2. ULTRAVIOLET ABSORPTION STUDIES OF CINCHONA ALKALOIDS :

2.1

Introduction :

In this section, the ultraviolet absorption study of cinchona alkaloids (quinine, quinidine, cinchonine and cinchonidine) in aliphatic alcohols and aqueous alcohols is described.

2.2

Experimental :

Quinine sulfate (Government Quinine Factory, Tamilnadu(Madras)) was crystallised eight times from hot water. Cinchonidine sulfate (Fluka, A.G. Switzerland) was crystallised five times from hot water. Quinidine sulfate (B.P. Howard, London) was crystallised three times from hot water. Cinchonine sulfate was prepared by dissolving cinchonine (pure crystals ; Riedel, Germany) in aqueous sulfuric acid and crystallising out the sulfate ; this was then crystallised twice from hot water.

From samples of cinchona alkaloid sulfates, the bases were obtained as follows : calculated amount of about 0.5 N sodium hydroxide (A.R.) solution was added to alkaloid sulfate solution and to ensure complete precipitation, a few more drops of the alkali were added. This was then heated to about 80°C, filtered, washed free of alkali, recrystallised (quinine from 40 % (by volume) ethyl alcohol, quinidine from 80 % (by volume) ethyl alcohol, cinchonine and

cinchonidine from distilled ethyl alcohol), dried at 100°C (± 2) and stored.

The alcohols used were of C.P.grade.

To study the ultraviolet absorption of the four cinchona alkaloid bases in 0 % methanol, ethanol and n-propanol, ultraviolet absorption spectra of the alkaloid sulfates in aqueous solutions at about pH 7 (adjusted by addition of sodium hydroxide solution) at room temperature were taken.

The ultraviolet absorption measurements were made with Beckman Model DU Spectrophotometer using 10 mm. matched quartz cells in the range 250 - 350 mμ. The values of the extinction coefficients, ϵ , were calculated by dividing the observed optical density by the concentration of the alkaloid base/sulfate in gm equiv./litre.

2.3

Nomenclature :

λ = wavelength in mμ.

ϵ = extinction coefficient.

λ_x = wavelength at which absorption is maximum.

2.4

Results :

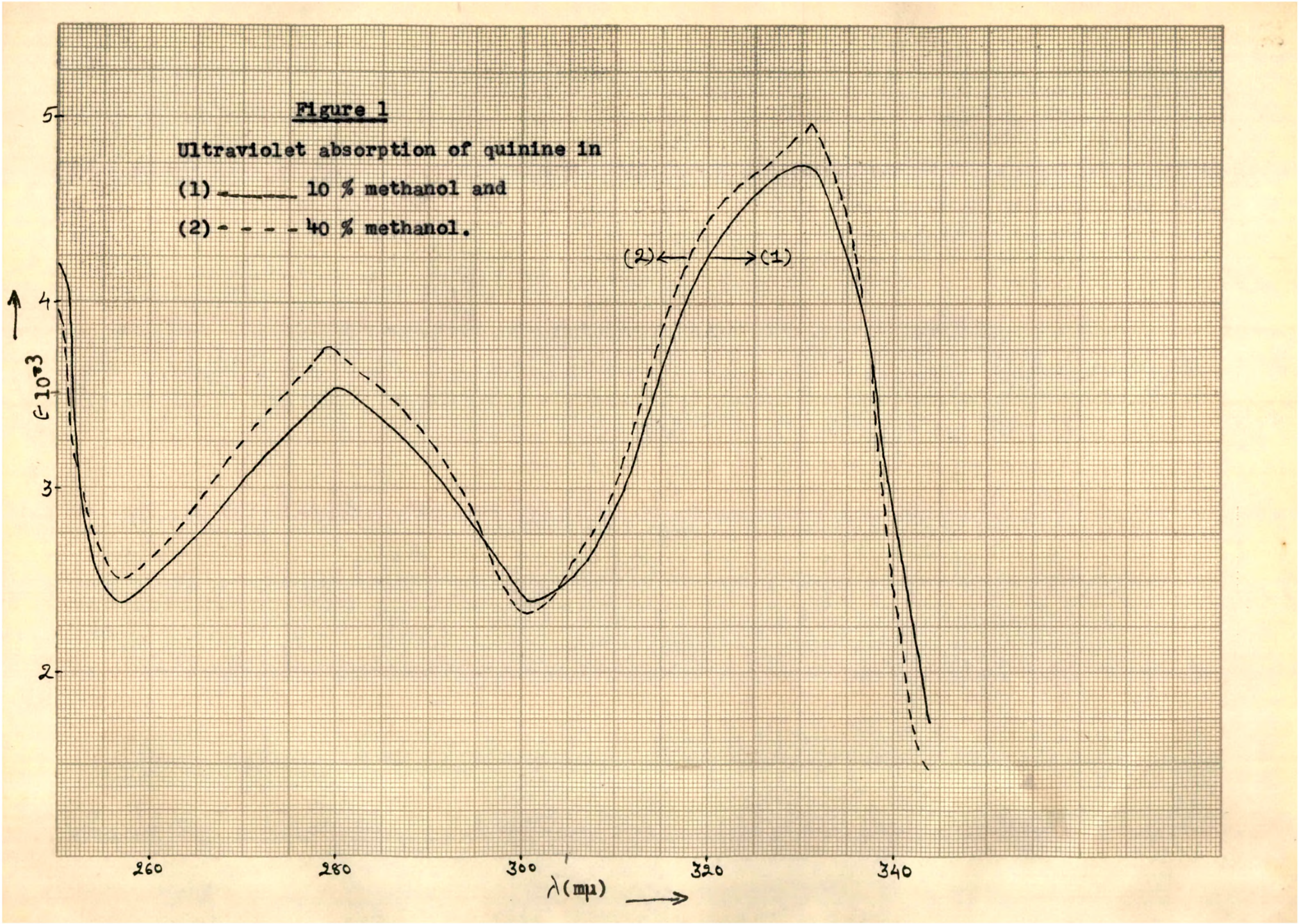
Figure 1
Ultraviolet absorption of quinine in
(1) _____ 10 % methanol and
(2) - - - - 40 % methanol.
(2)
(1)
5
4
3
2
ε·10^-3
260
280
300
320
340
λ(mμ)

Table 2.01

Ultraviolet absorption of quinine in aqueous methanols.

% Methanol =	0	10	40	100
λ		ε/10 =		
250	434	423	397	352
252	306	305	302	283
254	249	259	258	254
256	227	240	252	254
260	230	248	261	269
264	247	267	283	293
268	269	294	315	326
272	289	317	340	349
276	305	341	359	370
278	310	347	372	381
279	-	-	-	387
280	315	354	372	381
282	314	347	365	373
284	309	342	353	358
288	296	325	340	341
292	277	303	309	312
294	264	287	290	283
298	235	254	250	231
300	226	243	236	222
302	-	240	236	225
304	-	244	246	237
305	229	-	-	-
306	-	256	262	248
310	265	291	296	289
314	-	349	359	352
315	331	-	-	-
318	-	408	422	433
320	389	429	447	450
324	-	453	466	459
325	421	-	-	-
328	-	471	485	474
329	-	476	485	-
330	438	476	491	497
331	-	474	497	-
332	-	472	485	514
334	-	448	460	491
335	414	-	-	-
340	303	284	271	248
344	-	171	145	127
345	175	-	-	-
350	92	66	54	38

Table 2.02

Ultraviolet absorption of cinchonine in aqueous methanols.

% Methanol =	0	20	100
λ		ε/10 =	
250	154	164	189
254	188	193	223
258	228	228	268
262	276	278	325
266	323	325	378
270	366	374	431
274	411	420	480
278	443	456	514
282	459	478	525
283	-	481	-
284	466	478	528
286	469	478	521
288	471	478	518
289	472	474	506
290	471	471	476
292	453	439	446
296	411	392	382
298	387	392	378
300	389	396	386
301	397	399	-
302	402	407	386
303	394	388	-
304	376	378	340
308	306	307	261
311	254	250	212
312	253	253	227
314	311	307	302
315	337	328	299
316	325	314	261
320	115	100	76
325	24	23	27

Table 2.03

Ultraviolet absorption of quinidine in aqueous methanols.

% Methanol =	0	10	20	40	100
λ		ε/10 =			
250	456	416	401	387	347
254	271	252	249	255	260
256	252	237	234	248	257
258	249	237	234	251	264
260	253	243	241	265	276
264	274	265	264	292	302
268	300	296	293	323	345
272	323	322	319	346	363
276	342	345	342	367	388
278	350	354	353	374	396
280	354	354	357	374	399
282	353	357	360	366	389
284	349	351	349	356	376
288	331	334	338	339	358
292	310	310	316	312	327
294	292	296	297	292	297
298	258	258	260	248	242
300	248	246	249	241	237
302	-	240	245	238	240
304	-	249	253	242	247
305	253	-	-	-	-
306	-	258	260	255	261
310	296	293	297	292	298
314	-	351	357	350	366
315	371	-	-	-	-
320	439	433	438	435	465
324	-	457	461	455	469
325	474	-	-	-	-
326	-	468	468	462	475
328	-	480	475	468	488
329	-	480	483	475	-
330	499	480	490	475	515
331	-	480	490	475	525
332	-	474	475	475	528
334	-	457	449	448	502
335	464	-	-	-	-
340	328	270	357	272	248
344	-	164	178	160	-
345	183	-	-	-	-
350	91	64	61	61	36

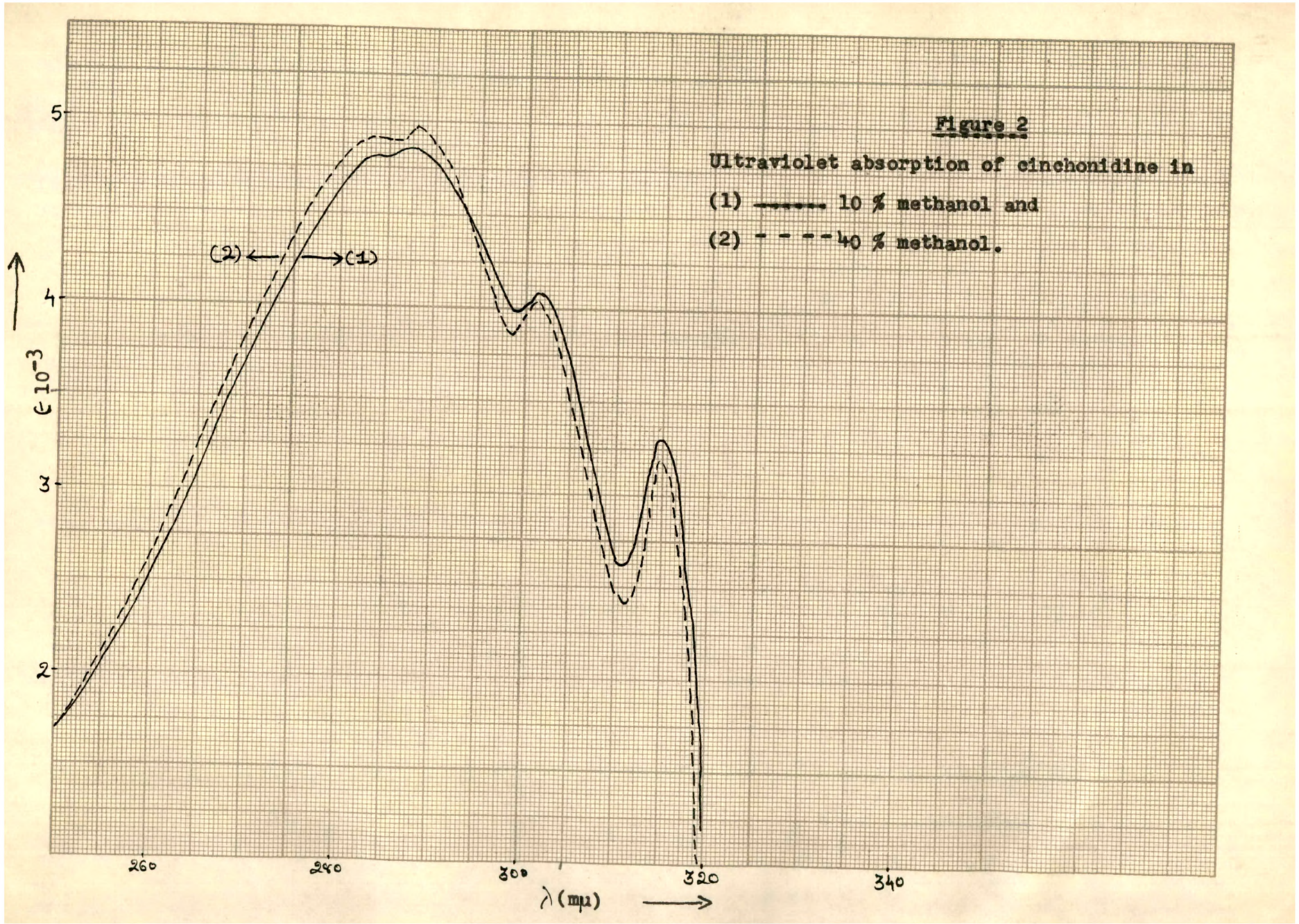

Figure 2

Ultraviolet absorption of cinchonidine in

(1) ——— 10 % methanol and

(2) - - - - 40 % methanol.

Table 2.04

Ultraviolet absorption of cinchonidine in aqueous methanols.

% Methanol =	0	10	40	100
λ		ε/10 =		
250	159	164	166	191
254	181	195	196	228
258	219	233	250	271
262	261	278	282	325
266	307	325	331	379
270	351	372	381	433
274	393	421	427	477
278	424	453	462	506
282	441	476	486	516
283	-	479	490	519
284	446	479	490	516
286	448	482	490	513
287	-	485	490	-
288	450	486	497	509
289	452	-	-	-
290	450	481	490	498
294.5	418	442	437	441
296	396	427	416	405
298	371	399	391	379
299	-	399	384	376
300	372	401	395	387
301	382	405	402	394
302	385	408	405	383
303	358	399	395	-
306	333	346	334	303
310	264	270	254	220
311	252	262	240	211
312	255	267	247	224
314	308	307	310	264
315	331	321	331	300
316	322	309	317	260
320	132	118	100	75
325	38	25	23	25

Table 2.05

Ultraviolet absorption of quinine in aqueous ethanols.

% Ethanol =	0	10	40	100
λ		ε/10 =		
250	434	431	378	318
254	249	261	257	244
256	227	247	250	244
258	225	250	256	250
262	237	261	273	273
266	258	288	300	302
270	281	313	328	330
274	296	333	346	350
278	310	347	364	372
280	315	354	368	372
282	314	351	360	359
284	309	347	353	340
286	304	337	341	334
288	296	327	328	327
290	289	320	318	314
294	264	292	282	270
298	235	254	241	218
302	-	243	231	218
304	-	247	239	228
305	229	-	-	-
310	265	295	285	279
314	-	354	353	370
315	331	-	-	-
318	-	398	421	411
320	389	431	446	430
324	-	458	467	430
325	421	-	-	-
328	-	479	485	443
329	-	479	489	-
330	438	483	492	462
331	-	476	496	472
332	-	469	491	478
334	-	445	467	456
335	414	-	-	-
340	303	292	289	202
346	175	132	116	-
350	92	70	57	29

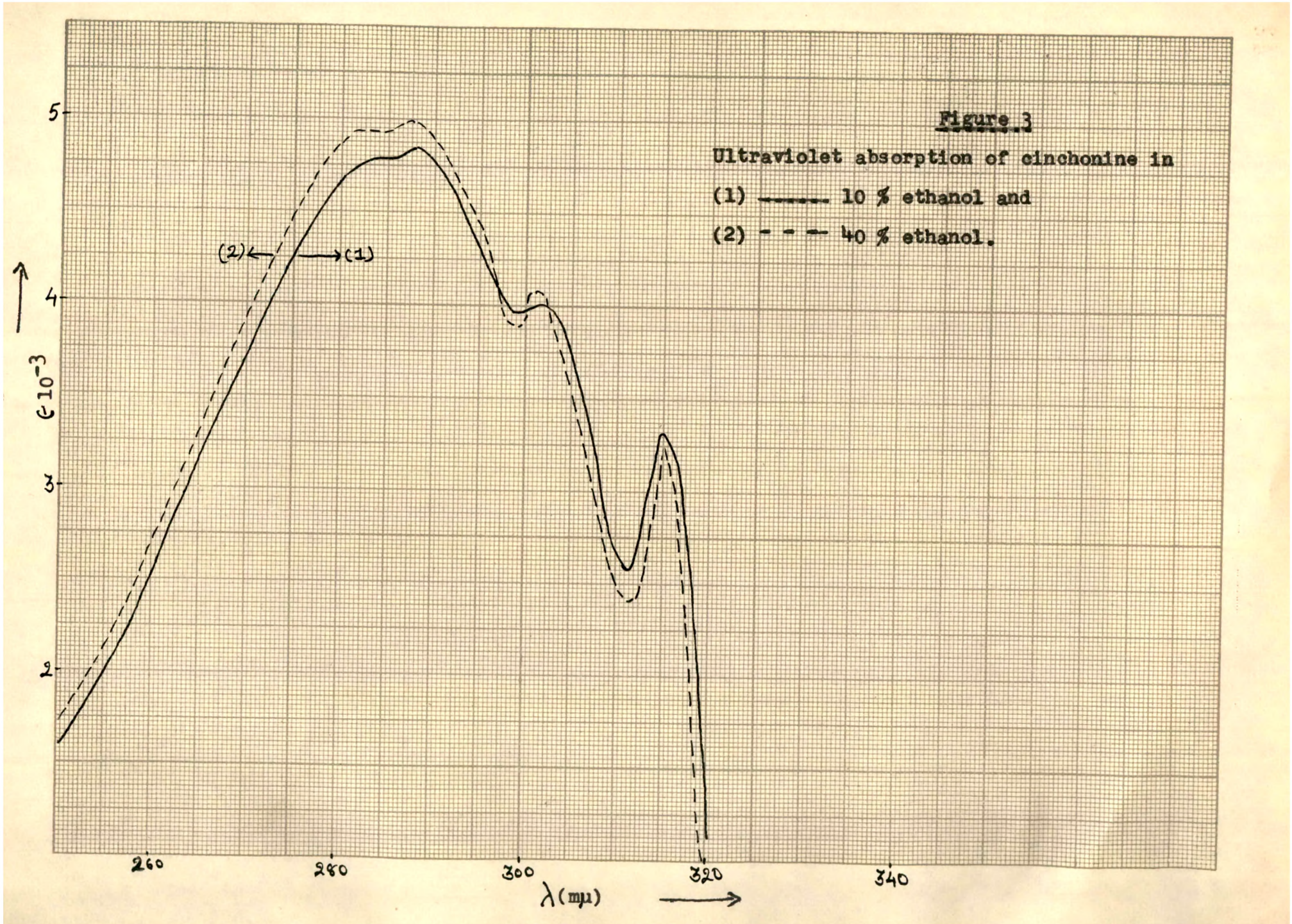

Figure 3

Ultraviolet absorption of cinchonine in

(1) ——— 10 % ethanol and

(2) - - -- 40 % ethanol.

Table 2.06

Ultraviolet absorption of cinchonine in aqueous ethanols.

% Ethanol =	0	10	20	40	100
λ			C/10 =		
250	154	158	178	167	185
254	188	187	203	200	218
258	228	232	243	243	265
262	276	277	287	289	316
266	322	325	341	342	378
270	366	377	385	389	428
274	411	418	428	435	490
278	443	455	464	472	508
282	459	473	479	493	523
283	-	477	482	493	523
284	466	477	486	493	523
286	469	477	493	495	515
288	471	484	490	498	515
289	472	-	-	-	-
290	471	480	490	491	501
294.5	433	439	443	450	425
298	387	397	399	393	370
299	-	394	392	388	370
300	389	394	399	388	385
301	402	401	406	404	385
302	394	401	406	404	374
303	376	398	-	395	-
304	359	387	377	378	327
308	306	311	305	297	247
311	254	256	250	240	200
312	253	259	254	243	214
314	311	312	305	302	290
315	337	332	326	325	283
316	325	320	312	312	250
320	115	111	109	99	62
325	24	24	29	26	18

Table 2.07

Ultraviolet absorption of quinidine in aqueous ethanols.

% Ethanol =	0	10	20	40	100
λ		ε/10 =			
250	456	411	393	373	310
254	271	255	247	248	244
256	252	243	236	239	244
258	249	246	242	245	250
260	253	249	247	253	259
264	274	274	275	278	291
268	300	298	304	309	323
272	323	322	332	332	342
276	342	340	348	350	367
278	350	350	360	361	380
280	354	353	360	364	376
282	353	350	360	360	367
284	349	345	354	353	348
288	331	330	337	329	332
290	322	319	326	320	323
294	292	287	292	284	272
298	258	254	253	242	222
300	248	242	242	232	212
302	-	240	236	229	218
304	-	246	247	234	231
305	253	-	-	-	-
306	-	254	253	245	244
310	296	289	292	283	278
314	-	347	354	344	345
315	371	-	-	-	-
320	439	426	421	428	430
324	-	448	450	450	427
325	474	-	-	-	-
328	-	468	466	463	443
329	-	471	472	466	-
330	499	474	478	472	468
331	-	474	472	472	-
332	-	468	466	469	481
334	-	444	444	449	456
335	464	-	-	-	-
338	-	356	343	347	285
340	328	292	275	274	209
344	-	176	160	154	85
345	183	-	-	-	-
350	91	67	56	55	25

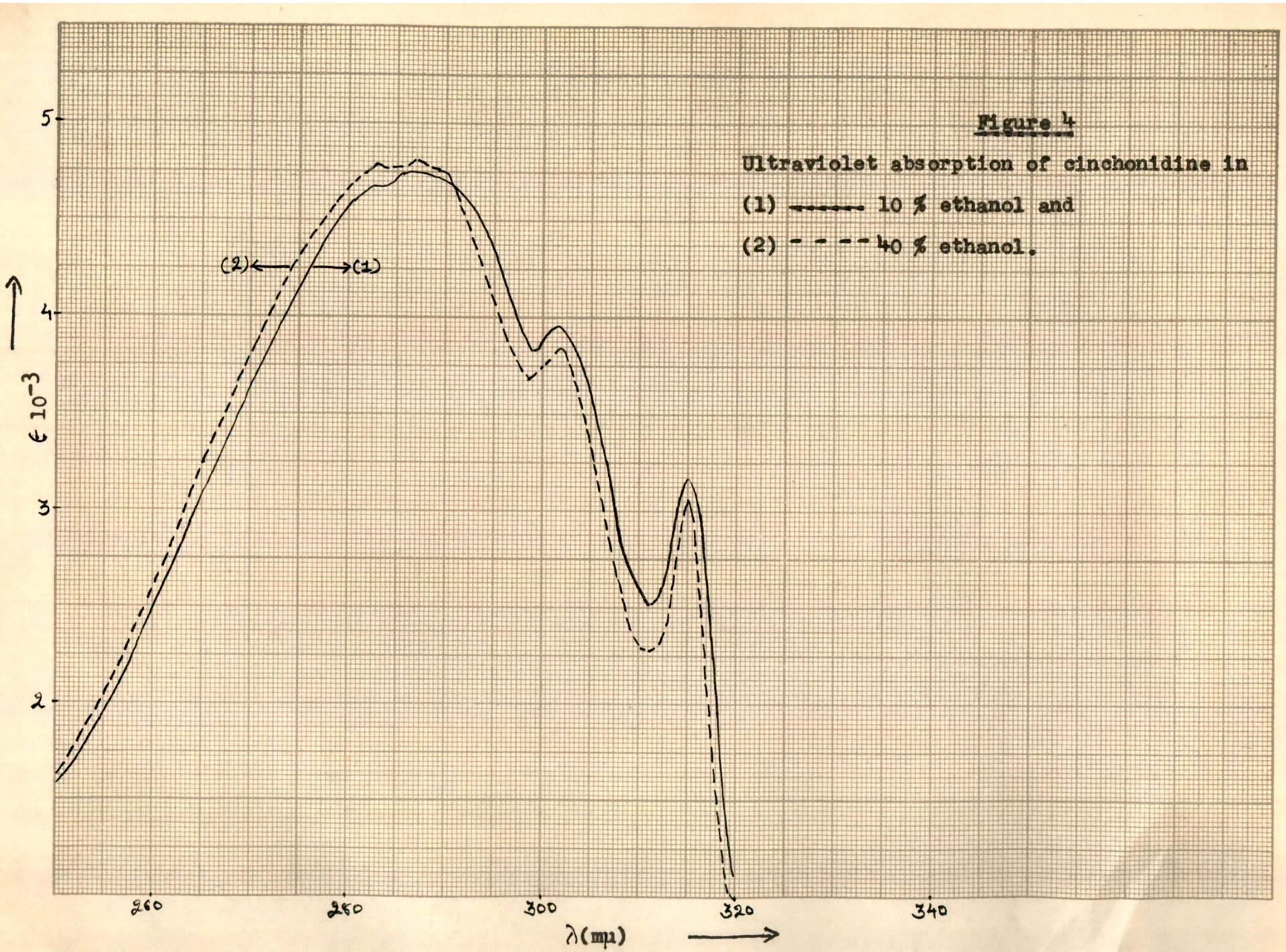

Figure 4

Ultraviolet absorption of cinchonidine in

(1) ——— 10 % ethanol and

(2) - - - - 40 % ethanol.

Table 2.08

Ultraviolet absorption of cinchonidine in aqueous ethanols.

% Ethanol =	0	10	20	40	100
λ		ε/10 =			
250	159	157	151	157	182
254	181	186	187	191	217
258	219	226	228	233	263
262	261	274	275	280	313
266	307	321	325	332	367
270	351	365	375	378	420
274	393	412	414	424	470
278	424	445	450	455	498
282	441	467	471	474	506
283	-	467	471	477	506
284	446	467	478	477	506
286	448	474	478	477	498
287	-	474	478	480	-
288	450	474	478	477	498
290	451	471	471	474	484
292	436	460	457	452	452
296	396	416	407	400	392
298	371	387	382	375	363
299	-	383	378	369	360
300	372	394	385	375	370
301	382	394	392	381	376
302	385	394	392	384	363
303	358	387	385	372	342
306	333	336	328	314	283
310	264	259	253	240	207
311	252	251	243	228	199
312	255	256	246	233	210
314	308	303	300	289	283
315	331	318	314	308	283
316	322	303	296	286	242
320	132	110	104	86	64
325	38	26	18	15	21

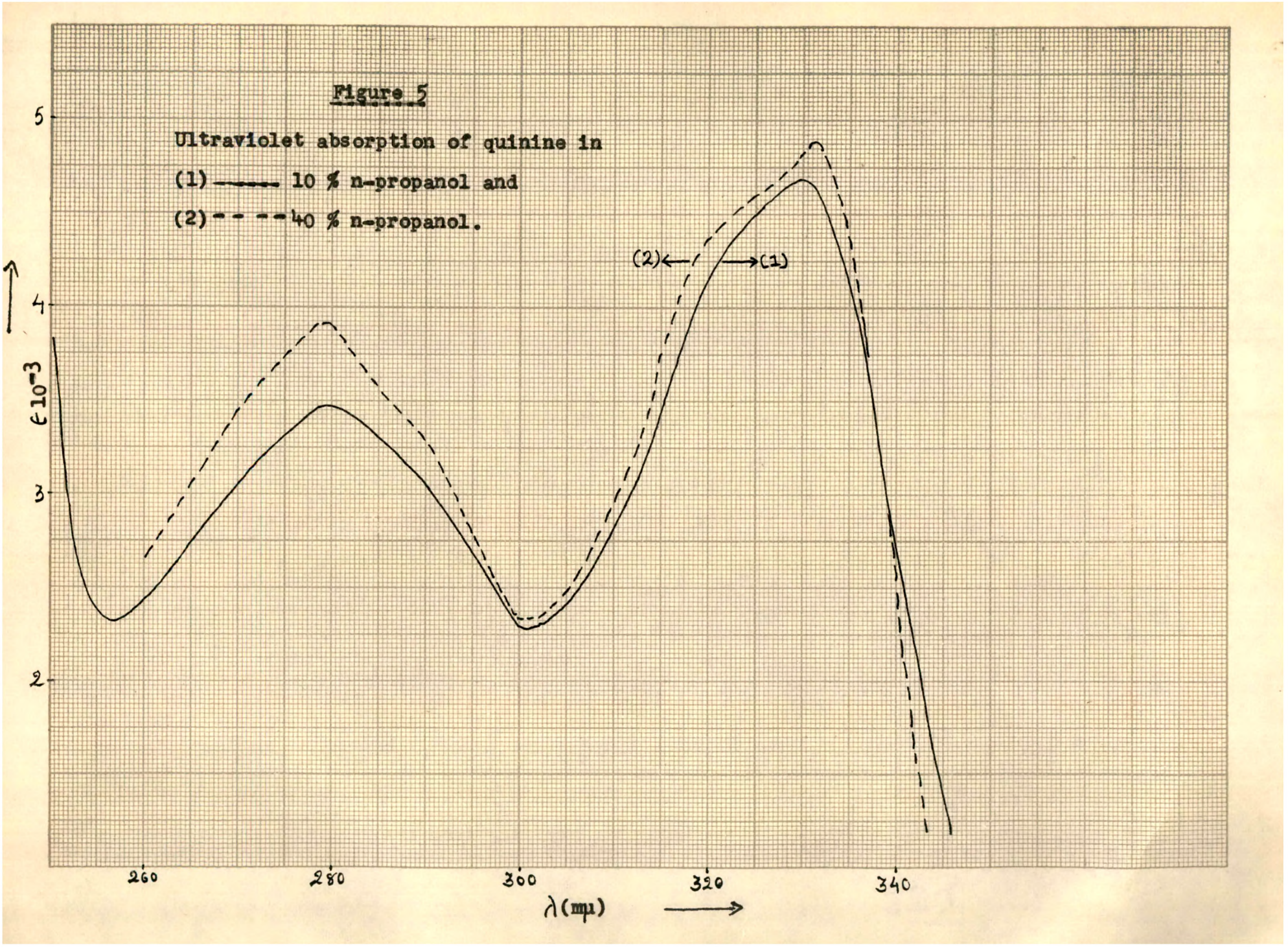
Figure 5
Ultraviolet absorption of quinine in
(1) ——— 10 % n-propanol and
(2) - - - - 40 % n-propanol.
(2)
(1)
5
4
3
2
ε10⁻³
260
280
300
320
340
λ(mμ)

Table 2.09

Ultraviolet absorption of quinine in aqueous n-propanols.

% n-Propanol =	0	10	20	40	100
λ		ε/10 =			
250	434	384	378	-	349
254	249	246	264	-	270
258	225	236	253	-	276
260	230	244	262	264	282
264	247	267	282	296	313
268	269	294	312	333	347
272	289	317	334	354	369
276	305	337	354	376	386
278	310	344	369	389	400
280	315	347	365	389	403
282	314	342	360	372	392
286	304	326	338	351	-
290	289	309	320	333	349
294	264	276	279	286	299
298	235	240	238	245	237
299	-	234	-	235	231
300	226	229	231	232	230
301	-	227	-	235	230
302	-	229	228	235	232
304	-	234	236	241	239
305	229	-	-	-	-
310	265	282	289	297	293
314	-	336	353	354	358
315	331	-	-	-	-
318	-	397	413	423	439
320	389	420	432	445	461
324	-	444	450	456	456
325	421	-	-	-	-
328	-	465	469	470	468
329	-	465	475	477	-
330	438	468	480	485	490
331	-	462	479	485	501
332	-	459	472	485	513
334	-	429	437	456	-
335	414	-	-	-	-
336	-	387	321	398	417
340	303	270	245	246	225
346	175	116	109	87	85
350	92	58	43	36	34

Table 2.10

Ultraviolet absorption of cinchonine in aqueous n-propanols.

% n-Propanol =	0	10	40	100
λ		ε/10 =		
250	154	141	-	210
254	188	169	205	239
258	228	205	244	282
262	276	250	290	340
266	322	292	340	398
270	366	339	384	443
274	411	381	436	500
278	443	415	470	521
282	459	435	486	545
283	-	437	491	547
286	469	440	491	543
287	-	445	491	-
288	471	442	491	540
289	472	-	-	-
290	471	438	481	529
294.5	433	400	426	463
298	387	362	380	392
299	-	359	368	391
300	389	361	376	402
301	397	367	382	409
302	402	367	378	402
303	394	359	369	-
306	334	309	303	307
310	265	240	223	225
311	254	227	214	214
312	253	233	220	225
313	276	248	247	-
314	311	275	283	308
315	337	294	299	314
316	325	255	275	272
320	115	94	68	72
325	24	12	8	29

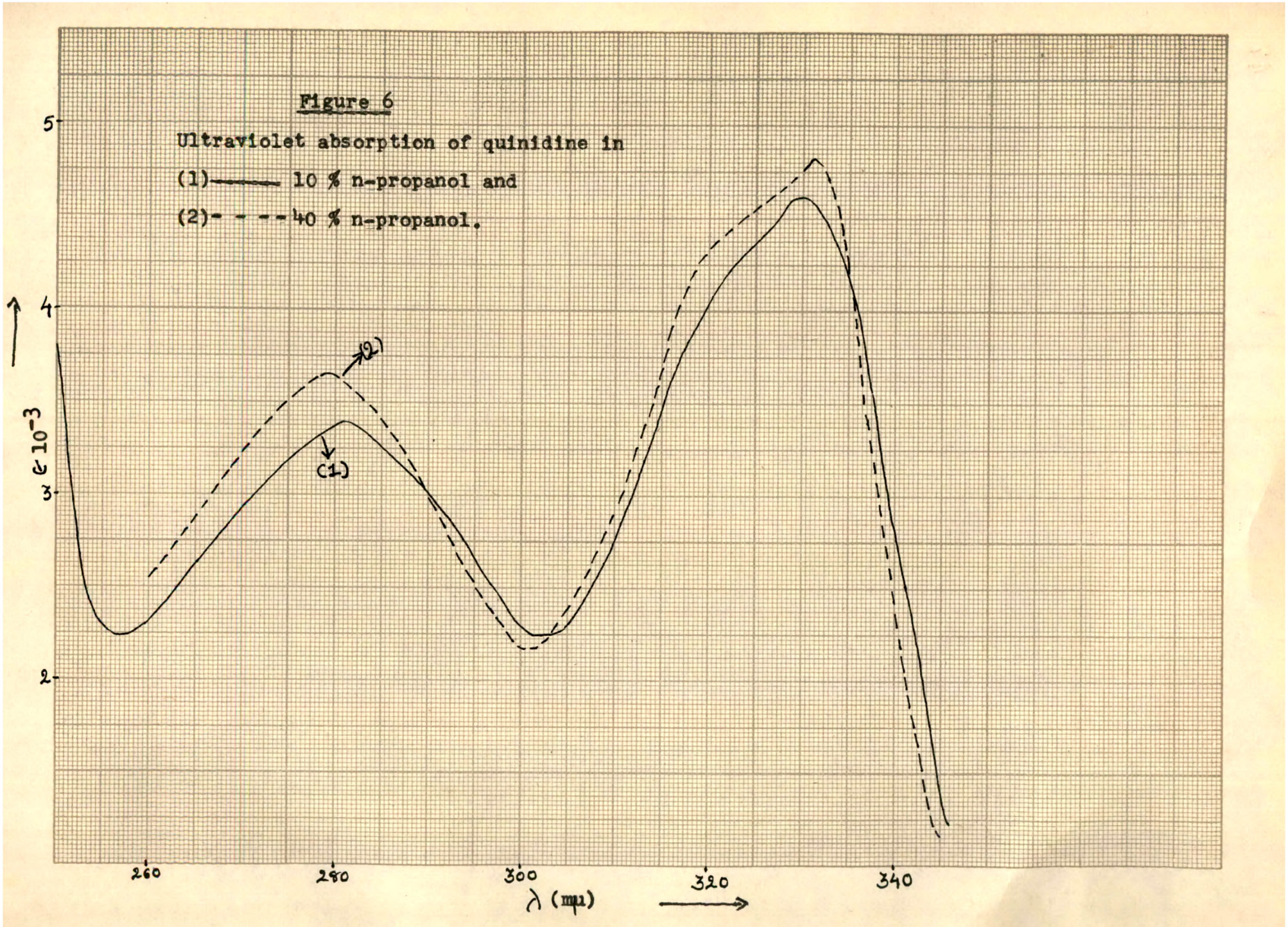
Figure 6
Ultraviolet absorption of quinidine in
(1)——— 10 % n-propanol and
(2)- - - - 40 % n-propanol.
5
4
3
2
ε 10⁻³
(2)
(1)
260
280
300
320
340
λ (mμ)

Table 2.11

Ultraviolet absorption of quinidine in aqueous n-propanols.

% n-Propanol =	0	10	20	40	100
λ			ε/10 =		
250	456	382	357	-	393
254	271	237	245	-	267
258	249	225	241	-	275
260	253	231	248	255	285
264	274	254	270	275	312
268	300	282	298	308	353
272	323	305	318	335	376
276	342	324	328	355	398
278	350	333	347	362	407
279	-	-	350	362	414
280	354	337	352	365	411
281	-	339	350	362	-
282	353	337	347	355	401
284	349	330	340	348	382
288	331	312	320	328	363
292	310	292	298	302	337
296	274	258	257	245	267
300	248	227	230	218	233
302	-	225	226	221	238
304	-	228	236	228	248
305	253	-	-	-	-
306	-	235	245	245	255
310	296	274	279	285	296
314	-	329	341	348	-
315	371	-	-	-	-
316	-	364	378	389	401
320	439	410	422	436	458
324	-	431	447	449	452
325	474	-	-	-	-
328	-	454	459	462	465
329	-	459	462	476	-
330	499	459	465	476	490
331	-	458	471	482	503
332	-	456	465	479	509
333	-	-	459	469	506
334	-	433	447	456	490
335	464	-	-	-	-
340	328	279	270	245	213
346	183	121	104	84	76
350	91	62	50	37	29

Table 2.12

Ultraviolet absorption of cinchonidine in aqueous n-propanols.

% n-Propanol =	0	10	40	100
λ		ε/10 =		
250	159	139	-	204
254	181	169	213	236
258	219	212	264	277
262	261	259	312	338
266	307	306	366	393
270	351	353	414	447
274	393	399	459	494
278	424	431	492	527
282	441	448	504	538
283	-	451	507	538
284	446	454	510	538
286	448	454	507	531
288	450	459	504	531
290	451	455	498	513
294.5	418	418	438	451
298	371	374	384	389
299	-	370	381	385
300	372	374	387	393
301	382	379	390	400
302	385	382	387	393
303	358	374	372	-
306	333	324	309	305
310	264	253	234	222
311	252	242	222	209
312	255	245	237	222
313	-	264	263	258
314	308	289	290	302
315	331	311	305	309
316	322	297	272	262
320	132	108	81	70
325	38	18	24	29

Table 2.13

Maxima and log ϵ of cinchona alkaloids in aqueous alcohols.

Solvent	QN		QND		CN		CND	
	λx	log ϵ	λx	log ϵ	λx	log ϵ	λx	log ϵ
0 % M	280	3.50	280	3.55	289	3.67	289	3.66
	330	3.64	330	3.70	302	3.60	302	3.59
	-	-	-	-	315	3.53	315	3.52
10 % M	280	3.55	282	3.55	-	-	288	3.69
	329-30	3.68	328-31	3.68	-	-	302	3.61
	-	-	-	-	-	-	315	3.51
20 % M	-	-	282	3.56	283	3.68	-	-
	-	-	330-31	3.69	302	3.61	-	-
	-	-	-	-	315	3.52	-	-
40 % M	278-80	3.57	278-80	3.57	-	-	288	3.70
	331	3.70	329-32	3.68	-	-	302	3.61
	-	-	-	-	-	-	315	3.52
100 % M	279	3.59	280	3.60	284	3.72	283	3.72
	332	3.71	332	3.72	300-2	3.59	301	3.60
	-	-	-	-	314	3.48	315	3.48
0 % E	280	3.50	280	3.55	289	3.67	290	3.65
	330	3.64	330	3.70	301	3.60	302	3.59
	-	-	-	-	315	3.53	315	3.52
10 % E	280	3.55	280	3.55	288	3.68	286-88	3.68
	330	3.68	330-31	3.68	301-2	3.60	300-2	3.60
	-	-	-	-	315	3.52	315	3.50
20 % E	-	-	278-82	3.56	286	3.69	284-88	3.68
	-	-	330	3.68	301-2	3.60	301-2	3.59
	-	-	-	-	315	3.51	315	3.50

Table 2.13 (Contd.)

Solvent	QN		QND		CN		CND	
	λx	log ϵ	λx	log ϵ	λx	log ϵ	λx	log ϵ
40 % E	280	3.57	280	3.56	288	3.70	287	3.68
	331	3.70	330-31	3.67	301-2	3.61	302	3.58
	-	-	-	-	315	3.51	315	3.49
100 % E	278-80	3.57	278	3.58	282-84	3.72	282-84	3.70
	332	3.68	332	3.68	300-1	3.59	301	3.58
	-	-	-	-	314	3.46	314-15	3.45
0 % P	280	3.50	280	3.55	289	3.67	290	3.65
	330	3.64	330	3.70	302	3.60	302	3.59
	-	-	-	-	315	3.53	315	3.52
10 % P	280	3.54	281	3.53	287	3.65	288	3.66
	330	3.67	329-30	3.66	301-2	3.57	302	3.58
	-	-	-	-	315	3.47	315	3.49
20 % P	278	3.57	280	3.55	-	-	-	-
	330	3.68	331	3.67	-	-	-	-
40 % P	278-80	3.59	280	3.56	283-88	3.69	284	3.71
	330-32	3.69	331	3.68	301	3.58	301	3.59
	-	-	-	-	315	3.48	315	3.48
100 % P	280	3.61	279	3.62	283	3.74	282-84	3.73
	332	3.71	332	3.71	301	3.61	301	3.60
	-	-	-	-	315	3.50	315	3.49

M = Methanol, E = Ethanol, P = n-Propanol.

2.5

Discussion :

The ultraviolet absorption spectra of the optical isomers quinine and quinidine in a given solvent are similar and so are those of cinchonine and cinchonidine. However, ultraviolet absorption spectra of quinine and quinidine are distinctly different from those of cinchonine and cinchonidine. The values of maxima for the ultraviolet absorption of the alkaloids are practically unaffected by the nature of aliphatic alcohols used. However, the value of logarithm of extinction coefficient, log ϵ , is, in some cases, affected to some extent.

On comparing the ultraviolet absorption of alkaloids in water and in alcohols, the values of maxima of quinine and quinidine are almost unaffected and the value of log ϵ is either not affected or affected by small amount. Same is true for cinchonine and cinchonidine except that first maximum (at lower wavelength) is significantly shifted to lower wavelength side, when solvent is changed from water to alcohol.

It appears that solvent-solute interaction, when the dielectric constant is reduced i.e. when solvent is changed from water to alcohol, does not affect the values of maxima appreciably except the first maximum at lower wavelength for cinchonine and cinchonidine.

The ultraviolet absorption provides a simple and convenient method for the estimation of the alkaloids in aqueous or alcoholic solutions and this was used in further studies.