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CHAPTER 2
ULTRAVIOLET ABSORPTION

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2.1 INTRODUCTION

The interactions of the carboxyl group with the electromagnetic fields show some very interesting features. In the range of ultraviolet radiation, light absorption by the group may occur through the $n \rightarrow \pi^*$ or the $\pi \rightarrow \pi^*$ mechanisms. When the group is bound to a residue able to undergo conjugation, as in benzoic acid, charge transfer can occur and show up in the appropriate band.[1-7] This gives an insight into the relationship between absorption and molecular structure. In addition, the ultraviolet absorption measurement serves as a reliable and convenient method for the analysis of dilute solutions. In fact, use of light absorption as a means of detection dates back to the earliest days of liquid chromatography, when, near the turn of this century Day and Tswett followed separation of their zones by visually observing the color and intensity of the zones. Therefore, a systematic study of the ultraviolet absorption spectra is of theoretical as well as practical importance.

Although, the ultraviolet absorption spectra of substituted benzoic acids have been studied by several workers,[8-52] a fuller study of the effect of pH and the determination of isosbestic points (invariant wavelengths) appears to be lacking. Such a study should be of interest for the estimation of dilute solutions of benzoic acids of variable pH. For example, such a situation arises when a dilute solution of an organic acid or its salt with or without a small amount of an inorganic acid or its salt is contacted with a strongly acidic cation exchange resin.

The present work includes a study of ultraviolet absorption spectra of substituted benzoic acids in water or aqueous dioxan over a pH range of about 1-8 and in methanol. The isosbestic points have been measured and the results are discussed.

2.2 EXPERIMENTAL

The solvents used were water (distilled), dioxan and methanol (G.R.).

Dioxan was purified[53] as follows :

A mixture of dioxan (1 liter), concentrated hydrochloric acid (14 ml) and water (100 ml) was refluxed for 10-12 hours during which time a slow stream of nitrogen was bubbled through the solution. The solution was cooled and potassium hydroxide pellets were added slowly with shaking until they no longer dissolved and a second layer had separated. The dioxan was decanted and transferred over potassium hydroxide pellets. If any water separated, it was removed and the dioxan was allowed to stand over fresh potassium hydroxide pellets for a longer time. It was next refluxed with sodium for 10-12 hours till reaction ceased, leaving a part of sodium unreacted. The solvent was then distilled from sodium and stored out of contact with air (B.P. 101-102°C).

Aqueous dioxan was prepared by volume, for example, 10% aqueous dioxan was prepared by diluting 100 ml of dioxan to 1 liter with distilled water. The pH of each solution was adjusted by adding hydrochloric acid (A.R.) or sodium hydroxide (A.R.) and measured with a Beckman Model H-2 or Leeds and Northrup pH meter.

The solutions of benzoic acids were prepared by dissolving weighed amount of sample in the particular solvent in volumetric flasks and then suitably diluting.

The ultraviolet absorption measurements were carried out with the Beckman Model DU or DU-2 spectrophotometer, using 10 mm matched quartz cells, in the range 226-350 nm. The values of molar absorptivity (molar extinction coefficient) ϵ, at each wavelength, were calculated by dividing the measured absorbance (optical density) by the concentration of the sample in gram moles per liter of the solution. The results were represented in the graphical form (Section 2.3) by plotting molar absorptivity, ϵ, at different pH against wavelength, λ nm. The curves at different pH intersect at some fixed wavelengths called isosbestic points (invariant wavelengths). The wavelength of maximum absorption, λ_{max} and isosbestic points, λ_{inv}, were read directly from the graph.

2.3 RESULTS

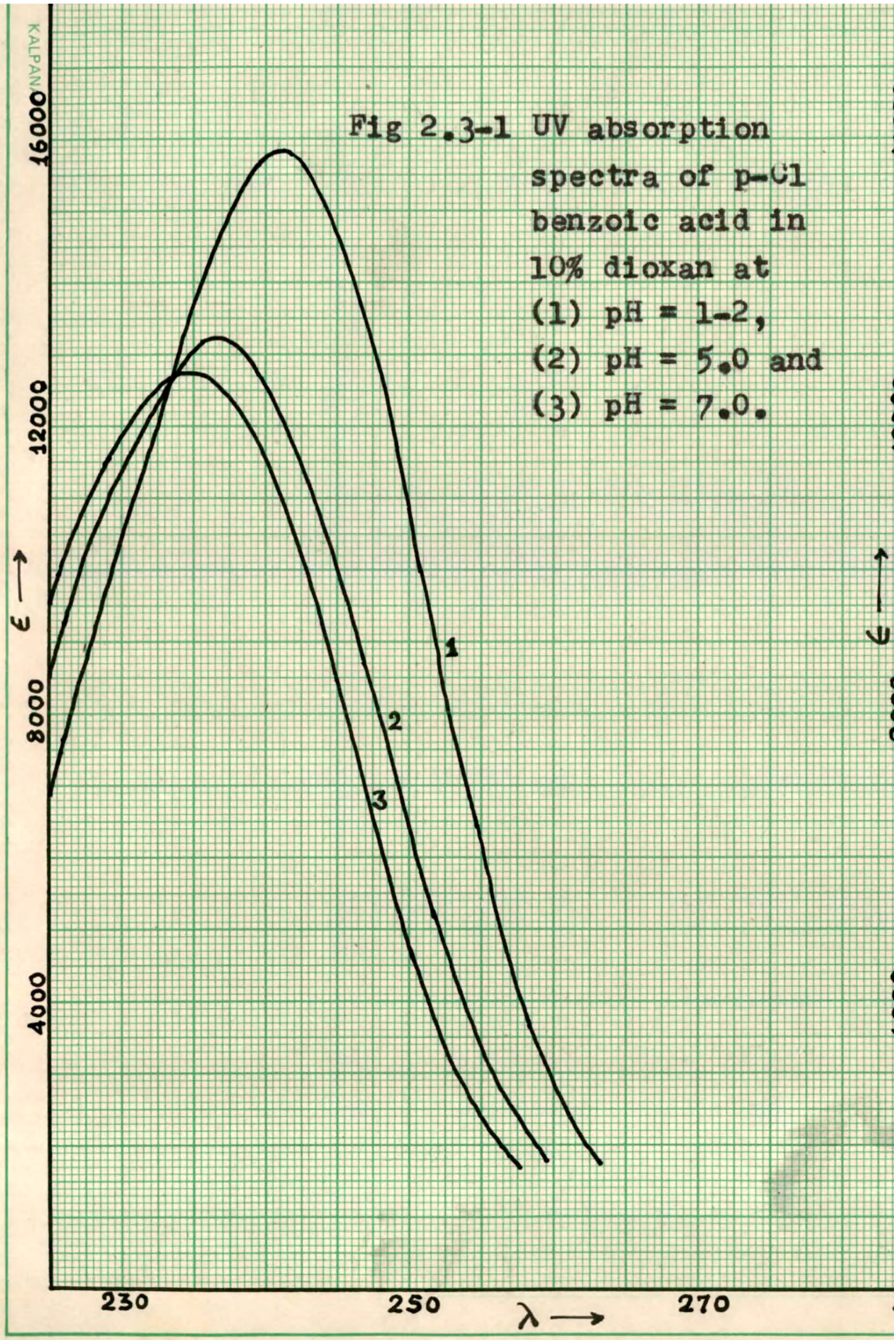

Fig 2.3-1 UV absorption spectra of p-Cl benzoic acid in 10% dioxan at
(1) pH = 1-2,
(2) pH = 5.0 and
(3) pH = 7.0.

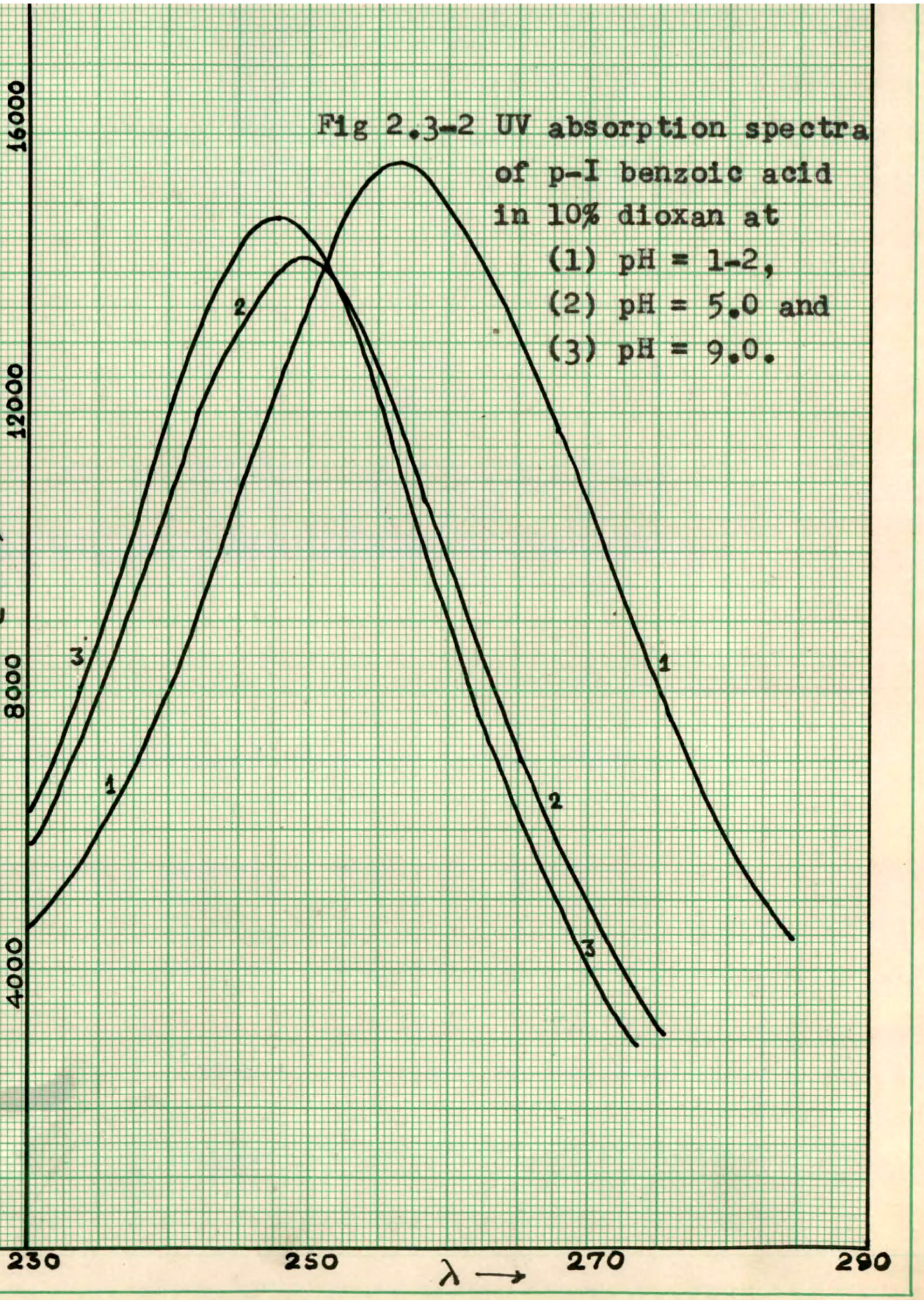

Fig 2.3-2 UV absorption spectra of p-I benzoic acid in 10% dioxan at
(1) pH = 1-2,
(2) pH = 5.0 and
(3) pH = 9.0.

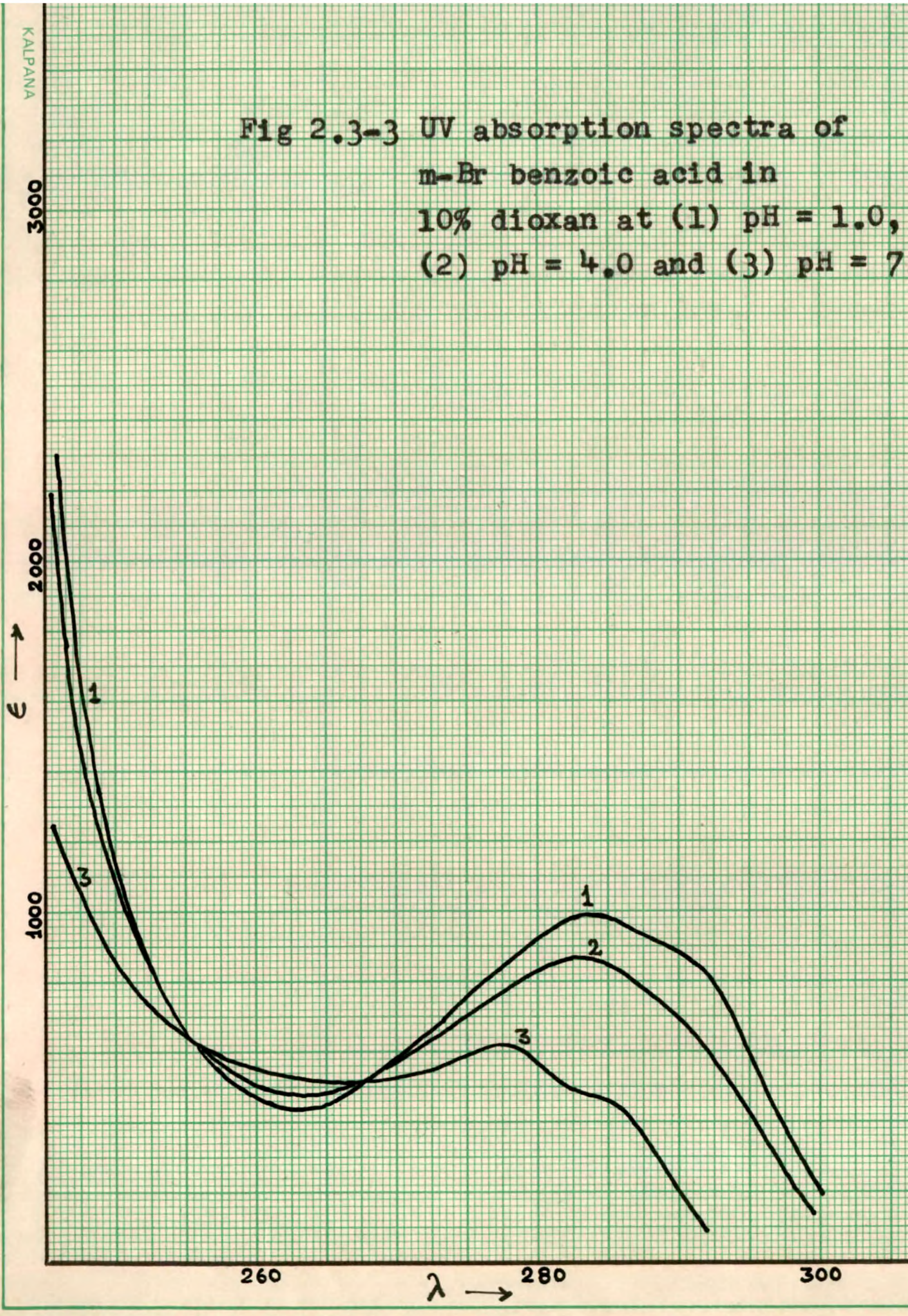

Fig 2.3-3 UV absorption spectra of m-Br benzoic acid in 10% dioxan at (1) pH = 1.0, (2) pH = 4.0 and (3) pH = 7.0.

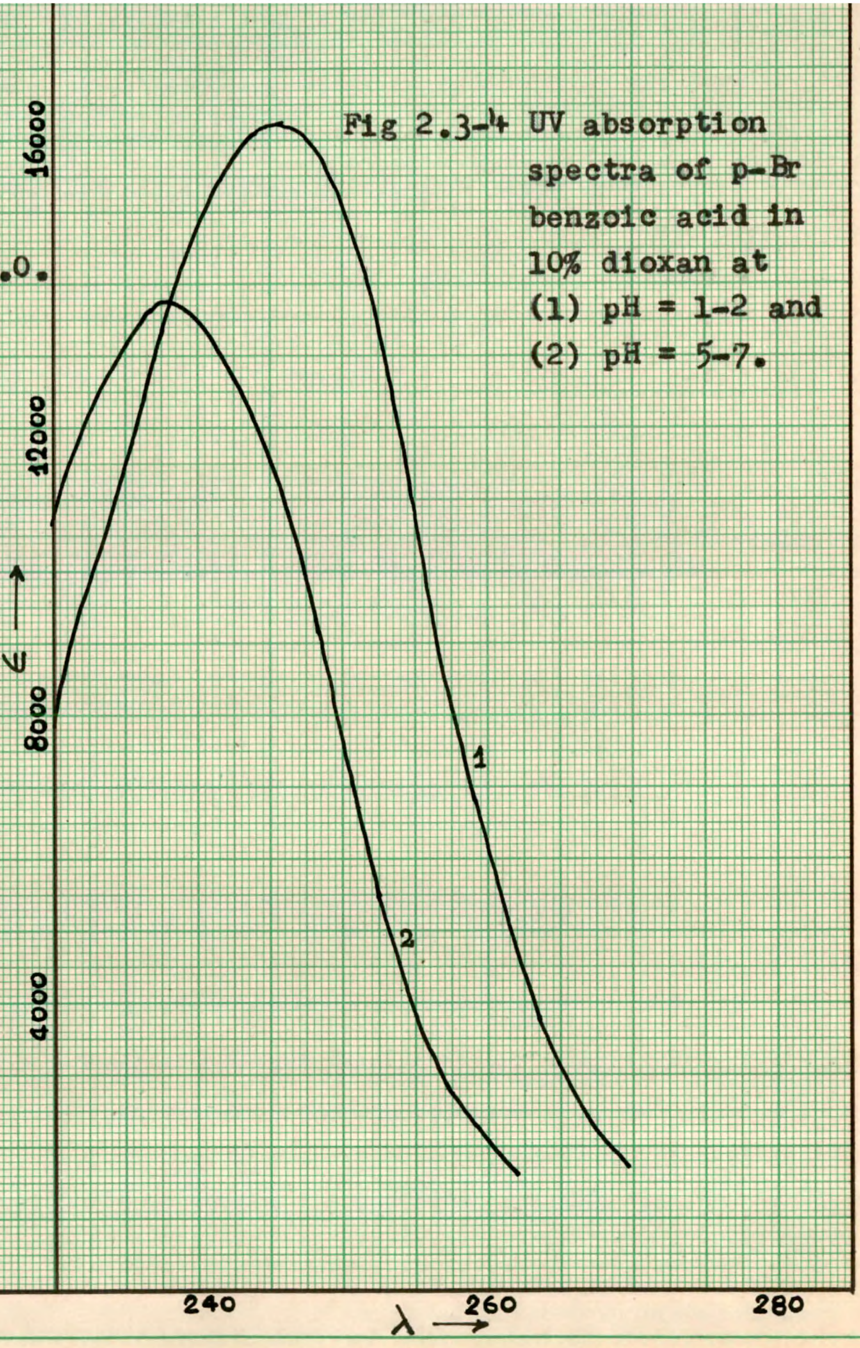

Fig 2.3-4 UV absorption spectra of p-Br benzoic acid in 10% dioxan at (1) pH = 1-2 and (2) pH = 5-7.

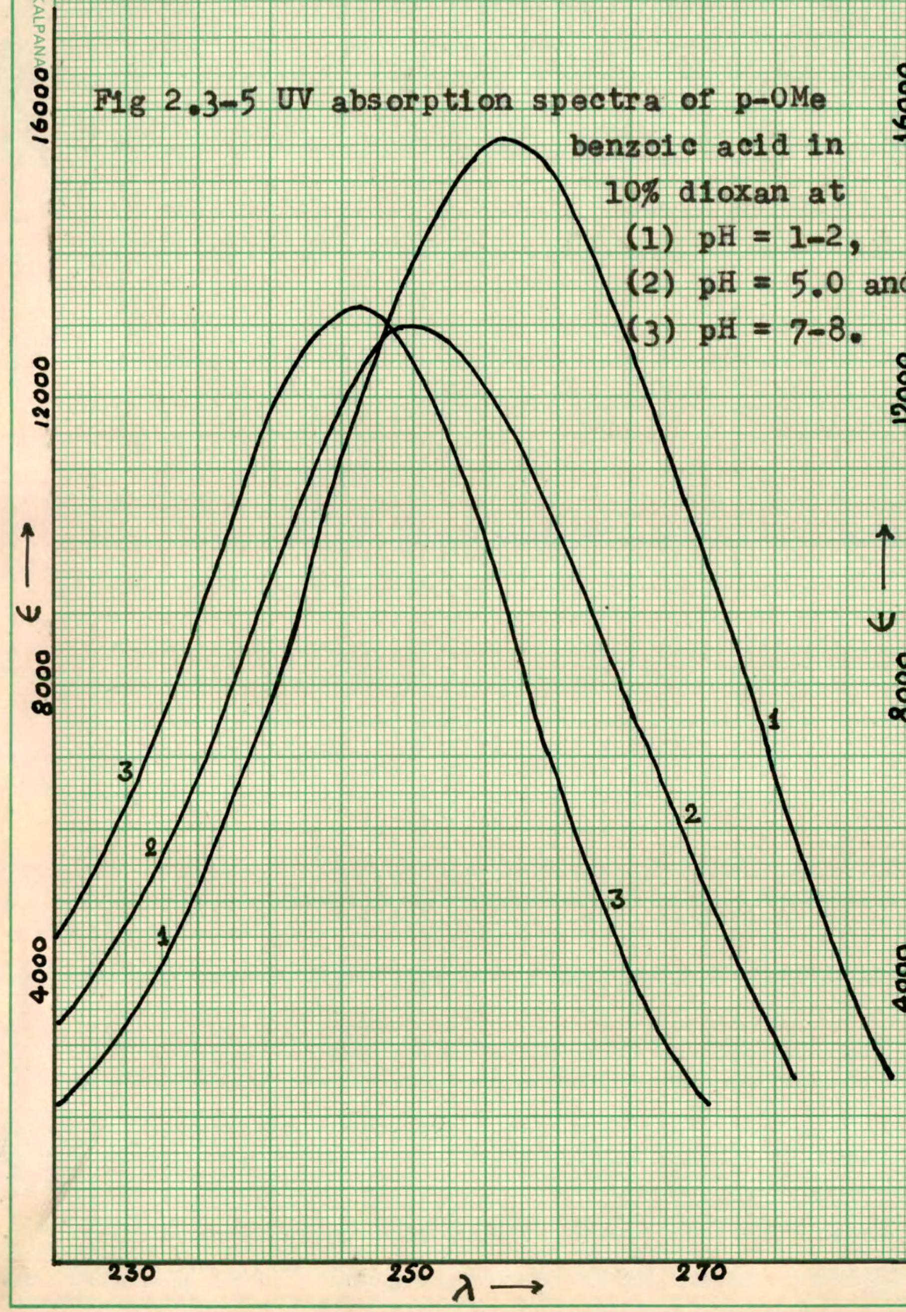

Fig 2.3-5 UV absorption spectra of p-OMe benzoic acid in 10% dioxan at
(1) pH = 1-2,
(2) pH = 5.0 and
(3) pH = 7-8.

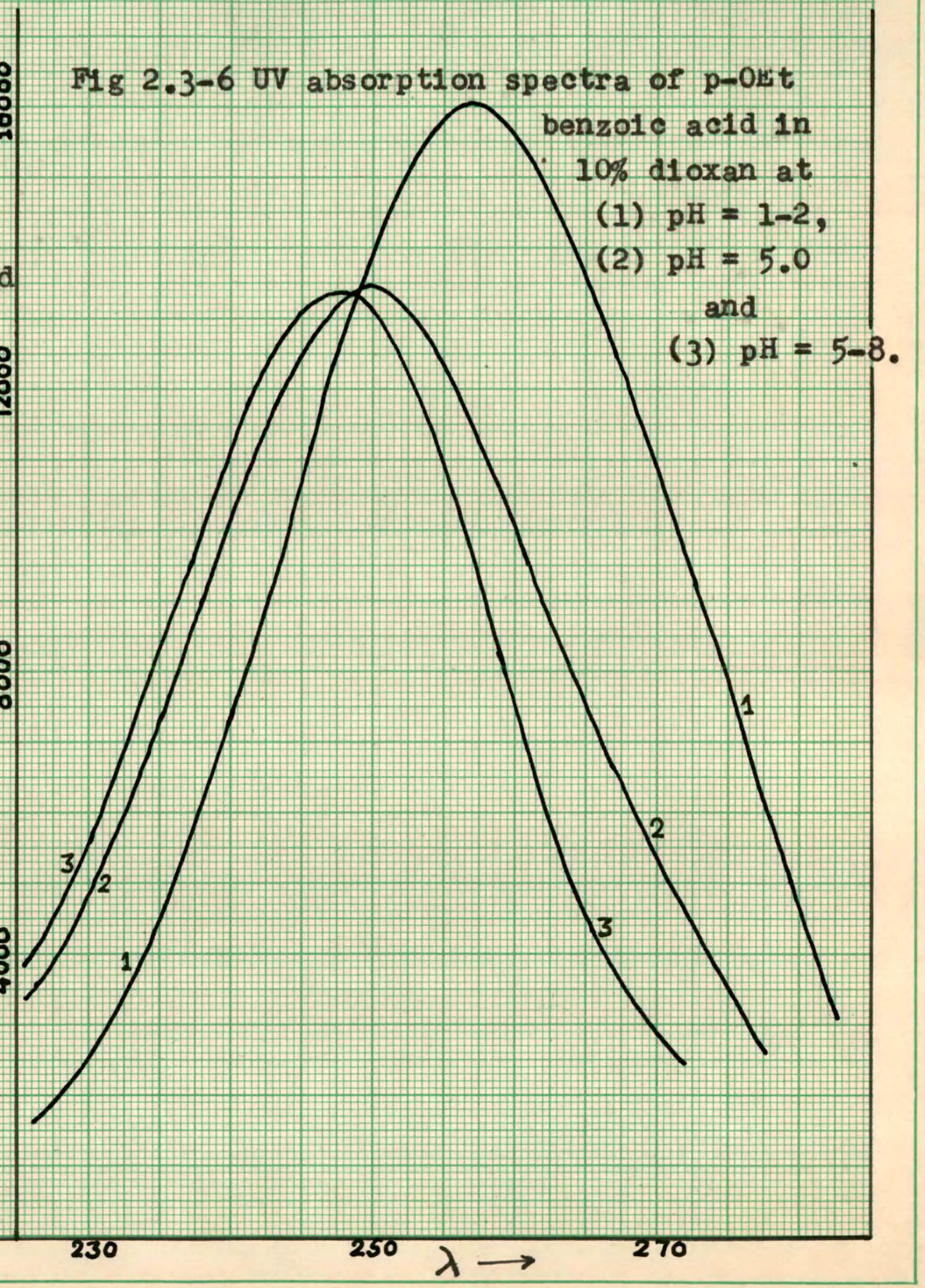

Fig 2.3-6 UV absorption spectra of p-OEt benzoic acid in 10% dioxan at
(1) pH = 1-2,
(2) pH = 5.0
and
(3) pH = 5-8.

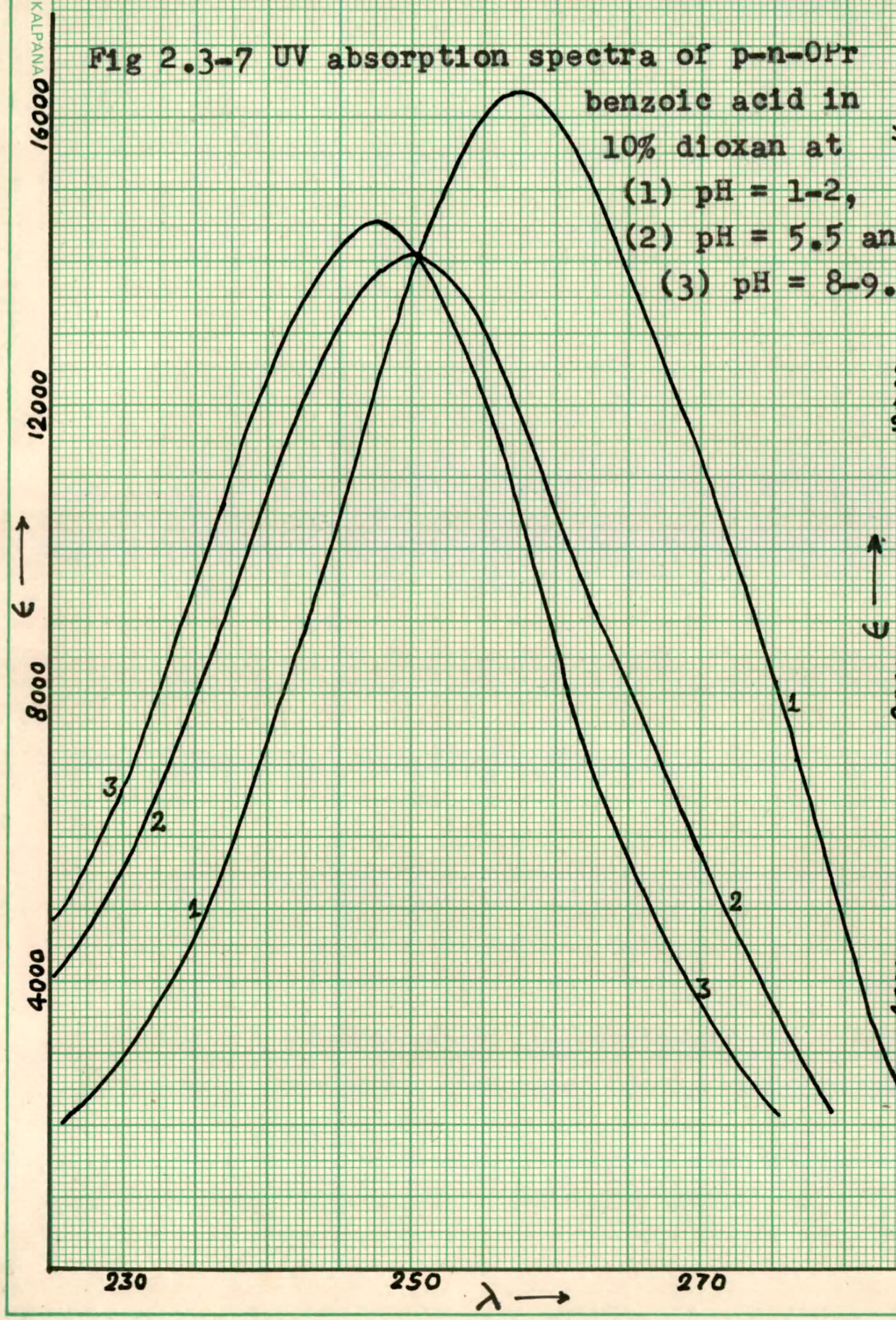

Fig 2.3-7 UV absorption spectra of p-n-OPr benzoic acid in 10% dioxan at (1) pH = 1-2, (2) pH = 5.5 and (3) pH = 8-9.

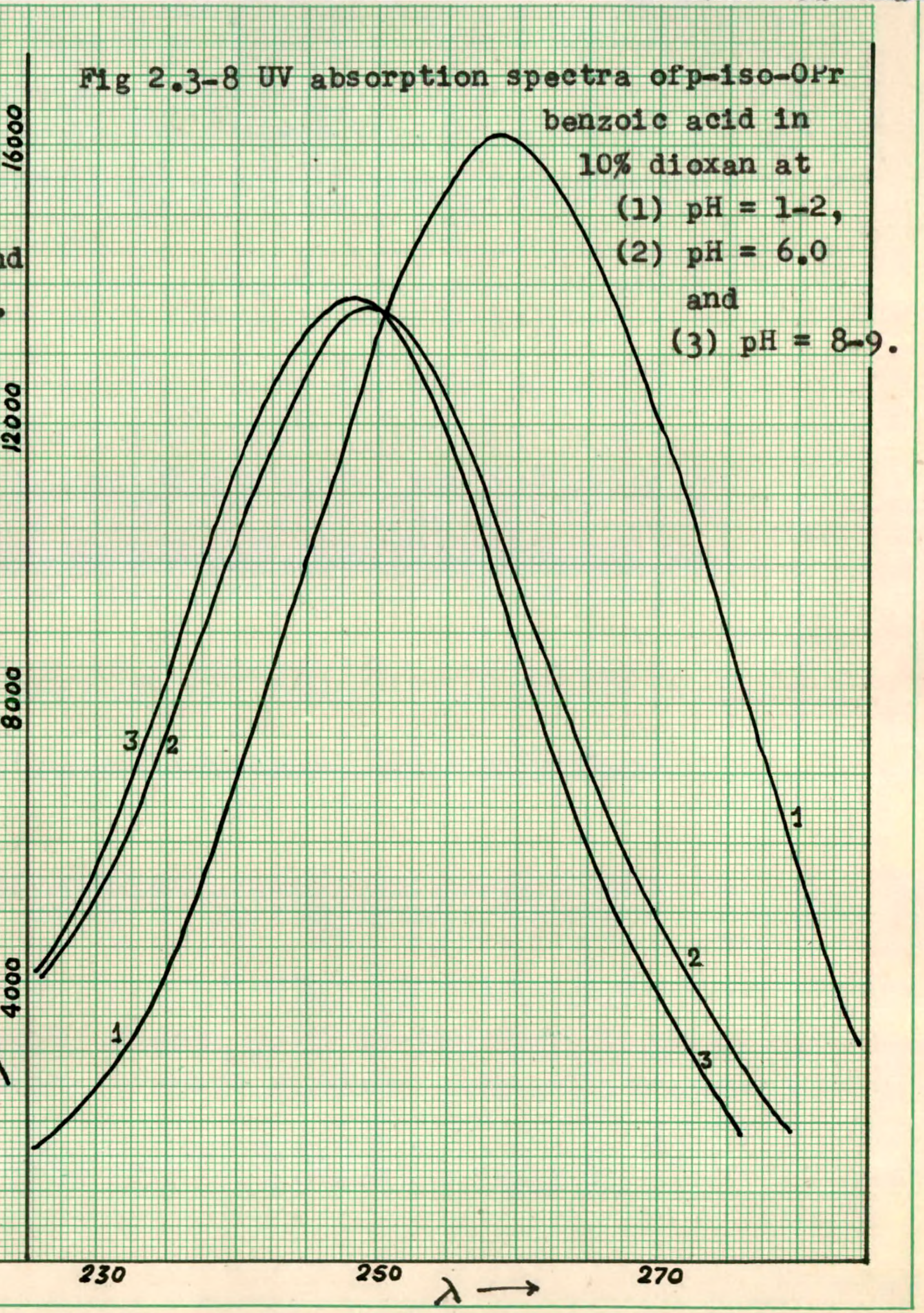

Fig 2.3-8 UV absorption spectra of p-iso-OPr benzoic acid in 10% dioxan at (1) pH = 1-2, (2) pH = 6.0 and (3) pH = 8-9.

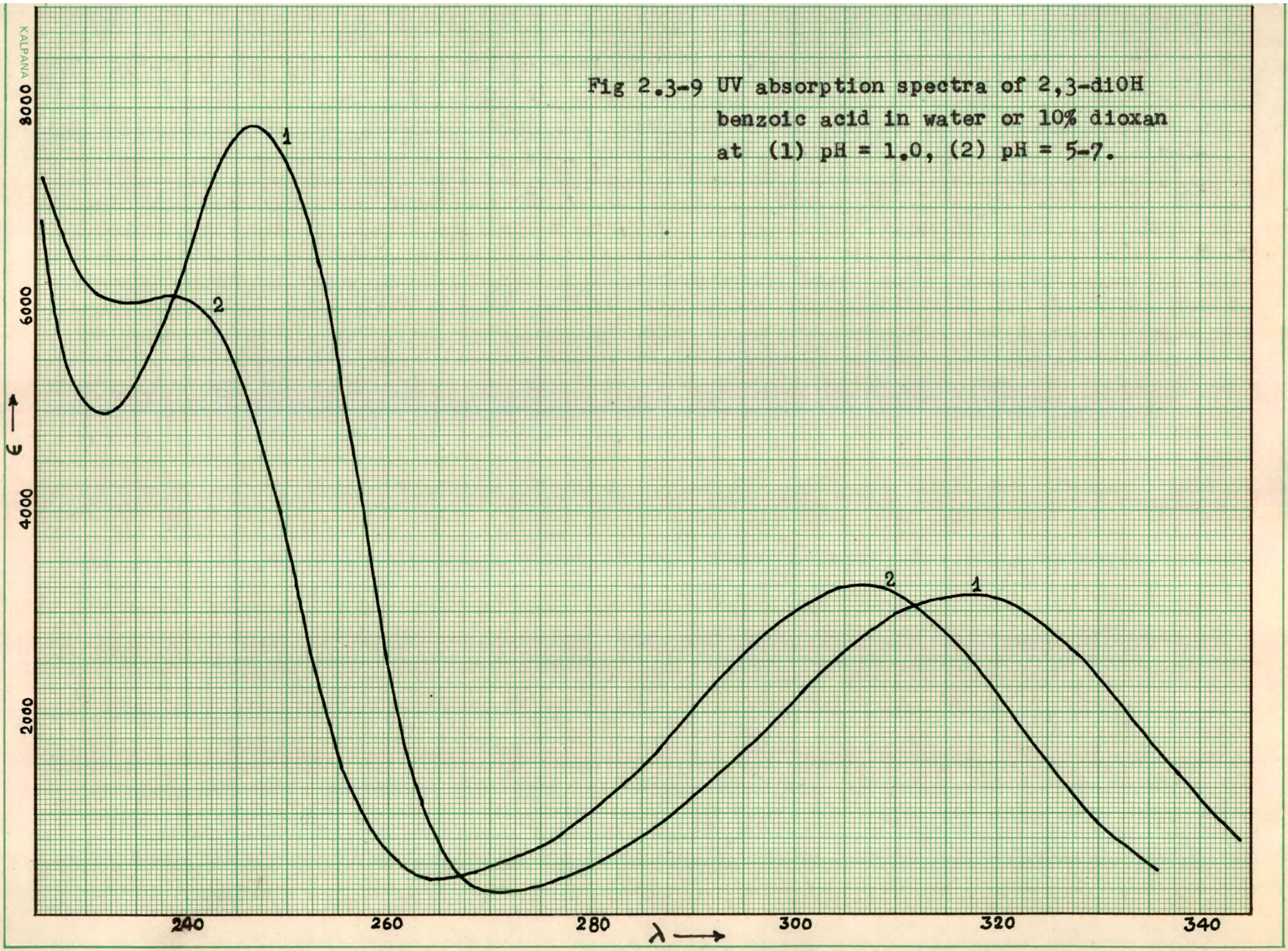

Fig 2.3-9 UV absorption spectra of 2,3-diOH benzoic acid in water or 10% dioxan at (1) pH = 1.0, (2) pH = 5-7.

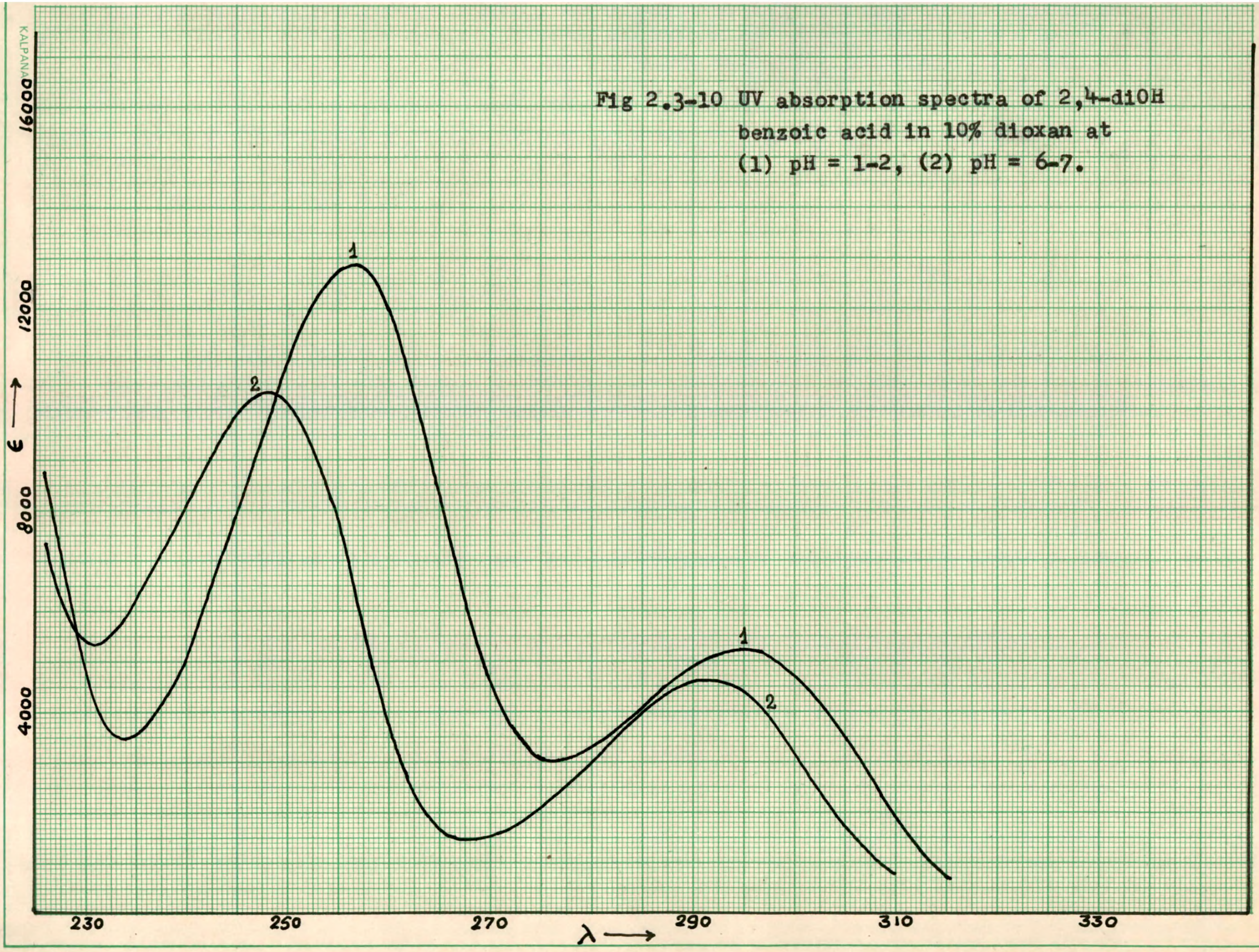
Fig 2.3-10 UV absorption spectra of 2,4-diOH benzoic acid in 10% dioxan at (1) pH = 1-2, (2) pH = 6-7.

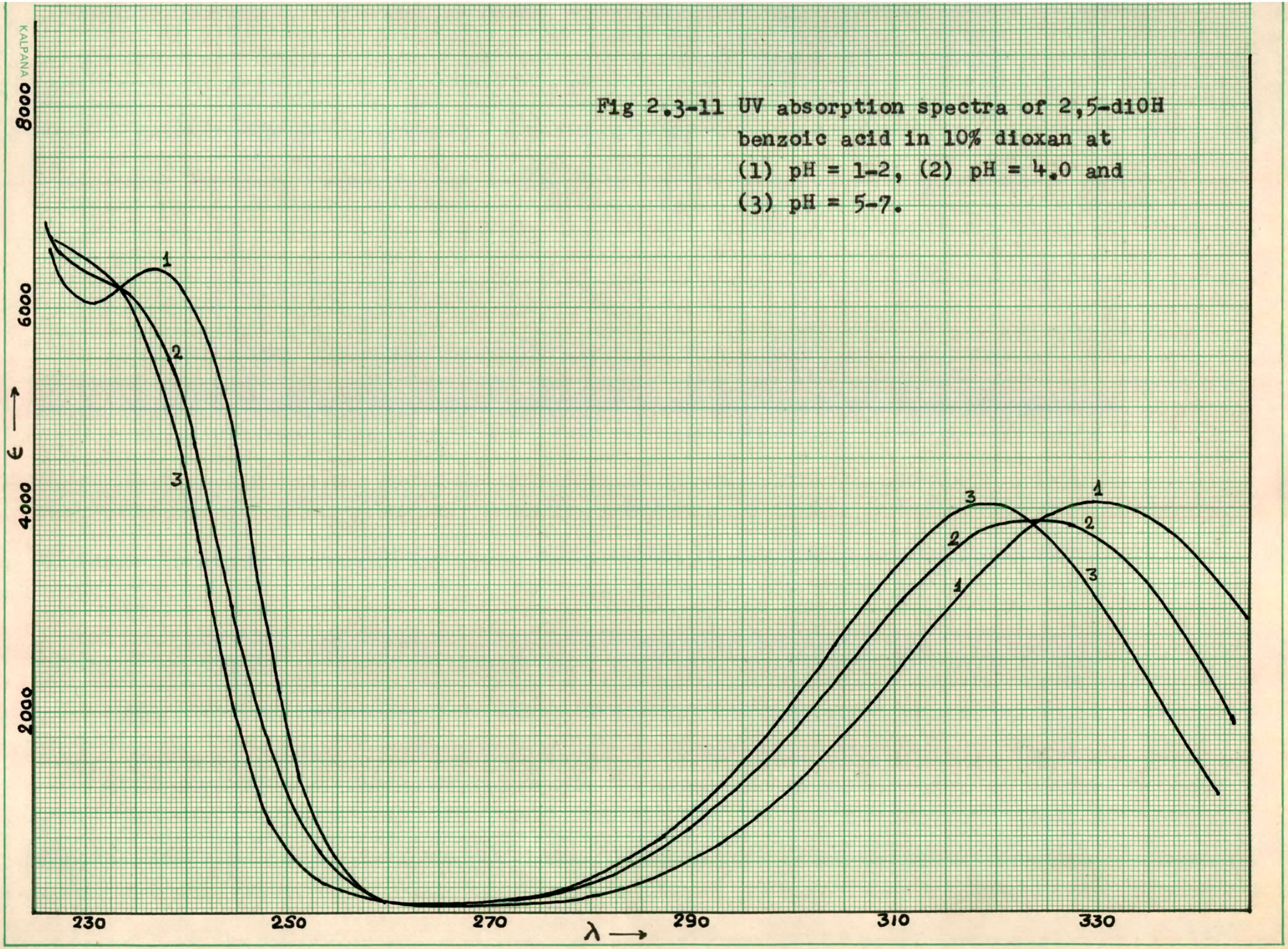

Fig 2.3-11 UV absorption spectra of 2,5-diOH benzoic acid in 10% dioxan at (1) pH = 1-2, (2) pH = 4.0 and (3) pH = 5-7.

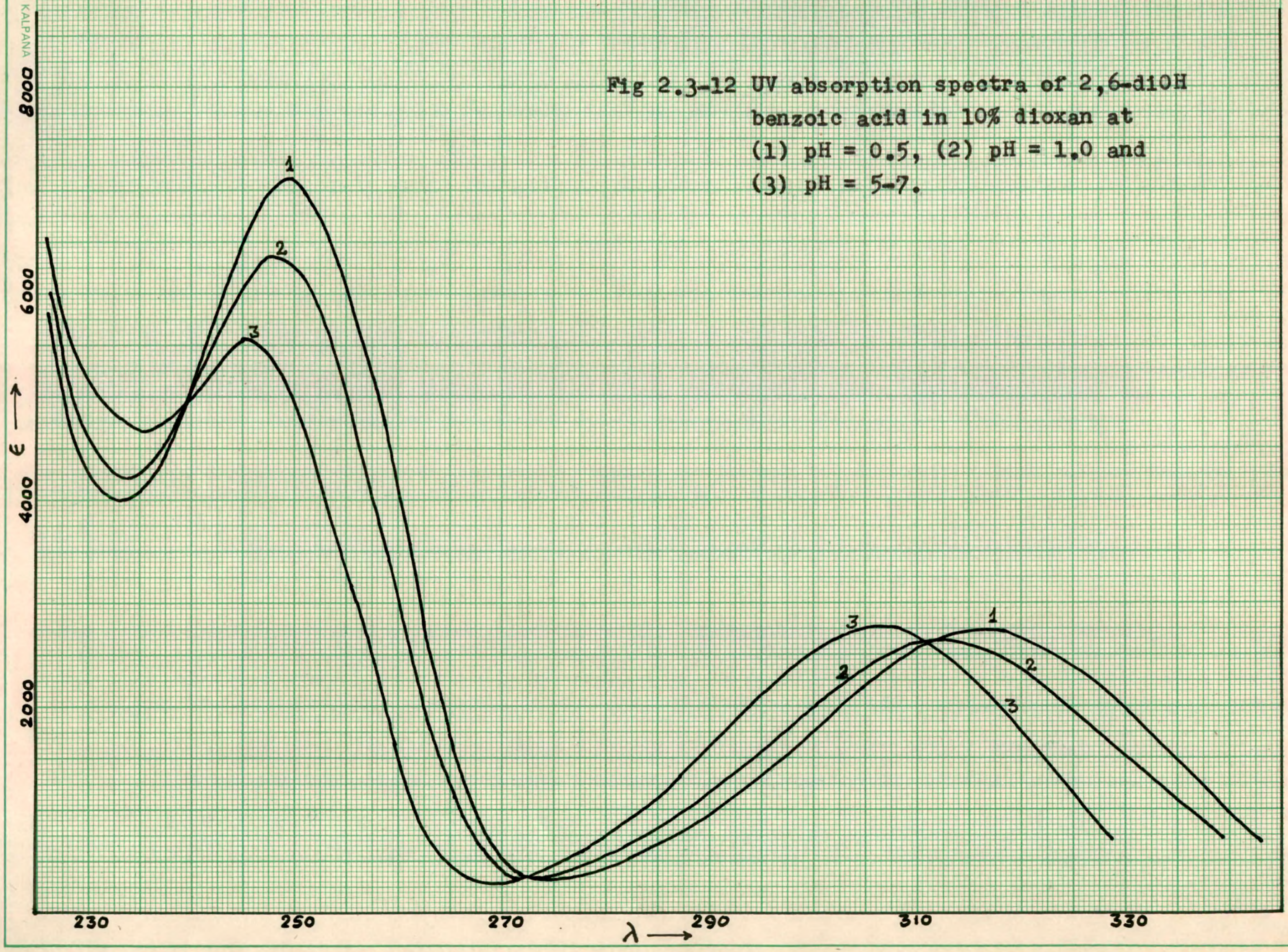

Fig 2.3-12 UV absorption spectra of 2,6-diOH benzoic acid in 10% dioxan at (1) pH = 0.5, (2) pH = 1.0 and (3) pH = 5-7.

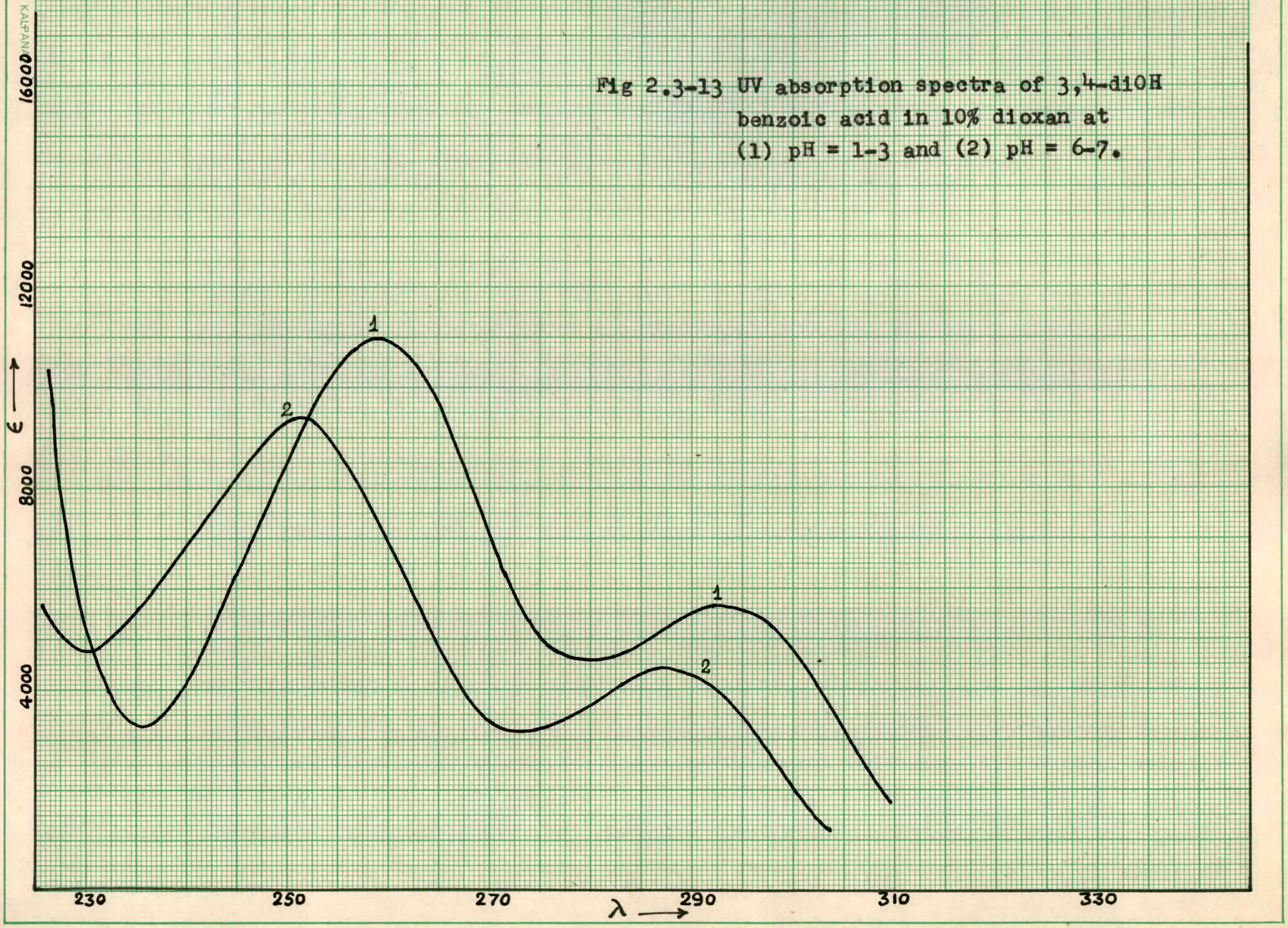

Fig 2.3-13 UV absorption spectra of 3,4-diOH benzoic acid in 10% dioxan at (1) pH = 1-3 and (2) pH = 6-7.

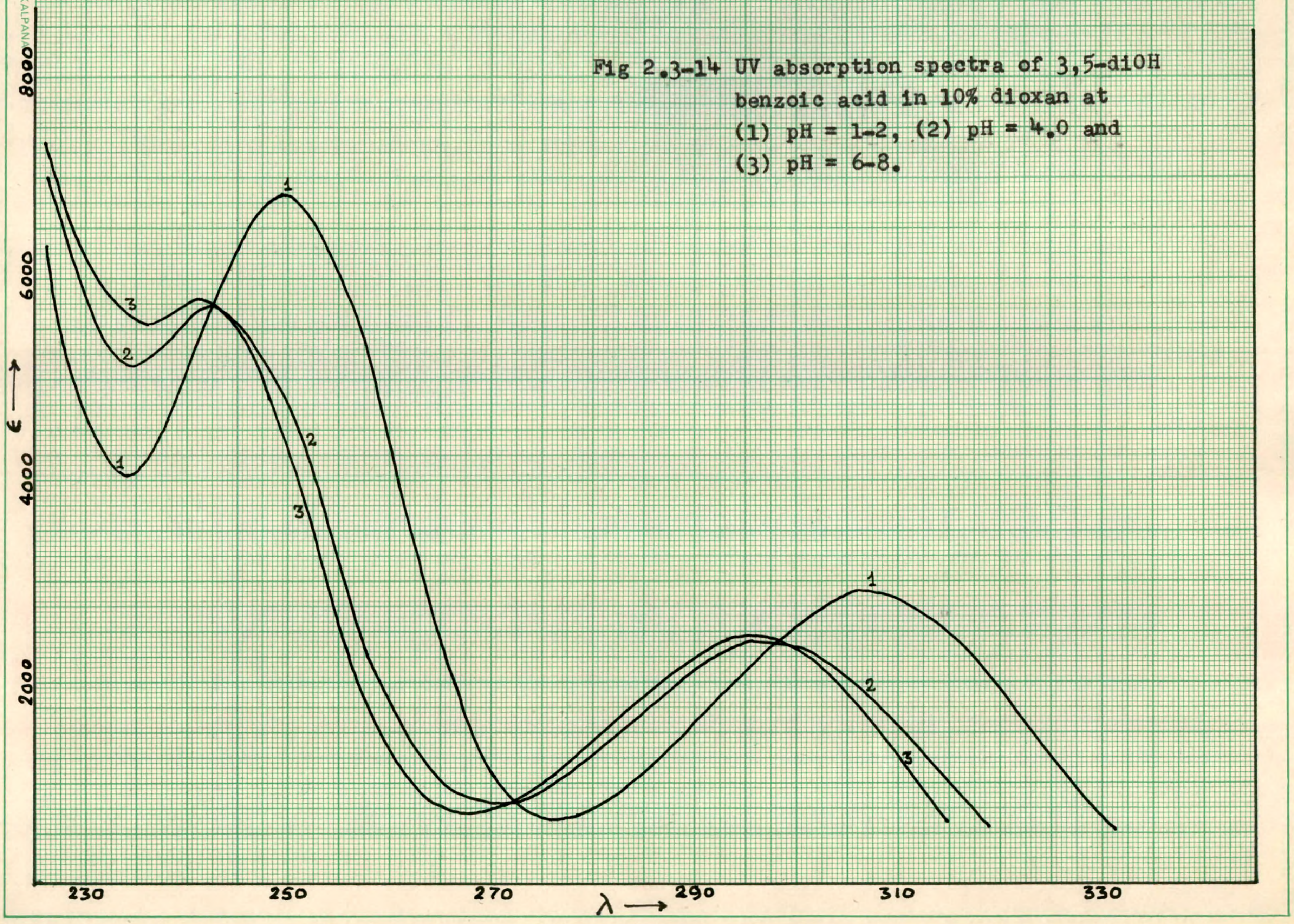

Fig 2.3-14 UV absorption spectra of 3,5-diOH benzoic acid in 10% dioxan at (1) pH = 1-2, (2) pH = 4.0 and (3) pH = 6-8.

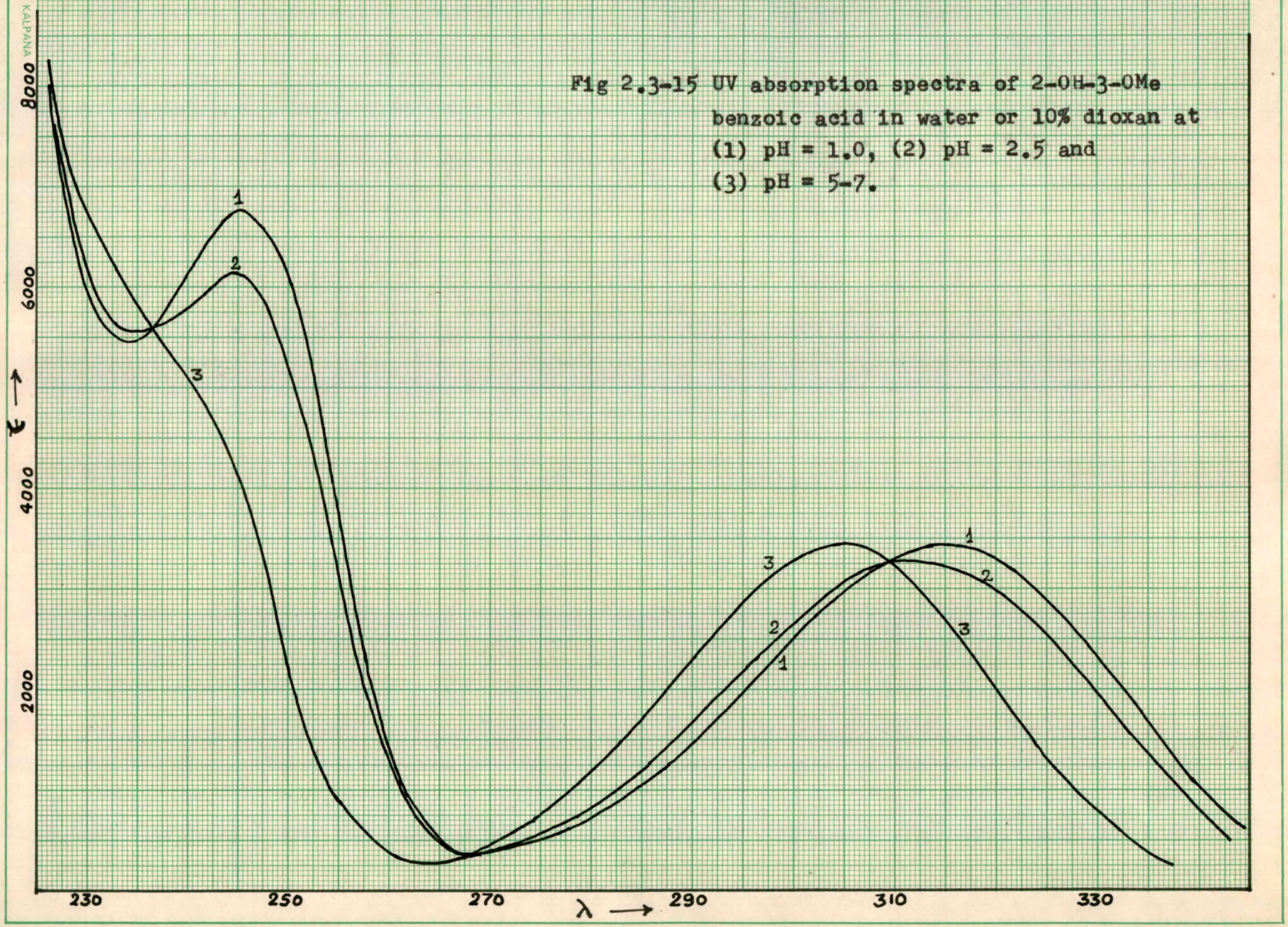

Fig 2.3-15 UV absorption spectra of 2-OH-3-OMe benzoic acid in water or 10% dioxan at (1) pH = 1.0, (2) pH = 2.5 and (3) pH = 5-7.

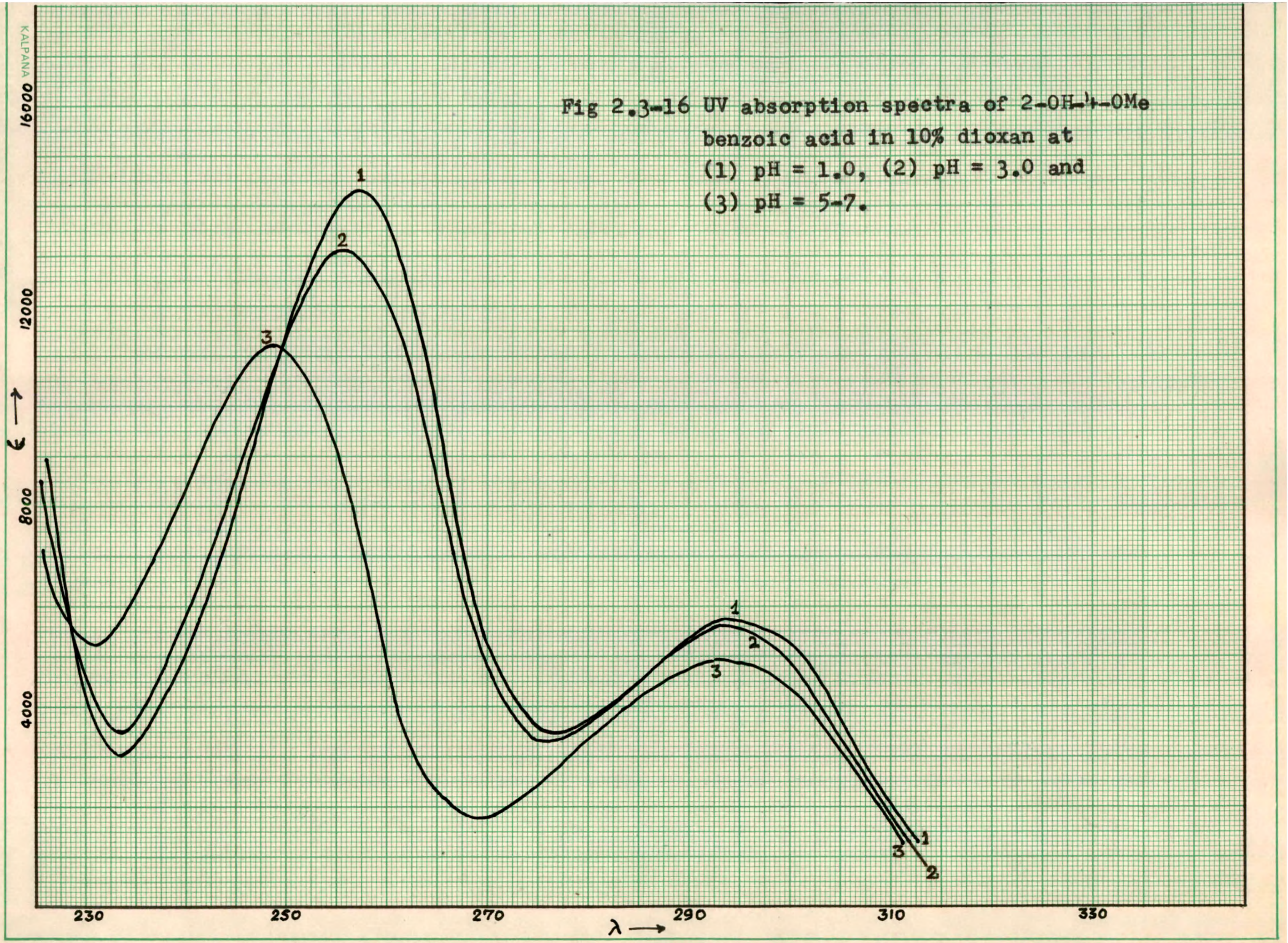

Fig 2.3-16 UV absorption spectra of 2-OH-4-OMe benzoic acid in 10% dioxan at
(1) pH = 1.0, (2) pH = 3.0 and
(3) pH = 5-7.

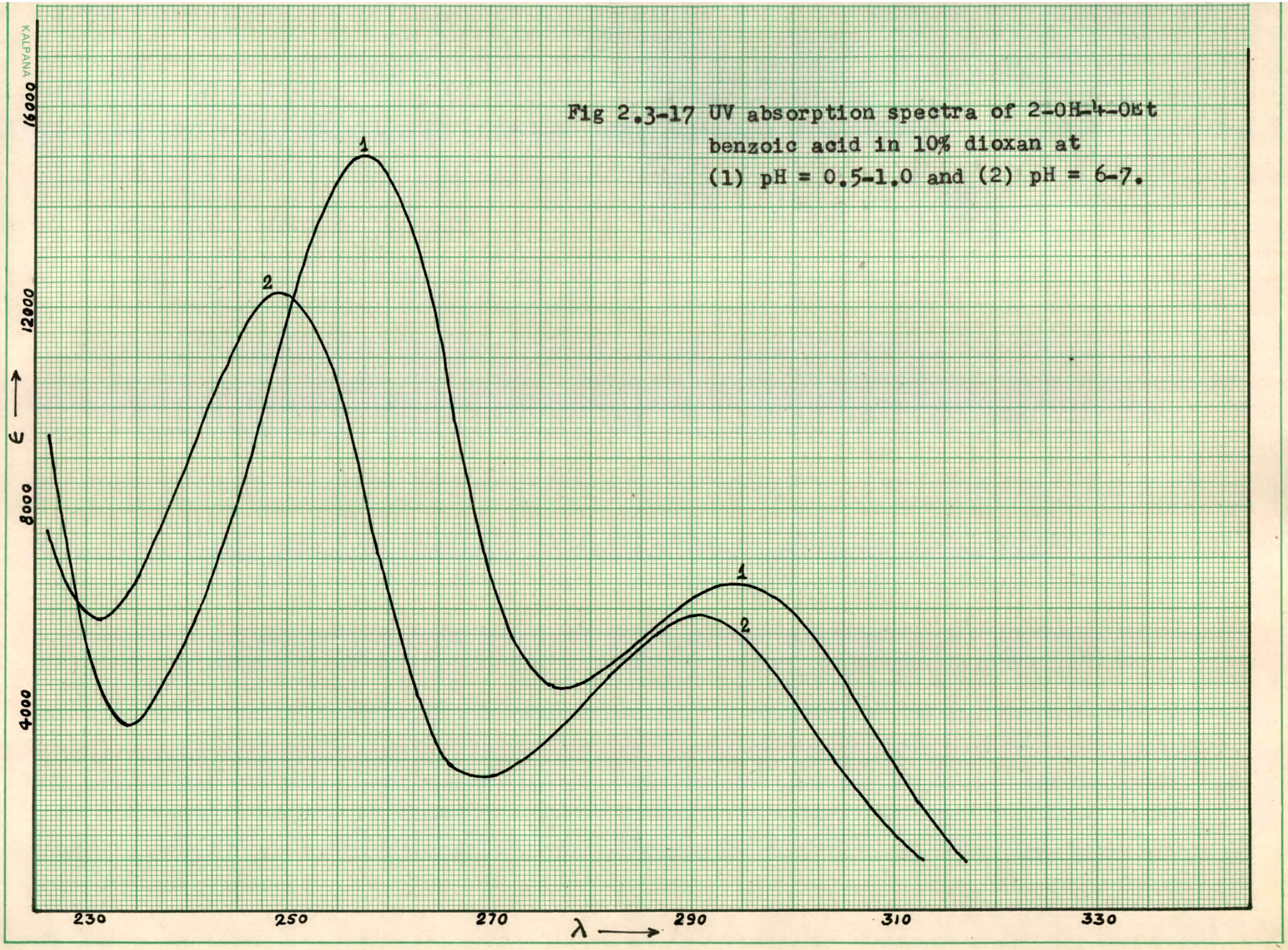

Fig 2.3-17 UV absorption spectra of 2-OH-4-OEt benzoic acid in 10% dioxan at (1) pH = 0.5-1.0 and (2) pH = 6-7.

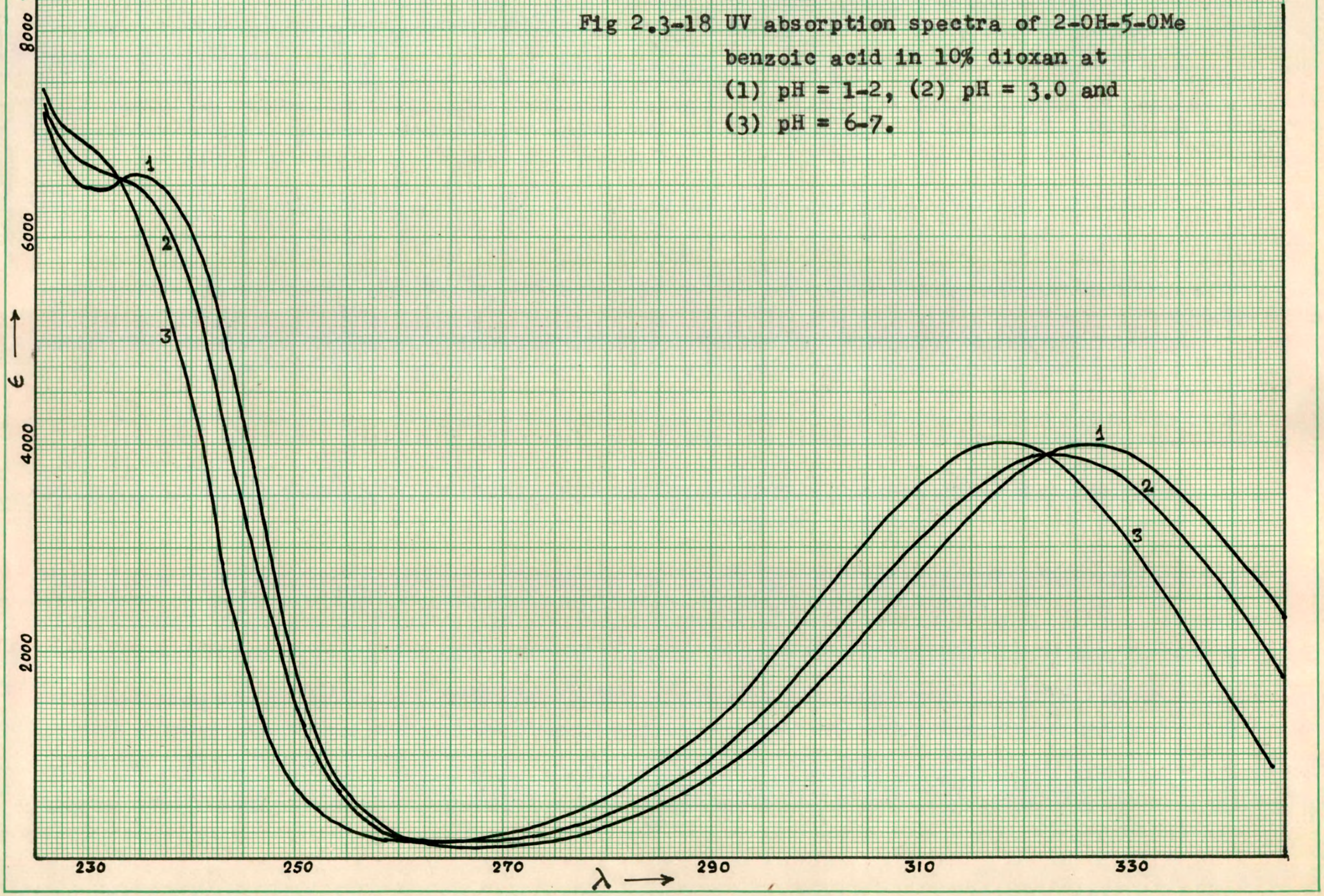

Fig 2.3-18 UV absorption spectra of 2-OH-5-OMe benzoic acid in 10% dioxan at (1) pH = 1-2, (2) pH = 3.0 and (3) pH = 6-7.

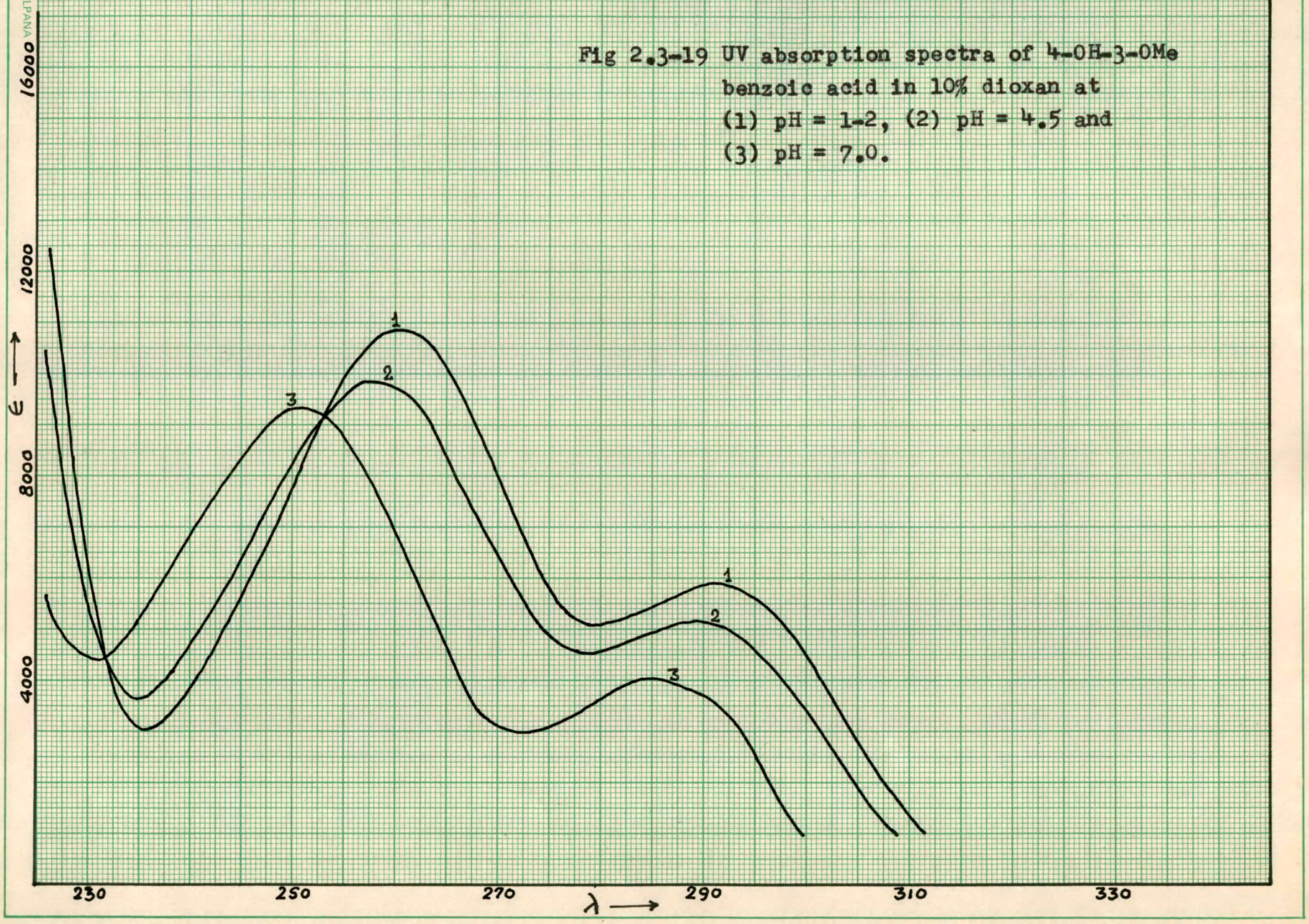

Fig 2.3-19 UV absorption spectra of 4-OH-3-OMe benzoic acid in 10% dioxan at
(1) pH = 1-2, (2) pH = 4.5 and
(3) pH = 7.0.

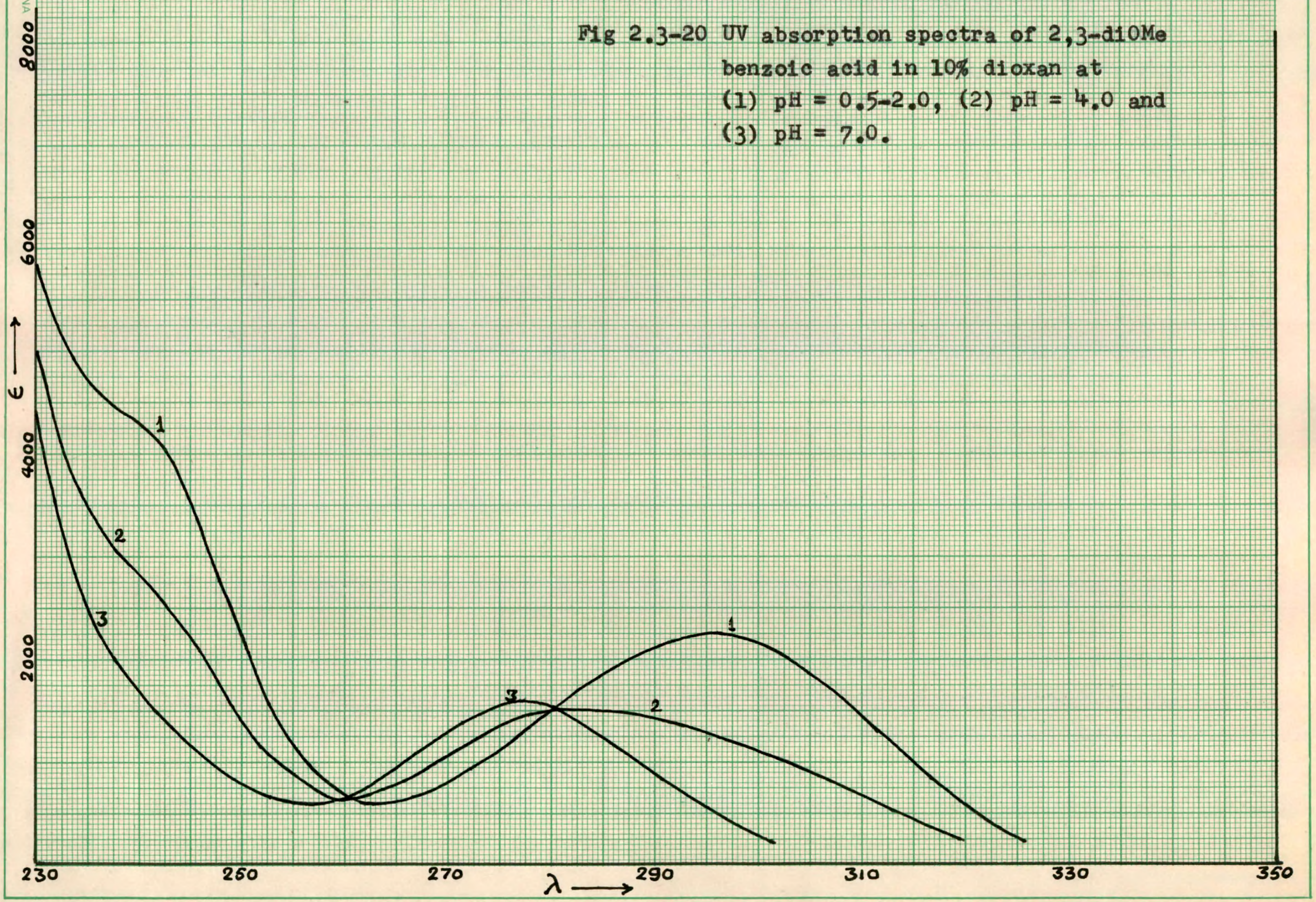

Fig 2.3-20 UV absorption spectra of 2,3-diOMe benzoic acid in 10% dioxan at (1) pH = 0.5-2.0, (2) pH = 4.0 and (3) pH = 7.0.

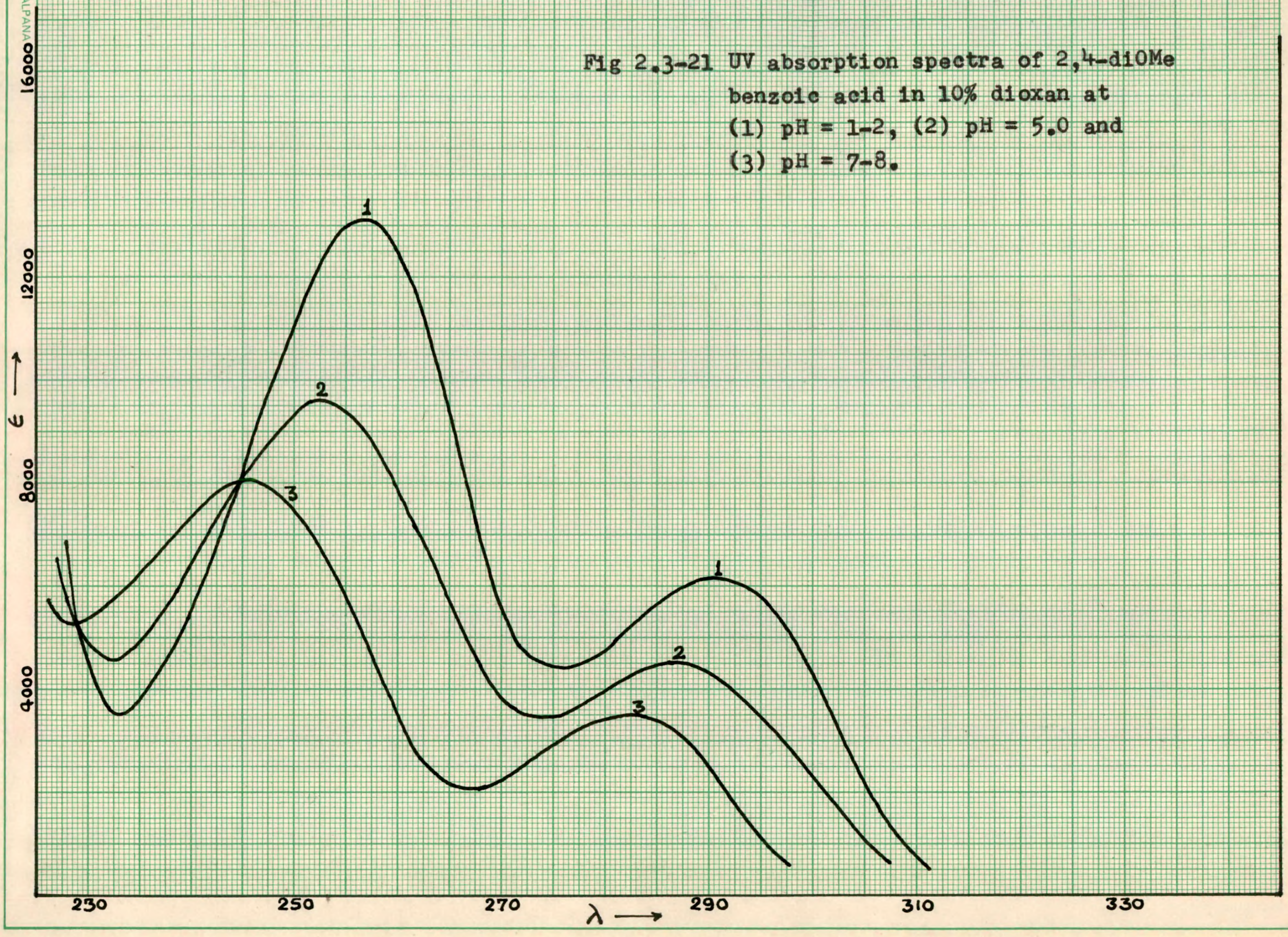

Fig 2.3-21 UV absorption spectra of 2,4-diOMe benzoic acid in 10% dioxan at (1) pH = 1-2, (2) pH = 5.0 and (3) pH = 7-8.

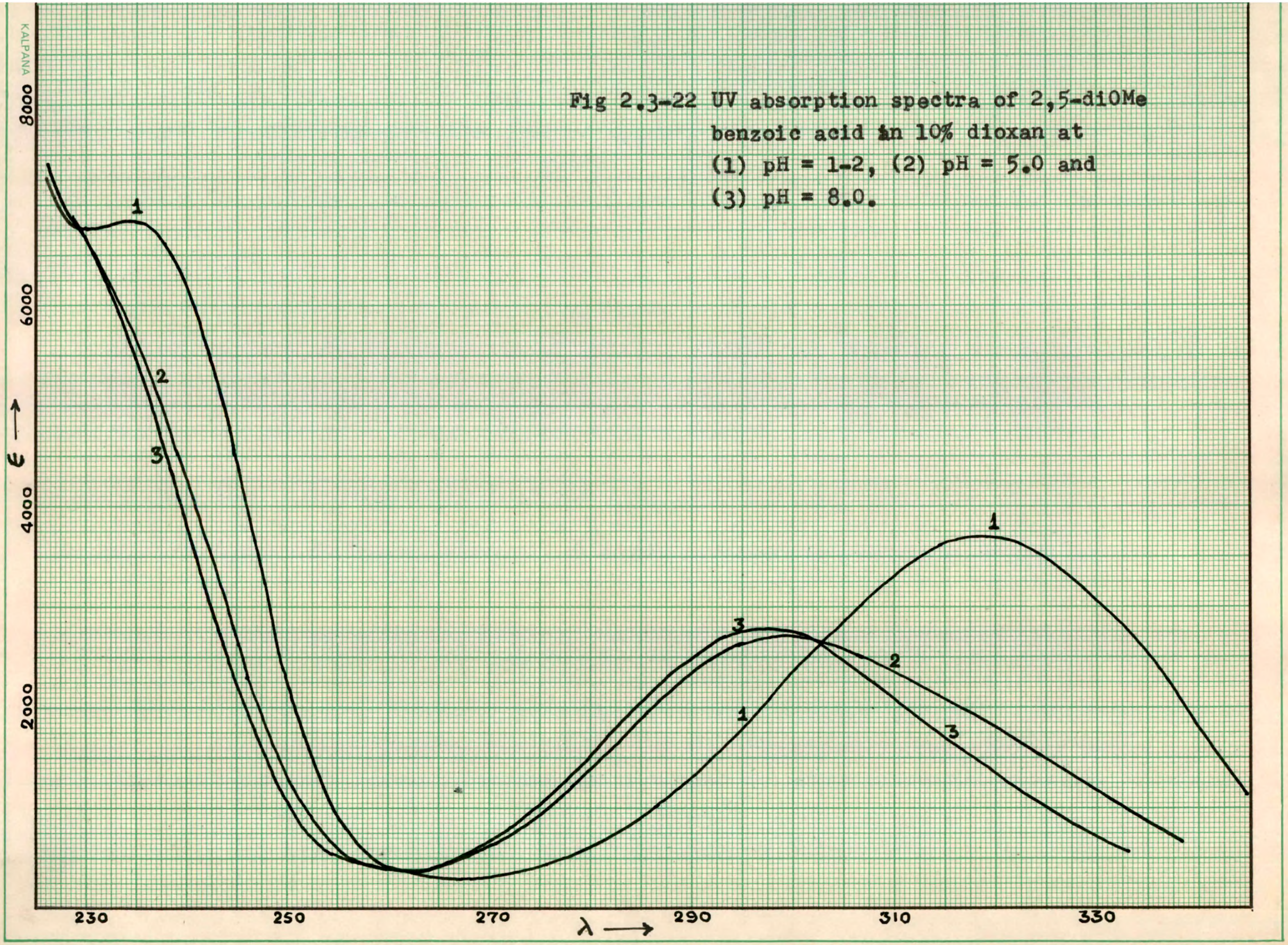

Fig 2.3-22 UV absorption spectra of 2,5-diOMe benzoic acid in 10% dioxan at (1) pH = 1-2, (2) pH = 5.0 and (3) pH = 8.0.

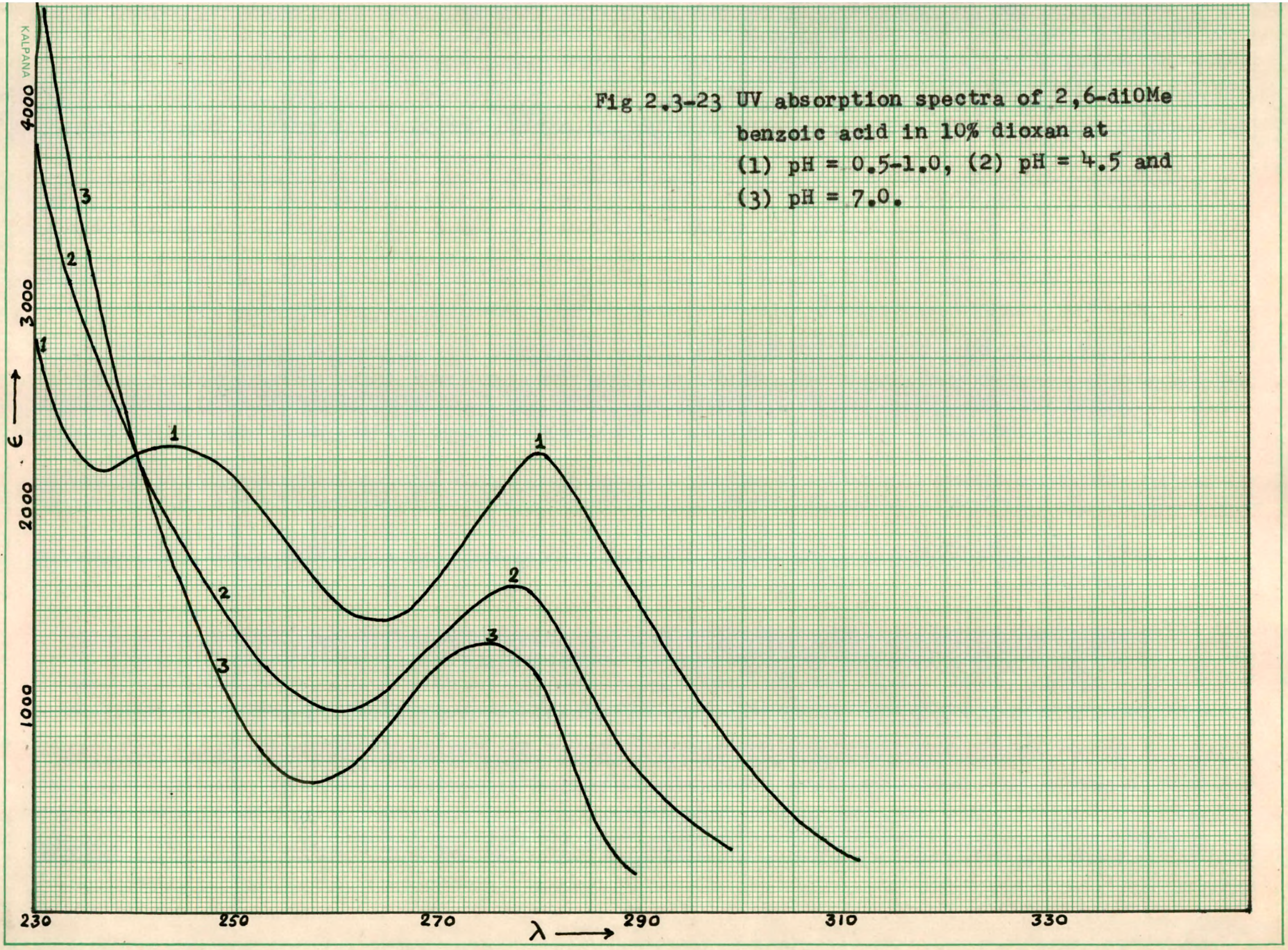

Fig 2.3-23 UV absorption spectra of 2,6-diOMe benzoic acid in 10% dioxan at (1) pH = 0.5-1.0, (2) pH = 4.5 and (3) pH = 7.0.

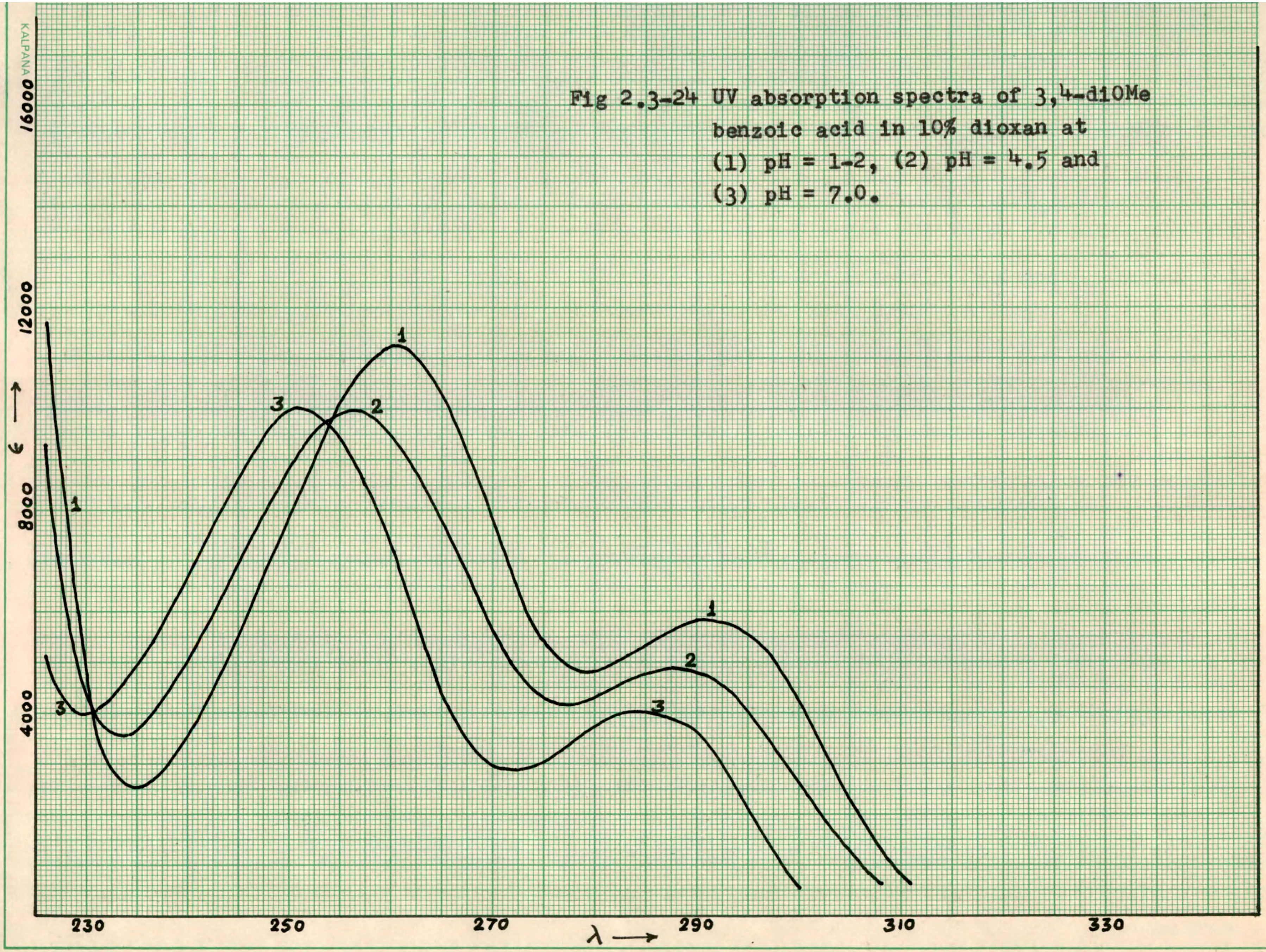

Fig 2.3-24 UV absorption spectra of 3,4-diOMe benzoic acid in 10% dioxan at (1) pH = 1-2, (2) pH = 4.5 and (3) pH = 7.0.

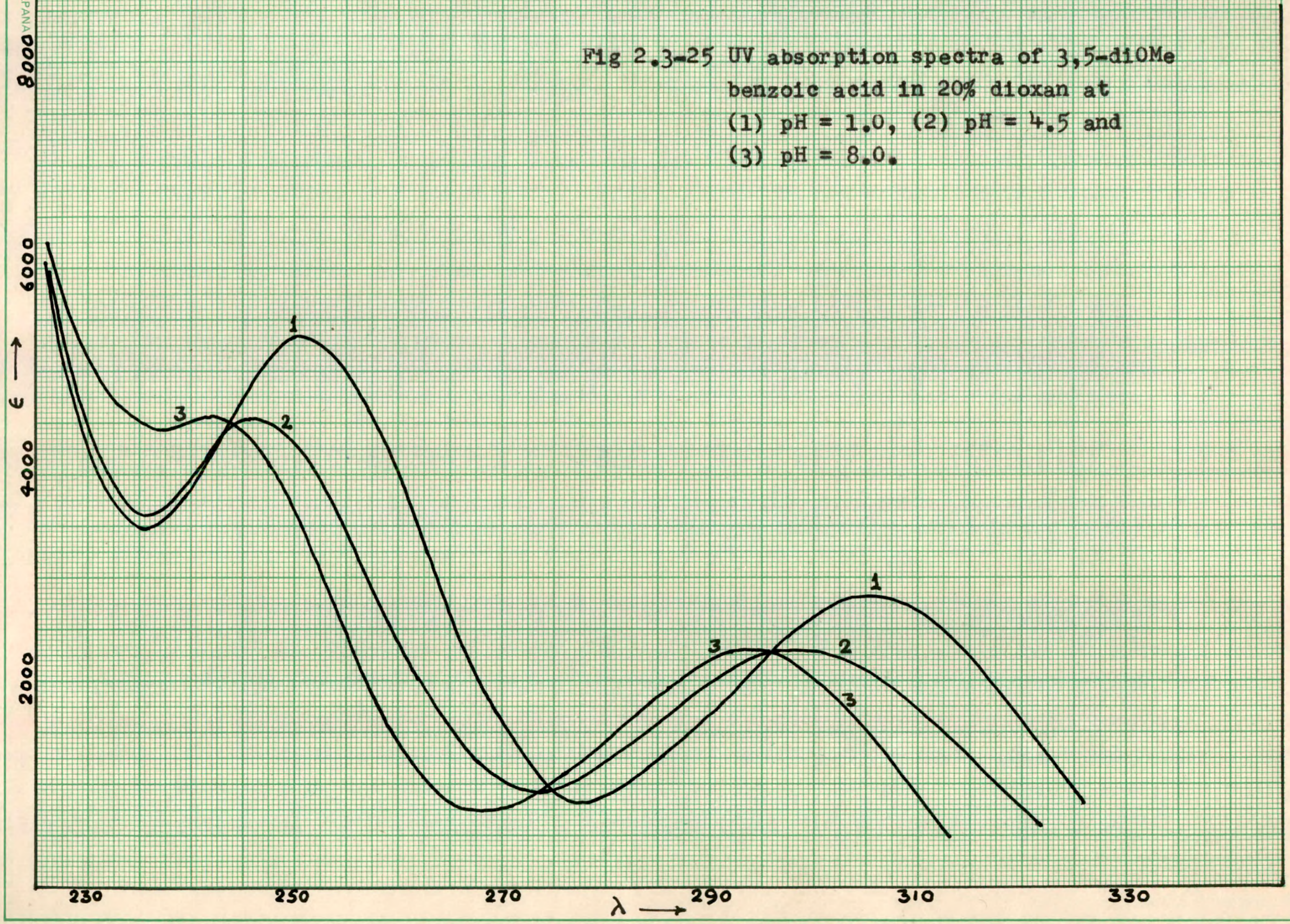

Fig 2.3-25 UV absorption spectra of 3,5-diOMe
benzoic acid in 20% dioxan at
(1) pH = 1.0, (2) pH = 4.5 and
(3) pH = 8.0.

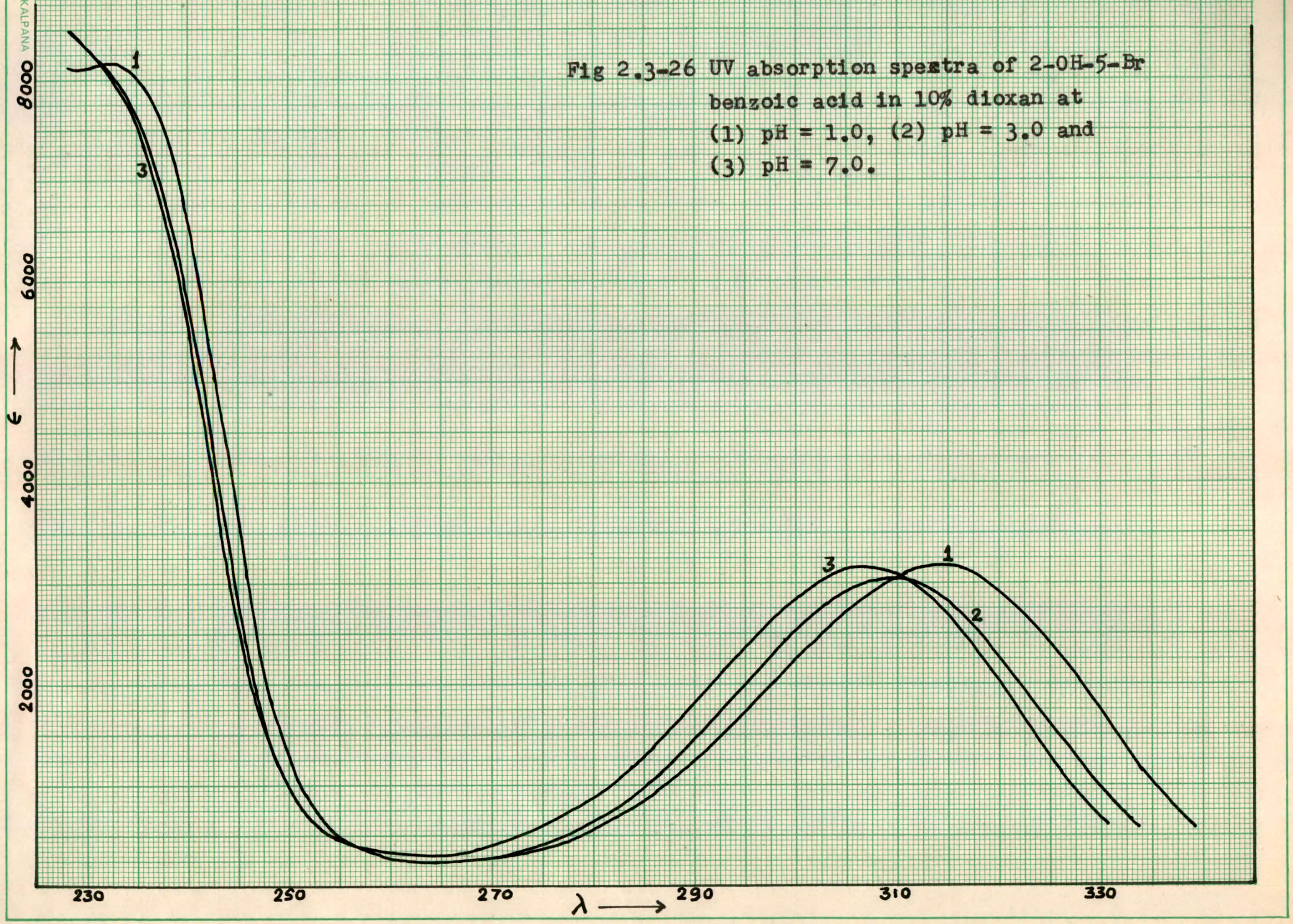

Fig 2.3-26 UV absorption spectra of 2-OH-5-Br benzoic acid in 10% dioxan at (1) pH = 1.0, (2) pH = 3.0 and (3) pH = 7.0.

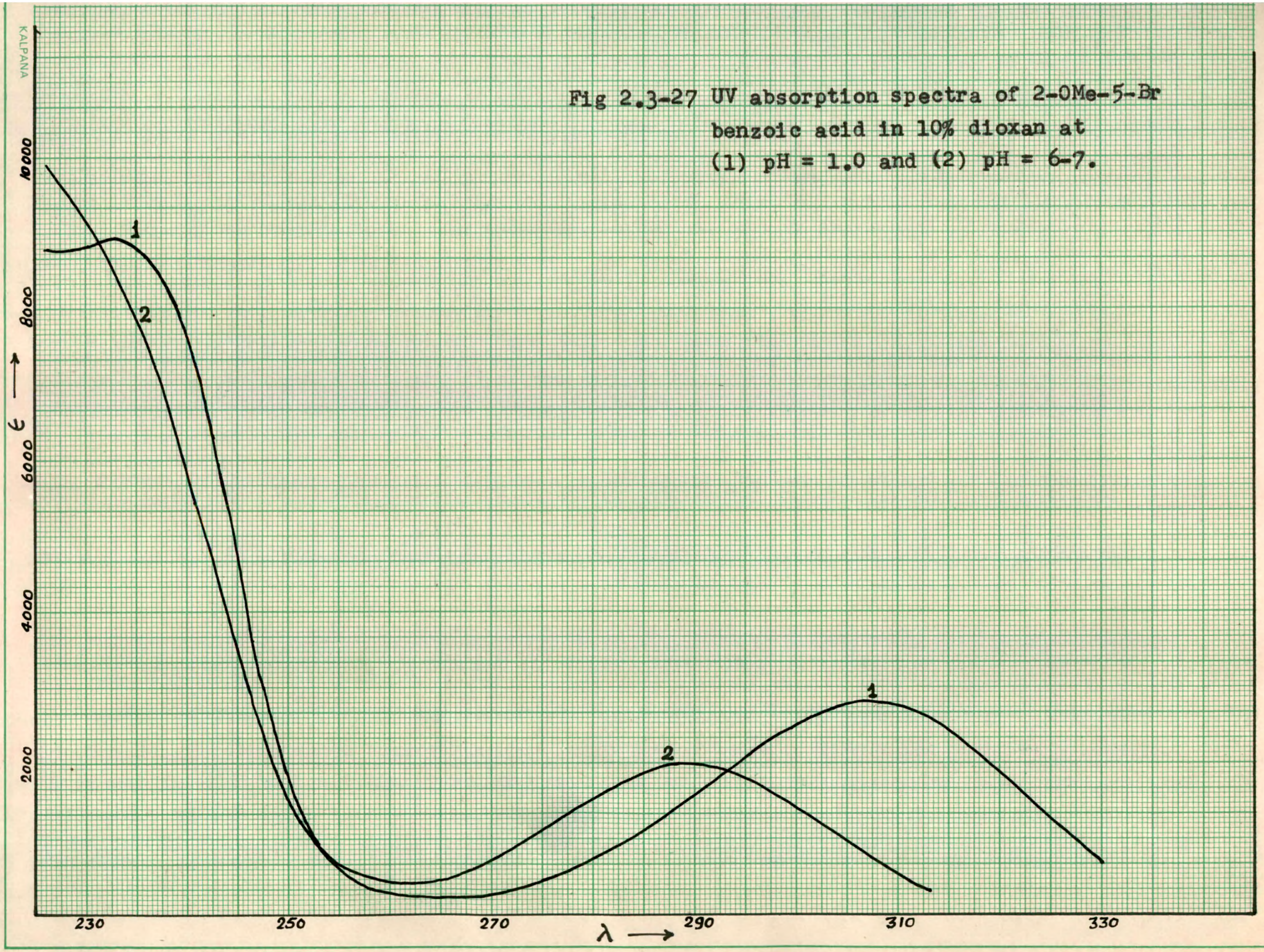

Fig 2.3-27 UV absorption spectra of 2-OMe-5-Br benzoic acid in 10% dioxan at (1) pH = 1.0 and (2) pH = 6-7.

2.4 DISCUSSION

The spectral properties of benzenoid compounds are conditioned by the closed cyclic conjugation of three ethylinic double bonds. Benzene, the aromatic parent, shows three groups of absorption bands with pronounced fine structure, first at ∽ 185 nm (log ϵ =4.60); second, at ∽ 200 nm (log ϵ =3.70) and third, at ∽ 260 nm (log ϵ =2.40). From the symmetry of the wavefunctions it is possible to predict the probability of transitions responsible for these bands. The point group to which the nuclear skeleton of benzene belongs is D_{6h} and the symmetry is so high that the possibilities for excited states are severely restricted. The calculations have shown that the ground electronic state is totally symmetric and is a singlet. The excited state is a fourfold degenerate state. The introduction of electronic repulsion splits the excited state into a twofold degenerate level transitions to which are allowed and two nondegenerate states transitions to which are forbidden. However, the forbidden bands become partially allowed because of vibronic interaction between the allowed and the forbidden states and thus 'steal' some intensity. The three main bands of benzene are ascribed to transitions to these levels.[2-7]

Substitution perturbs the benzene ring both by resonance and inductive effects. Resonance effect which results in the migration of charge between the ring and the substituent offers a strong perturbation and is often considered more important cause of intensification and wavelength shift.

In benzoic acid, the carboxyl group has got a conspicuous electron attracting tendency (-I, -M effects) and hence can conjugate with the benzene ring. One result of this conjugation is to bring about a change in the spectrum, the bands being shifted bathochromically. Tables 1 and 2 give the values of λmax (logϵ) nm in water or aqueous dioxan at different pH and in methanol or ethanol. The values at low pH and in methanol or ethanol are comparable for most of the compounds but in some cases there is a bathochromic shift.

Benzoic acid shows two absorption bands, first at 230 nm (log ϵ =4.04) and second at 273 nm (log ϵ =2.97). These bands have been interpreted as the shifted benzene bands[8-12] on the basis of resonance between polar and nonpolar structures. Such an explanation is not unreasonable since the carboxyl group is known to have fairly high resonance effect. On the other hand, Nagakura and Tanaka[13,14] have ascribed the 230 nm band to an intramolecular charge transfer or electron transfer (ET) absorption, corresponding to the two new orbitals formed by the interaction of the highest occupied orbital of the benzene ring and the lowest vacant orbital of the carboxyl group. In the ground state one of these orbitals is occupied by two electrons and the excitation to the other level is accompanied by a large electron transfer. Hence the name intramolecular charge transfer absorption. This assignment seems superior because the wavelength of this kind of band is too long to be regarded as the shift from the 200 nm band of benzene. The band at 273 nm is the shifted benzenoid band.[15]

2.4-1 : Monosubstituted Benzoic Acids :

With the monosubstituted benzoic acids there is appreciable interaction between the orbitals of the monosubstituted benzene and those of the carboxyl group. Such an interaction leads to the appearance of two ET bands for the ortho and meta isomers, whereas in the para isomer, the appearance of only one intense band at wavelengths larger than those of the principal ET bands of the ortho and meta isomers is possible.[13] The following generalizations may be made about the spectra of monosubstituted benzoic acids carrying electronically complementary groups.(Table 1)

(i) The ortho and meta isomers may exhibit similar spectra because the possibility of primary resonance interaction, which is absent in the meta isomer, is also ruled out in the case of the ortho isomer due to steric interaction between the carboxyl group and the ortho substituent.[5,16,17] It is generally considered that the carboxyl group is twisted out of the plane of the benzene ring and the resulting loss of coplanarity reduces its resonance interaction with the phenyl system. The inductive and resonance contribution of the substituent is not large enough to counterbalance the loss of coplanarity. The larger the deviation from coplanarity the smaller will be the resonance contribution. A direct consequence of steric interaction is to make the principal ET band to appear as an inflection with a hypsochromic shift or the band is completely removed from the spectrum. e.g. o-chlorobenzoic acid, o-bromobenzoic acid.

In the meta isomers also an indirect steric interaction between the carboxyl group and the meta substituent through the hydrogen in the ortho position may hinder the carboxyl group resonance. As a result of this effect, called the buttressing effect,[18] the principal ET band may lose prominence and appear only as an inflection. e.g. m-bromobenzoic acid.

(ii) The wavelength maximum and intensity for the principal ET band are in the order para > meta ⩾ ortho, because the steric interaction is maximum in the ortho isomer. However, hydroxybenzoic acids exhibit a different trend viz. para > ortho > meta. The reversal of the usual order has been attributed to the possibility of hydrogen bonding[19,20] between the ortho hydroxy group and the carboxyl group. The hydrogen bonding is thought to lower the excited state thereby shifting the band bathochromically and hyperchromically.

(iii) On substitution in the para position, the principal ET band of benzoic acid is shifted in the order
$OH > OMe > I > Br > Cl \simeq Me$ in methanol and
$I \simeq OMe > OH > Br > Cl > Me$ in water at low pH. Ortho or meta substitution may change this order because of steric interaction or buttressing effect respectively.

(iv) The halobenzoic acids are of interest because the inductive and mesomeric effects are of the opposite sign; in para substituted benzoic acids the bathochromic effect increases in the order $Cl < Br < I$. This corresponds to the order of net electron release by the substituent which in turn is a function of both electronegativity difference between the aromatic moiety and the substituent and the polarizability of the Ar-X bond[5,21,22,54] (X = Cl, Br or I).

(v) The second ET band shows slight bathochromic and hyperchromic shifts in both the ortho and meta isomers in the order ortho < meta, except in the case of hydroxybenzoic acids. The reversal of the usual order for hydroxybenzoic acids may be attributed to hydrogen bonding.

Table 1 : Absorption data for monosubstituted benzoic acids in water or aqueous dioxan at different pH and in methanol or ethanol.

Benzoic acid	Solvent	pH	λmax(log ϵ)nm	Ref.
H	W	1-3	230(4.04); 273(2.97)	55
o-Me		4.0	- ; 272(2.90)	
		7-10	- ; 268(2.75)	
	E	-	228(4.02); 273(2.94)	11
o-Me	W	1-2	230(3.86); 278(3.07)	55
		3.0	230(3.83); 278(2.92)	
		4-7	- ; 270(2.70)	
	E	-	228(3.71) ; 279(2.86)	11
m-Me	W	1-2	234(4.00); 280(3.09)	55
		4.0	234(3.99); 280(3.02)	
		5-8	230(3.88); 276(2.91)	
	E	-	232(3.95); 279(3.06)	11

p-Me	W	1-2	240(4.14);	-	55
		4.0	240(4.13);	-	
		6-9	234(4.05);	-	
	M	-	236(4.11);	-	
o-Cl	W	1.0	- ;	280(2.93)	55
		2.0	- ;	280(2.90)	
		3-4	- ;	272(2.62)	
	E	-	229(3.71)^{s};	278(2.88)	11
m-Cl	W	1-3	232(3.94);	282(3.02)	55
		4.0	230(3.93);	282(2.94)	
		6-9	- ;	278(2.82)	
	E	-	230(3.92);	284(2.98)	11
p-Cl	D1	1-2	242(4.20);	-	
		5.0	236(4.12);	-	
		7.0	234(4.11);	-	
	M	-	236(4.15);	-	
o-Br	W	1.0	- ;	280(3.05)	55
		2.0	- ;	280(2.91)	
		3-4	- ;	272(2.61)	
	E	-	224(3.80)^{s};	282(2.88)	11
m-Br	D2	1.0	- ;	284(3.01)	
		4.0	- ;	282(2.93)	
		7.0	- ;	278(2.80)	
	E	-	225(3.92)^{s};	280(2.92)	11
p-Br	D1	1-2	246(4.21);	-	
		5-7	238(4.14);	-	
	M	-	240(4.20);	-	
p-I	D1	1-2	257(4.20);	-	
		5.0	250(4.15);	-	
		9.0	248(4.17);	-	
	M	-	250(4.21);	-	
o-OMe	W	1-2	236(3.86);	296(3.50)	55
		4.0	- ;	282(3.31)	
		6-8	- ;	278(3.32)	
	E	-	230(3.79);	291(3.43)	11

m-OMe	W	1-2	235(3.84);	294(3.38)	55
		3.0	- ;	290(3.31)	
		5-8	- ;	286(3.30)	
	E	-	230(3.83);	293(3.39)	11
p-OMe	Dl	1-2	256(4.19);	-	
		5.0	250(4.11);	-	
		7-8	246(4.12);	-	
	M	-	252(4.18);	-	
p-OEt	Dl	1-2	257(4.20);	-	
		5.0	250(4.13);	-	
		7-8	248(4.12);	-	
	M	-	253(4.19);	-	
p-n-OPr	Dl	1-2	258(4.21);	-	
		5.5	250(4.15);	-	
		8-9	248(4.16);	-	
	M	-	253(4.19);	-	
p-iso-OPr	Dl	1-2	258(4.21);	-	
		6.0	250(4.14);	-	
		8-9	248(4.15);	-	
	M	-	253(4.19);	-	
o-OH	W	1-2	236(3.92);	302(3.55)	55
		4-7	- ;	296(3.56)	
	M	-	235(-);	302(-)	30
m-OH	W	1-3	236(3.86);	296(3.38)	55
		4.0	- ;	290(3.32)	
		7-9	- ;	288(3.31)	
	M	-	234(-);	295(-)	30
p-OH	W	1-3	254(4.11);	-	55
		5.0	248(4.06);	-	
		7-8	246(4.06);	-	
	E	-	251(4.09);	-	11
o-NO_2	W	1-2	264(3.68);	-	55
		4-7	268(3.71);	-	

m-NO_2	W	1-2	262(3.86);	-	55
		4-7	266(3.86);	-	
	M	-	260(3.83);	-	31
p-NO_2	W	1-3	262(4.07);	-	55
		6.0	272(4.00);	-	
		7-9	272(3.99);	-	
	M	-	260(4.05);	-	

In this and the subsequent tables, W = water; D1 = 10% dioxan; D2 = 20% dioxan; M = methanol; E = 95% ethanol and s = inflection.

When the substituent is not complementary the order of shifts is reversed.[23,24] In such a case the ortho isomer absorbs at a longer wavelength than the meta and para isomers. This is evident from the spectra of nitrobenzoic acids when compared at very low pH. In this case it is assumed that charge transfer from benzoic acid to the vacant orbital of the nitro group may also occur.

2.4-2 : Disubstituted Benzoic Acids :

The spectra of disubstituted benzoic acids are best understood in terms of the spectra of their constituent monosubstituted benzoic acids.[4,25-27] The compounds can be classified into three groups.

(i) The compounds which contain bulky groups in 2,3- or 2,6-positions, viz. 2,3-dimethoxy and 2,6-dimethoxybenzoic acids, where the effects of steric hindrance are apparent, for the principal ET band appears as an inflection or hump and the second ET band undergoes hypochromic and hypsochromic shifts when compared to the corresponding band of the constituent monosubstituted compounds. Lesser steric interaction or the possibility of hydrogen bonding with the ortho substituent, e.g. 2-hydroxy-3-methoxybenzoic acid, favours well-defined bands.

(ii) The disubstituted benzoic acids which contain a substituent para to the electronegative carboxyl group show a prominent principal ET band with hypochromic shift comparable in wavelength to the corresponding band of the para monosubstituted compound.[25] The other substituent exerts only a secondary effect and makes the second ET band, which is absent in the case of the para monosubstituted compound, reappear in the spectrum. The second ET band shows hyperchromic and hypsochromic shifts relative to the corresponding band of the monosubstituted reference compound.

(iii) In 2,5-disubstituted benzoic acids the effects of the two substituents are expected to become additive. The principal ET band appears only as a hump and the second ET band shows both bathochromic and hyperchromic shifts. The calculated and observed λmax generally differ at most by ± 5 nm but larger deviations suggest the interaction between 2,5 substituents resulting in changed bond distance and consequent nonadditivity due particularly to the group at the 2-position.[19]

Table 2 gives the absorption data for disubstituted benzoic acids.

Table 2 : Absorption data for some disubstituted benzoic acids in water or aqueous dioxan at different pH and in methanol or ethanol.

Benzoic acid	Solvent	pH	λ max(log ε)nm	Ref.
2,3-diOH	W,Di	1.0	247(3.89); 317(3.50)	
		5-7	- ; 306(3.51)	
	M	-	247(3.84); 317(3.51)	
2,4-diOH	Di	1-2	256(4.11); 295(3.72)	
		6-7	248(4.01); 292(3.66)	
	M	-	254(4.06); 294(3.71)	
2,5-diOH	Di	1-2	238(3.80); 330(3.61)	
		5-7	- ; 319(3.61)	
	M	-	237(-); 332(-)	30
2,6-diOH	Di	0.5	250(3.97); 316(3.56)	
		5-7	246(3.86); 306(3.55)	
	E	-	250(3.80); 311(3.54)	11
3,4-diOH	Di	1-3	260(4.03); 293(3.75)	
		6-7	252(3.97); 288(3.65)	
	M	-	258(3.98); 292(3.73)	
3,5-diOH	Di	1-2	250(3.84); 306(3.47)	
		4.0	242(3.76); 296(3.38)	
		6-8	240(3.75); 295(3.39)	
	M	-	248(-); 306(-)	30
2-OH-3-OMe	W,Di	1.0	246(3.83); 315(3.54)	
		2.5	245(3.78); 312(3.52)	
		5-7	- ; 306(3.53)	
	M	-	244(3.72); 312(3.57)	31
2-OH-4-OMe	Di	1.0	258(4.15); 294(3.76)	
		3.0	256(4.12); 294(3.75)	
		5-7	250(4.01); 290(3.69)	
	M	-	252(4.05); 294(3.72)	

2-OH-4-OEt	Dl	0.5-1.0	257(4.18);	294(3.81)
		6-7	249(4.02);	291(3.71)
	M	-	252(4.08);	294(3.76)
2-OH-5-OMe	Dl	1-2	235(3.82);	328(3.60)
		3.0	- ;	323(3.59)
		6-7	- ;	319(3.60)
	M	-	234(3.82);	327(3.64)
4-OH-3-OMe	W,Dl	1-2	261(4.03);	292(3.75)
		4.5	259(3.99);	290(3.71)
		7.0	251(3.97);	285(3.60)
	M	-	258(4.02);	289(3.73)
2,3-diOMe	Dl	0.5-2.0	- ;	295(3.35)
		4.0	- ;	280(3.17)
		7.0	- ;	277(3.20)
	M	-	240(3.53)^{s};	292(3.31)
2,4-diOMe	Dl	1-2	257(4.12);	291(3.79)
		5.0	253(3.98);	287(3.65)
		7-8	246(3.90);	283(3.54)
	M	-	253(4.07);	288(3.70)
2,5-diOMe	Dl	1-2	234(3.84);	320(3.56)
		5.0	- ;	298(3.43)
		8.0	- ;	295(3.47)
	M	-	232(3.84);	315(3.51)
2,6-diOMe	Dl	0.1-1.0	244(3.36);	280(3.36)
		4.5	- ;	278(3.21)
		7.0	- ;	275(3.12)
	M	-	- ;	278(3.33)
3,4-diOMe	Dl	1-2	261(4.05);	291(3.77)
		4.5	256(4.00);	289(3.69)
		7.0	251(4.00);	284(3.61)
	M	-	256(4.04);	289(3.71)
3,5-diOMe	D2	1.0	251(3.73);	305(3.46)
		4.5	246(3.66);	299(3.36)
		8.0	242(3.66);	293(3.36)
	M	-	249(3.70);	303(3.43)

2-OH-5-Br	D1	1.0	232(3.91); 315(3.52)	
		3.0	- ; 310(3.50)	
		7.0	- ; 307(3.51)	
	E	-	231(3.91); 314(3.53)	19
2-OMe-5-Br	D1	1.0	233(3.95); 307(3.44)	
		6-7	- ; 290(3.29)	
	E	-	231(3.95); 305(3.43)	19

2.4-3 : Effect of pH :

To study the effect of pH the spectra were recorded in the pH range of about 1-8 in water or aqueous dioxan. (Table 1 and 2). Below about pH 2 most of the acids may be regarded as undissociated to any appreciable extent while above pH 6 the dissociation was substantially complete. For most of the compounds studied the molar absorptivity curves at different pH intersect at some fixed wavelengths called isosbestic points (Table 3).

In the case of benzoic acid when the pH of the solution is increased the bands are shifted both hypsochromically and hypochromically because the ionisation of the carboxyl group is accompanied by a loss of single proton and the group is left with an isolated negative charge which diminishes the electron attracting tendency of the carboxyl group[8].

Monosubstituted benzoic acids : In the case of ortho and meta isomers as the pH of the solution is increased, the principal ET band loses prominence and appears only as an inflection. However, the shape of the principal ET band of the para isomer remains the same but shows both hypsochromic and hypochromic shifts.

Table 3 : The invariant wavelengths and log ε for the ultraviolet absorption of benzoic acids.

Benzoic acid	Solvent	λinv(log ε)nm			Ref.
H	W	-	-	-	55
o-Me	W	-	-	-	
m-Me	W	-	-	266(2.85)	55
p-Me	W	233(4.04)	-	-	55
o-Cl	W	-	-	-	
m-Cl	W	-	253(2.77)	269(2.75)	55
p-Cl	D1	233(4.10)	-	-	
o-Br	W	-	-	-	55
m-Br	D2	-	255(2.79)	269(2.73)	
p-Br	D1	239(4.14)	-	-	
p-I	D1	251(4.15)	-	-	
o-OMe	W	-	257(2.84)	281(3.31)	55
m-OMe	W	230(3.81)	258(2.76)	288(3.30)	55
p-OMe	D1	249(4.11)	-	-	
p-OEt	D1	249(4.12)	-	-	
p-n-OPr	D1	251(4.15)	-	-	
p-iso-OPr	D1	251(4.14)	-	-	
o-OH	W	-	258(2.44)	298(3.54)	55
m-OH	W	-	258(2.73)	288(3.31)	55
p-OH	W	248(4.05)	-	-	55
o-NO_2	W	-	251(3.62)	-	55
m-NO_2	W	-	264(3.85)	-	55
p-NO_2	W	-	275(3.99)	-	55
2,3-diOH	W,D1	238(3.78)	268(2.51)	312(3.47)	
2,4-diOH	D1	229(3.74)	249(4.00)	-	
2,5-diOH	D1	231(3.79)	259(2.60)	324(3.59)	
2,6-diOH	D1	239(3.82)	272(-)	310(3.54)	
3,4-diOH	W,D1	231(3.68)	252(3.97)	-	
3,5-diOH	W,D1	241(3.75)	273(2.93)	296(3.38)	
2-OH-3-OMe	W,D1	236(3.74)	266(2.55)	310(3.52)	
2-OH-4-OMe	D1	228(3.75)	250(4.05)	-	
2-OH-4-OEt	D1	229(3.79)	250(4.09)	-	

2-OH-5-OMe	D1	234(3.82)	262(-)	323(3.59)
4-OH-3-OMe	W,D1	231(3.64)	254(3.97)	-
2,3-diOMe	D1	-	261(2.81)	280(3.17)
2,4-diOMe	D1	228(3.73)	245(3.91)	-
2,5-diOMe	D1	229(3.83)	260(2.55)	303(3.42)
2,6-diOMe	D1	-	-	240(3.35)
3,4-diOMe	D1	231(3.60)	254(3.99)	-
3,5-diOMe	D2	244(3.65)	274(2.97)	296(3.36)
2-OH-5-Br	D1	231(3.91)	255(-)	310(3.49)
2-OMe-5-Br	D1	231(3.95)	253(2.97)	293(3.29)

Within the pH range studied, isosbestic points are not observed for benzoic acid, o-methyl, o-chloro, and o-bromobenzoic acids. (Table 3). o-Acetoxybenzoic acid also shows no isosbestic points.[28] o-Hydroxy and o-methoxybenzoic acids show two isosbestic points each, the first one of both at almost the same wavelength. The second isosbestic point for o-methoxybenzoic acid appears at a very much shorter wavelength than that of o-hydroxybenzoic acid because the increase in pH results in a large hypsochromic shift in the second band of o-methoxybenzoic acid, whereas the second ET band of o-hydroxybenzoic acid shows only a small shift. Such a difference in behaviour may be due to hydrogen bonding and/or steric interaction.

Two isosbestic points each are observed for all the meta substituted benzoic acids studied except m-methylbenzoic acid which shows only one such point. It may not be a real exception because it is likely that for this isomer the two isosbestic points may be very close so that they coincide. The first isosbestic points of all the isomers are very close and the wavelengths for the second isosbestic points are in the order

Me < Cl ≈ Br < OMe ≃ OH. The wavelength maximum for the second ET band is also in the same order except m-hydroxy benzoic acid which absorbs at a longer wavelength than m-methoxybenzoic acid.

All the para substituted benzoic acids studied show one isosbestic point each, which are in the same order as the one observed for λmax of the principal ET band at very low pH, i.e. Me ≃ Cl < Br < OH ≃ OMe ≃ OEt < n-OPr ≈ I.

In the case of nitrobenzoic acids the pH effect is reversed because in these acids the carboxyl group is opposed in the benzene ring by a more powerfully effective nitro group of the same type, which may change the electronic character of the carboxyl group. As the pH of the solution is increased from very low pH to higher values, bands are shifted bathochromically because a weak contributing effect may be conferred upon the carboxyl group by the presence of a free negative charge. The intensities of the bands are however, not changed much. All the three isomers show one isosbestic point each which are in the order para > meta > ortho in both wavelength and intensity.

Disubstituted benzoic acids : In the case of disubstituted benzoic acids also increase in pH results in the hypsochromic shifts of the bands (Table 2). At higher pH values for compounds containing an ortho substituent and no para substituent the principal ET band appears only as an inflection or is completely removed from the spectrum. In others the overall nature of absorption remains the same.

Depending upon the effect of pH, the disubstituted benzoic acids may be classified into two groups, acids with a para substituent, and acids without a para substituent. The compounds which belong to the former class are 2,4- and 3,4-disubstituted benzoic acids. The effect of pH is similar to that observed for para monosubstituted benzoic acid. As the pH of the solution is increased the principal ET band shows a hypsochromic shift. The second ET band shows both hypsochromic and hypochromic shifts. These acids show two isosbestic points each (Table 3). The difference between the λmax for the principal ET band and the second isosbestic point is almost a constant (Table 4), for all the acids studied except 2,4-dimethoxybenzoic acid which shows a larger difference because this compound only carries a bulky methoxy group in the ortho position.

Table 4 : The λmax and second λinv of some 2,4- and 3,4-disubstituted benzoic acids.

Benzoic acid	λmax	λinv	(λmax- λinv)
2,4-diOH	256	249	7
2-OH-4-OMe	258	250	8
2-OH-4-OEt	257	250	7
2,4-diOMe	257	245	12
3,4-diOH	260	253	7
4-OH-3-OMe	261	254	7
3,4-diOMe	261	254	7

The compounds which belong to the latter class show three isosbestic points each, except 2,3-diOMe and 2,6-diOMe benzoic acids, where steric interaction may be responsible. In 2,3-dimethoxybenzoic acid the first isosbestic point near the principal ET band is not observed and 2,6-dimethoxybenzoic acid the first two isosbestic points are not observed. However, all the acids show the third isosbestic point which is in the same order as the one observed for λmax for the second ET band, with the exception of compounds which contain a bulky group in the ortho position. In such cases the difference between λmax and λinv is relatively larger.

The results also indicate that the spectra in water and aqueous dioxan are essentially same.

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