV spectral range — see berberine, Table II).

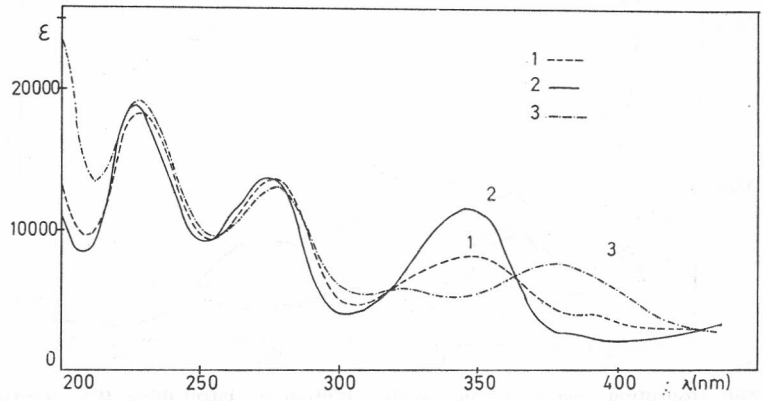

Figure 2. The absorption spectra of water solutions of jatrorubine (UV spectral range) 1 — pH = 5.03; 2 — pH = 3.13; 3 — pH = 11.50

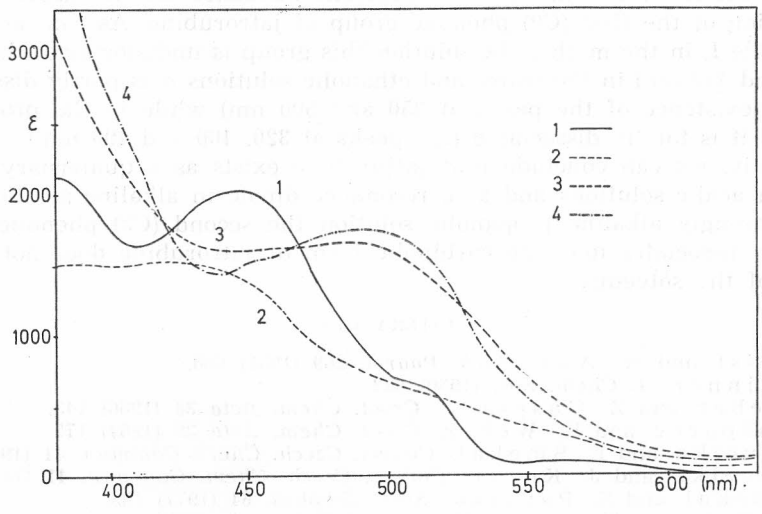

Figure 3. The absorption spectra of water solutions of jatrorubine (visible spectral range) 1 — pH = 3.13; 2 — pH = 4.11; 3 — pH = 5.03; 4 — pH = 12.70

In methanolic solutions (for pH > 6) the fifth peak at 540 (nm) appears, but in propanolic solutions (for pH > 11) greater differences between jatrorubine and berberrubine spectra arise. Beside the 540 (nm) maximum (which is now much bigger than in methanolic solutions), in the strongest alkaline solutions a second maximum at 460 (nm) appears so that now two absorption peaks exist in the visible range. At the same time the extinction coefficients of the peaks at 220 and 276 (nm) greatly increase (Figure 4). The maximum at 460 (nm) can be compared with the jatrorhizinic one at 457 (nm) (in the basic water solutions), so, all these changes may be considered as the result of the dissociation of the second phenolic group, that based on the C3 atom.

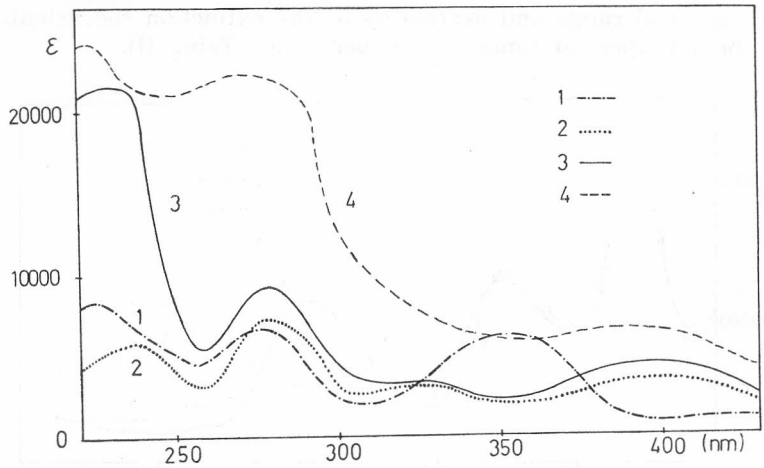

Figure 4. The absorption spectra of propanolic solution of jatrorubine (UV spectral range) 1 — pH = 1.13; 2 — pH = 6.21; 3 — pH = 12.14; 4 — pH = 13.95

The choice of solvent has a significant influence on the degree of the dissociation of the first (C9) phenolic group of jatrorubine. As can be noticed from Table I, in the methanolic solution this group is undissociated (the peaks at 350 and 450 nm) in the water and ethanolic solutions it is partly dissociated (parallel existence of the peaks at 350 and 500 nm) while in the propanolic, solutions it is totally dissociated (the peaks at 320, 400 and 490 nm.)

Finally, we can conclude that jatrorubine exists as a quaternary aminic cation in acidic solutions and as a resonance dipole in alkaline solutions, but in the strongly alkaline propanolic solution the second (C3) phenolic group, probably dissociates too. The carbinolic form of jatrorubine does not appear in any of the solvents.

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SAŽETAK

O apsorpcijskim spektrima jatrorubina

Š. Komorsky-Lovrić i Z. Gašparec

Opisane su apsorpcije vodenih, metanolnih, etanolnih i propanolnih otopina jatrorubina u ultraljubičastom i vidljivom dijelu spektra. Dodatkom HCl i KOH mijenjan je pH otopina od 2 do 13. Na osnovu zavisnosti apsorpcijskih karakteristika jatrorubina o pH otopina diskutirano je njegovo moguće ionsko stanje. Zaključeno je da se jatrorubin u kiselom nalazi u obliku kvartarnog aminskog kationa, a u bazičnim otopinama disocira fenolna grupa na C9 atomu i molekula postaje dipol. Nisu pronađeni dokazi o postojanju karbinolne forme jatrorubina niti kod najviših pH vrijednosti, ali postoje neke indicije da u jako alkalnim propanolnim otopinama dolazi do disocijacije i druge fenolne skupine (C3) jatrorubina. Rezultati su uspoređeni sa literaturnim podacima.

OUR »LJEKARNA« ZAGREB
i
FARMACEUTSKO-BIOKEMIJSKI FAKULTET
SVEUČILIŠTA U ZAGREBU

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