3. ULTRAVIOLET ABSORPTION STUDIES OF CINCHONA ALKALOIDS.

3. ULTRAVIOLET ABSOPTION STUDIES OF CINCHONA ALKALOIDS : (1)

Introduction :

Earlier (2-10), the ultraviolet absoption of the four major cinchona alkaloids (quinine, quinidine, cinchonine and cinchonidine) and their salts has been studied by a number of workers.

Stimson and Reuter (10) studied the ultraviolet absorption spectra of the four common naturally occuring alkaloids in alcoholic solutions or alcoholic / hydrochloric acid solutions and of some related compounds over a pH range 1-10 to facilitate the estimation of methoxy cinchona alkaloids.

Kanhere, Shah and Bafna (2) studied the ultraviolet absorption spectra of aqueous solutions of four cinchona alkaloid sulfates of different pH (adjusted by addition of sulfuric acid or sodium hydroxide) and the ultraviolet absorption at invarient wavelengths was used for the estimation of the alkaloid sulfates in dilute aqueous solutions.

In this chapter the ultraviolet absorption study of quinidine and cinchonine in twelve aliphatic alcohols is described. The results were used for the estimation of quinidine in the presence of cinchonine.

Experimental :

From samples of cinchona alkaloid sulfates used earlier (Chapter 2) 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 (quinidine from 80 % (by volume) ethyl alcohol and cinchonine from distilled ethyl alcohol (96 %) (), dried at 100°C (± 2) and stored.

The alcohols used were of C.P.grade. Absolute alcohol was obtained by refluxing the distilled ethyl alcohol in presence of anhydrous calcium oxide for six hours and then distilling it.

The ultraviolet absorption was measured with Beckman Model DU. Spectrophotometer using 10 mm. matched quartz cells.

Nomenclature :

λ = wavelength in mμ.

ϵ = extinction coefficient.

λ_X = wavelength at which absorption is maximum.

λ_N = wavelength at which absorption is minimum.

Results :

Figure 1.

Ultraviolet absorption of (A) quinidine (B) cinchonine in methyl alcohol.

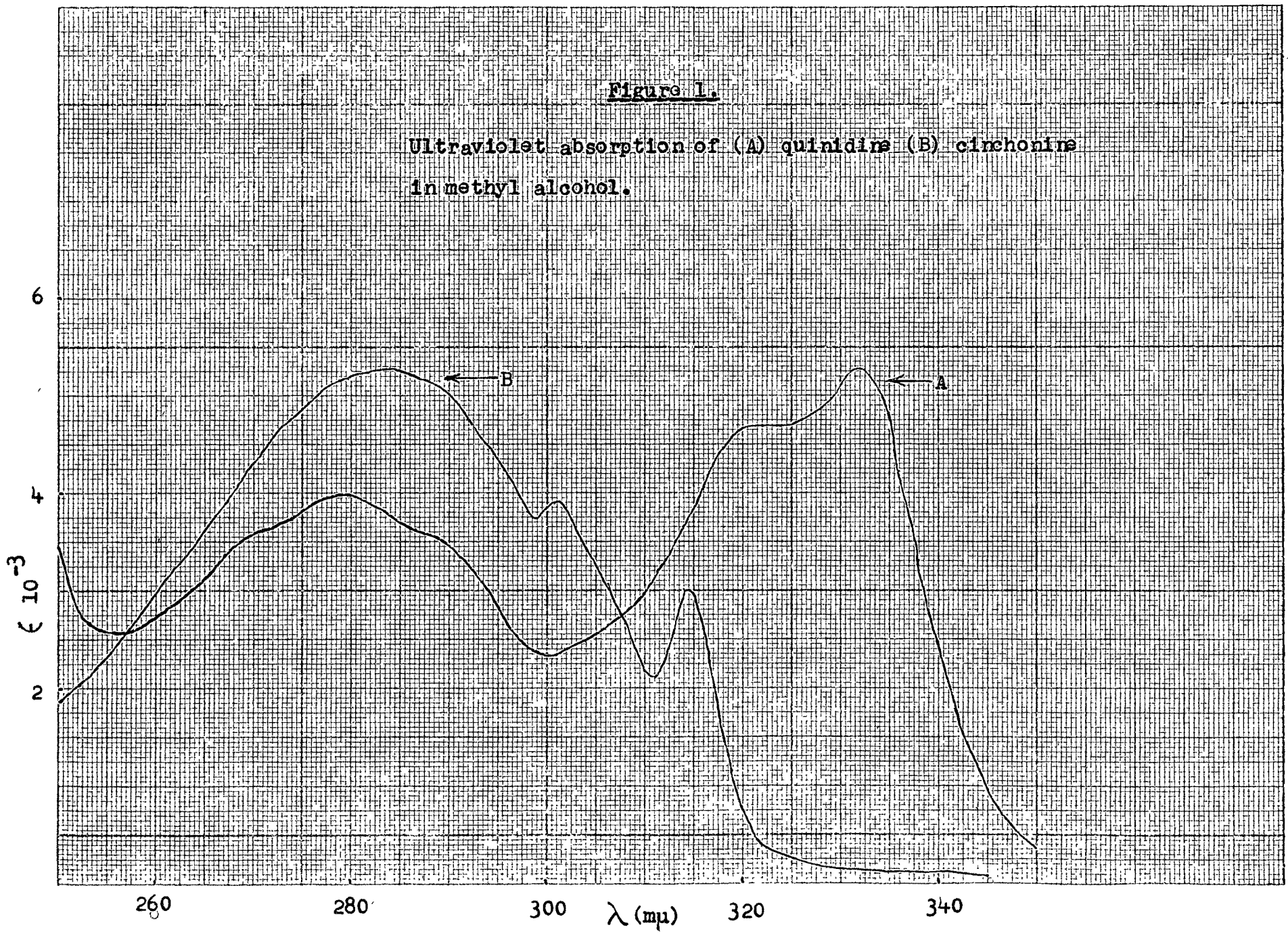

Table 3.01

Ultraviolet absorption of quinidine in methyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
250	347	284	376	316	409
252	281	286	363	318	449
254	260	288	358	320	465
256	257	290	348	322	469
258	264	292	327	324	469
260	276	294	297	326	475
262	285	296	264	328	488
264	302	298	242	330	515
266	322	299	239	331	525
268	345	300	237	332	528
270	358	301	237	333	521
272	363	302	240	334	502
274	371	304	247	336	422
276	388	306	261	338	330
278	396	308	265	340	248
279	399	310	298	342	234
280	399	312	327	346	76
282	389	314	366	350	36

Table 3.02

Ultraviolet absorption of cinchonine in methyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
250	189	282	525	310	218
252	204	284	528	311	212
254	223	286	521	312	227
256	246	288	518	313	257
258	268	290	506	314	302
260	295	292	476	315	299
262	325	294	446	316	261
264	3488	296	416	318	149
266	378	298	382	320	76
268	408	299	378	322	38
270	431	300	386	324	27
272	461	302	386	330	15
274	480	303	369	335	11
276	499	304	340	340	9
278	514	306	302	345	8
280	521	308	261		

Figure 2.

Ultraviolet absorption of (A) quinidine (B) cinchonine in ethyl alcohol (distilled).

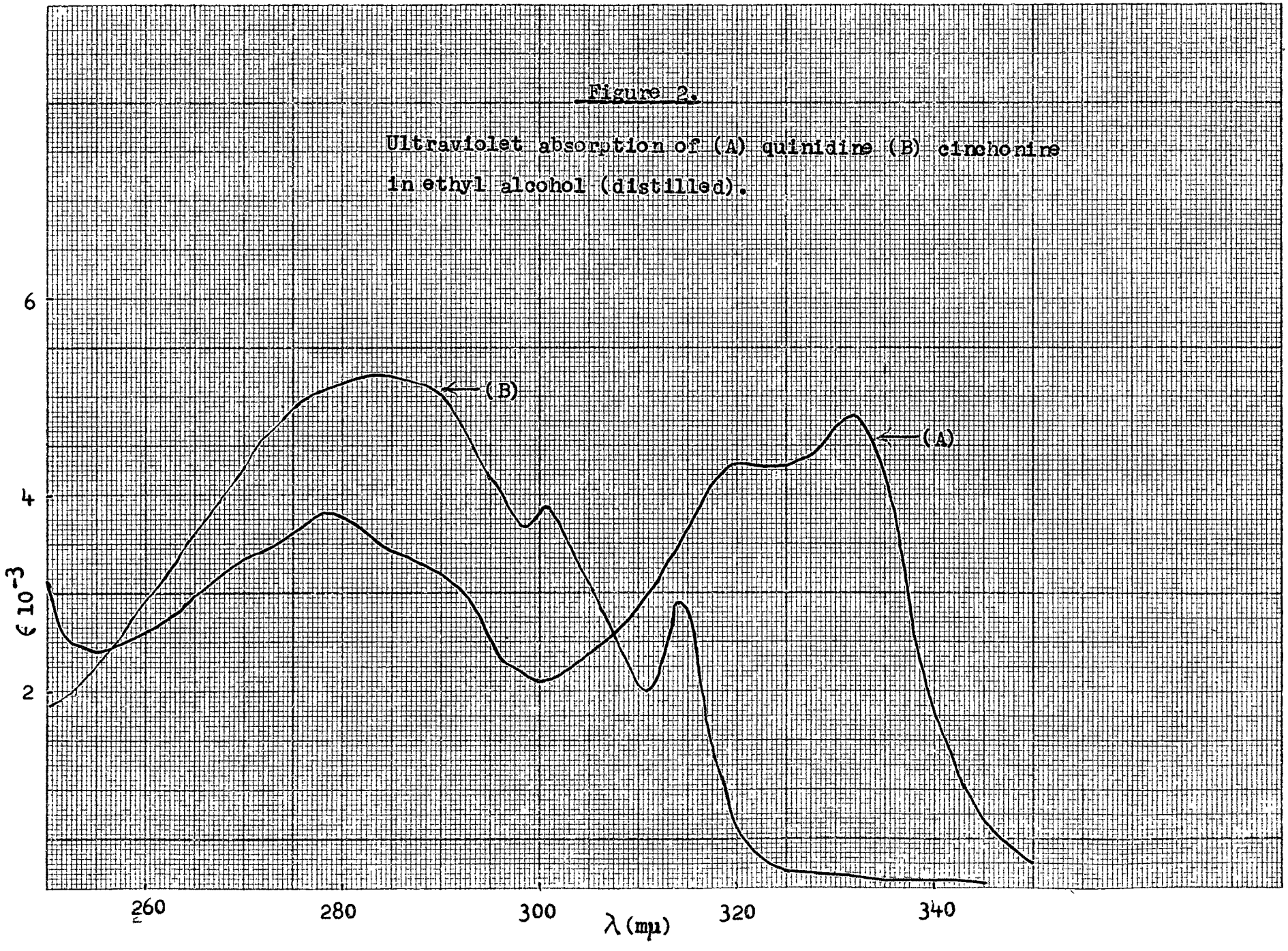

Table 3.03

Ultraviolet absorption of quinidine in distilled ethyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
250	310	282	367	314	345
252	253	284	348	316	386
254	244	286	342	318	418
255	240	288	332	320	430
256	244	290	323	322	430
258	250	292	304	324	427
260	259	294	272	326	437
262	272	296	233	328	443
264	291	298	222	330	468
266	304	299	215	332	481
268	323	300	212	334	456
270	335	301	212	336	386
272	342	302	218	338	285
274	354	304	231	340	209
276	367	306	244	342	136
278	380	308	263	344	85
279	380	310	278	346	57
280	376	312	310	350	25

Table 3.04

Ultraviolet absorption of cinchonine in distilled ethyl alcohol.

λ (mμ)	$\epsilon/10$	λ (mμ)	$\epsilon/10$	λ (mμ)	$\epsilon/10$
250	185	282	523	308	247
252	196	283	523	310	207
254	218	284	523	311	200
256	240	286	515	312	214
258	265	288	515	314	290
260	290	290	501	315	283
262	316	292	472	316	250
264	348	294	425	318	134
266	378	296	407	320	62
268	399	298	370	322	36
270	428	299	370	325	18
272	457	300	385	330	15
274	490	301	385	335	11
276	494	302	374	340	7
278	508	304	327	345	4
280	515	306	290		

Figure 3.

Ultraviolet absorption of (A) quinidine (B) cinchonine in ethyl alcohol (absolute).

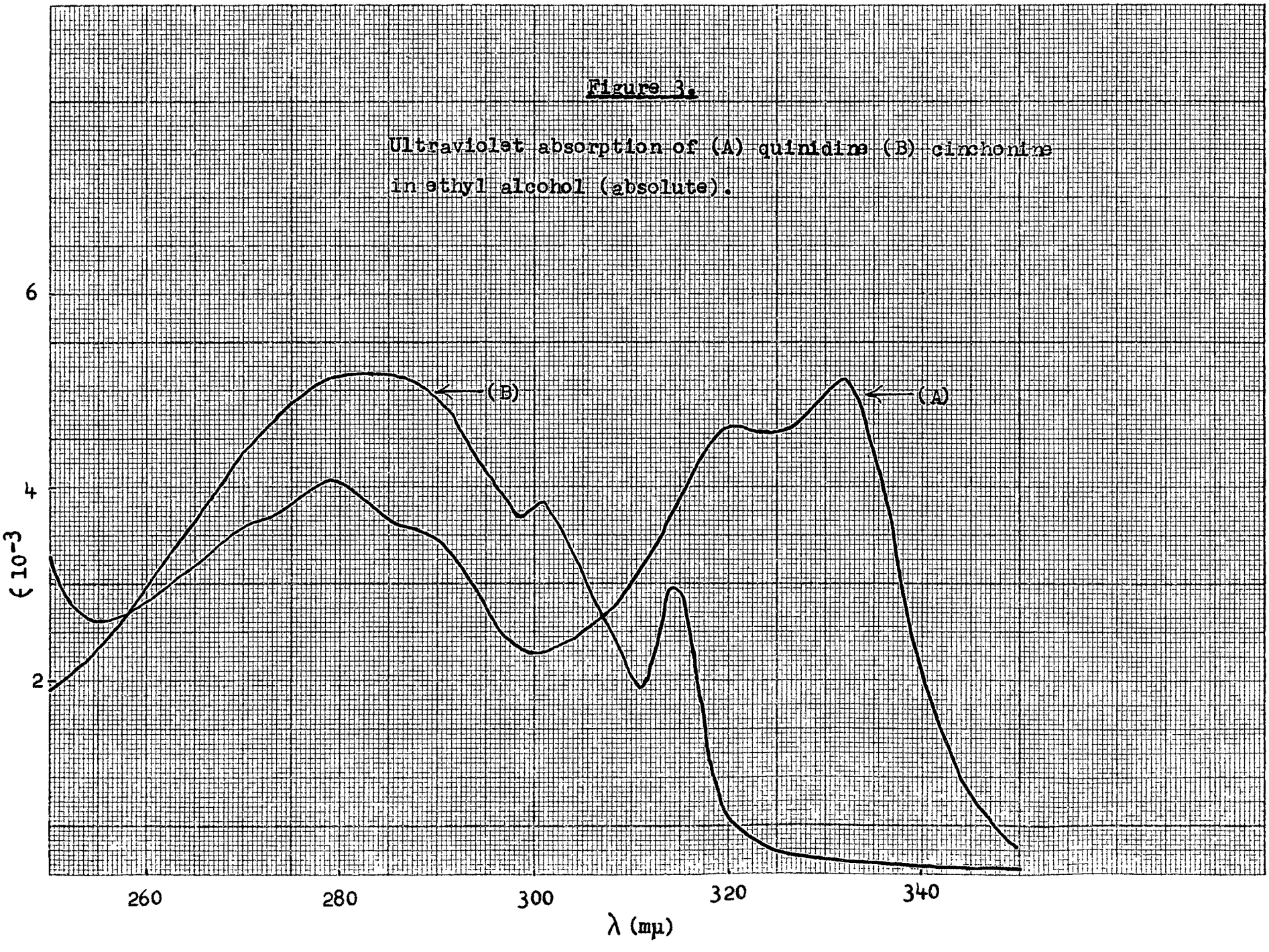

Table 3.05

Ultraviolet absorption of quinidine in absolute ethyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
250	328	282	392	316	404
252	278	284	373	318	442
254	262	286	360	320	461
255	259	288	354	322	458
256	262	290	347	324	458
258	272	292	322	326	461
260	281	294	291	328	474
262	297	296	253	330	498
264	309	298	234	331	502
266	328	300	227	332	512
268	347	301	231	333	502
270	360	302	232	334	479
272	366	304	243	336	398
274	379	306	256	338	300
276	392	308	275	340	215
278	404	310	297	345	76
279	405	312	328	350	28
280	404	314	366		

Table 3.06

Ultraviolet absorption of cinchonine in absolute ethyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	/10
250	190	282	516	310	202
252	206	284	518	311	194
254	227	286	515	312	210
256	245	288	507	313	257
258	269	290	491	314	296
260	297	292	459	315	289
262	325	294	429	316	241
264	348	296	400	318	123
266	376	298	368	320	59
268	404	300	378	325	20
270	435	301	384	330	16
272	459	302	372	335	10
274	480	303	351	340	8
276	495	304	325	345	6
278	507	306	289	350	6
280	514	308	249		

Figure 4.

Ultraviolet absorption of (A) quinidine (B) cinchonine in n-propyl alcohol.

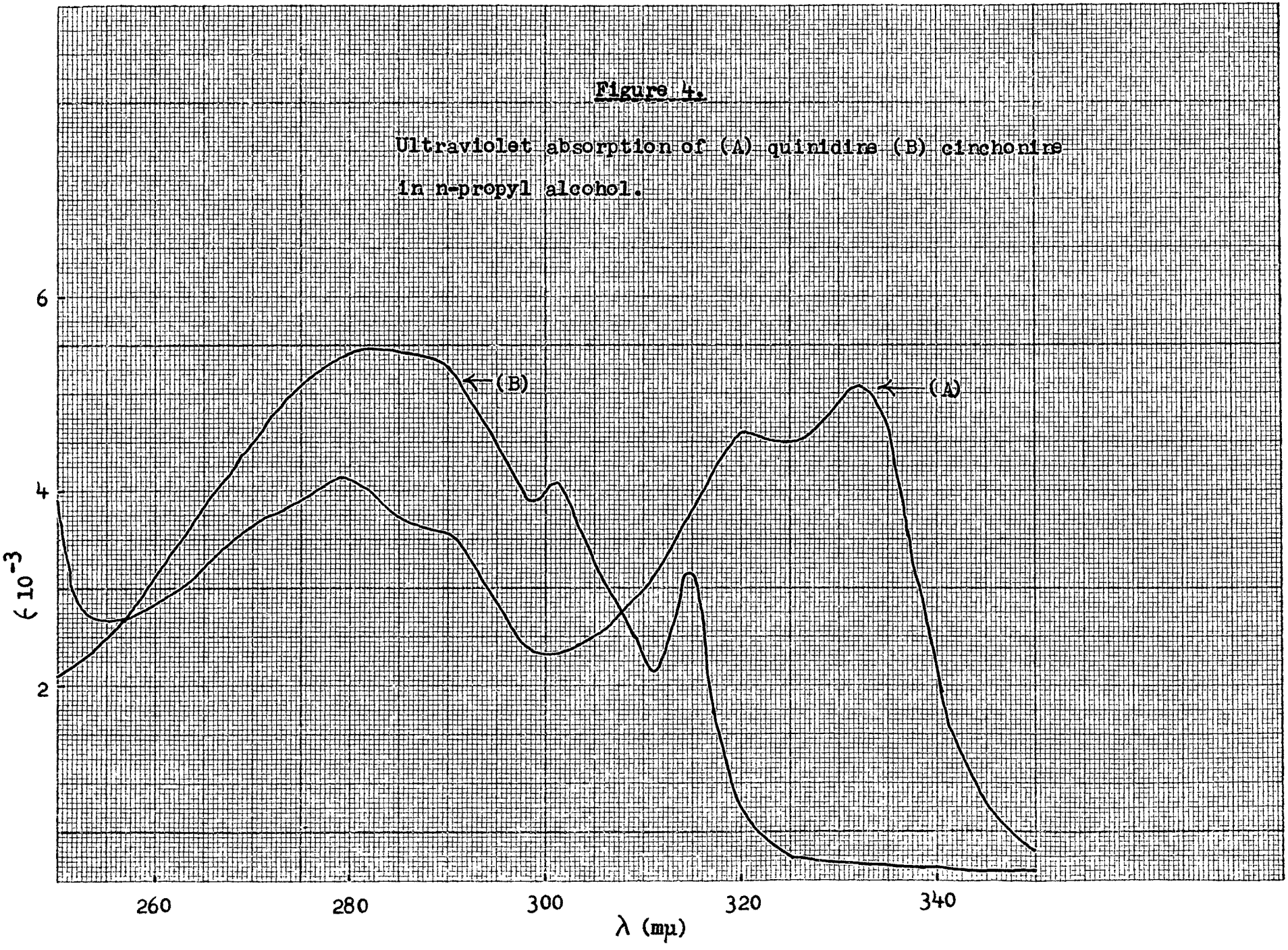

Table 3.07

Ultraviolet absorption of quinidine in n-propyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
250	393	282	401	314	325
252	286	284	382	316	401
254	267	286	372	318	439
255	266	288	363	320	458
256	269	290	357	322	455
258	275	292	337	324	452
260	285	294	302	326	452
262	299	296	267	328	465
264	312	298	242	330	490
266	334	299	236	331	503
268	353	300	233	332	509
270	366	301	234	333	506
272	376	302	238	334	490
274	382	304	248	336	404
276	398	306	255	338	308
278	407	308	283	340	213
279	414	310	296	345	76
280	411	312	325	350	29

Table 3.08

Ultraviolet absorption of cinchonine in n-propyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
250	210	282	545	308	271
252	225	283	547	310	225
254	239	284	543	311	214
256	261	286	543	312	225
258	282	288	540	314	308
260	311	290	529	315	314
262	340	292	492	316	272
264	366	294	463	318	145
266	398	296	427	320	72
268	427	298	392	325	29
270	443	299	391	330	22
272	478	300	402	335	18
274	500	301	409	340	15
276	518	302	402	345	15
278	521	304	348	350	12
280	543	306	307		

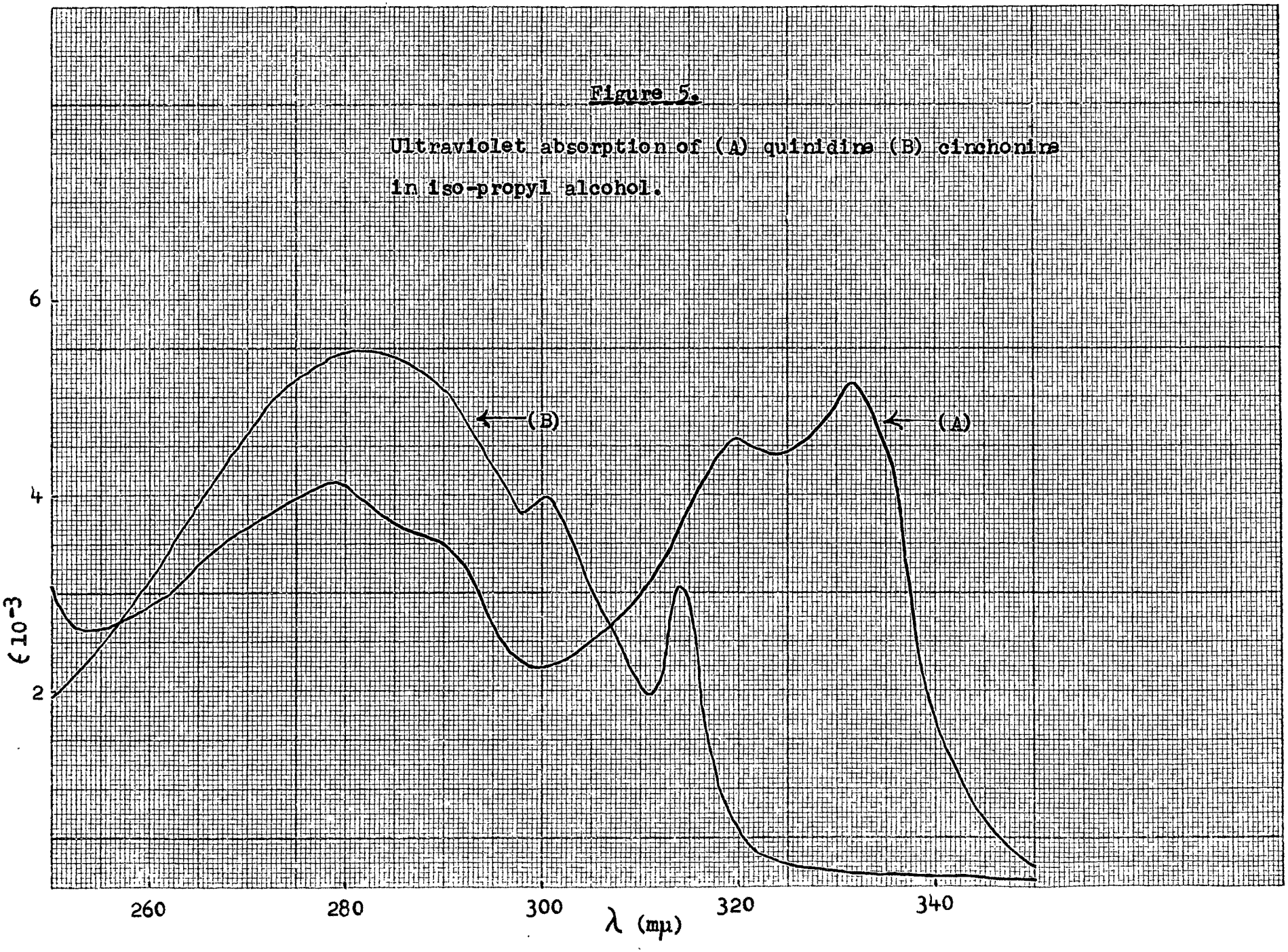
Figure 5.
Ultraviolet absorption of (A) quinidine (B) cinchonine in iso-propyl alcohol.
6
4
2
ε 10⁻³
(B)
(A)
260
280
300
320
340
λ (mμ)

Table 3.09

Ultraviolet absorption of quinidine in iso-propyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
250	307	282	395	316	407
252	269	284	377	318	443
254	260	286	366	320	457
255	263	288	360	322	448
256	264	290	354	324	443
258	275	292	331	326	451
260	286	294	289	328	466
262	295	296	248	330	490
264	319	298	230	331	508
266	336	300	225	332	513
268	354	301	224	333	502
270	366	302	230	334	472
272	377	304	248	336	384
274	384	306	260	338	277
276	401	308	275	340	183
278	410	310	298	345	65
279	413	312	325	350	24
280	410	314	363		

Table 3.10

Ultraviolet absorption of cinchonine in iso-propyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
250	195	282	547	306	287
252	212	283	549	308	247
254	234	284	545	310	204
256	258	286	538	311	194
258	283	288	538	312	212
260	312	290	513	314	305
262	341	292	481	315	298
264	373	294	441	316	240
266	402	296	412	318	116
268	430	298	380	320	54
270	459	299	380	325	22
272	488	300	395	330	14
274	509	301	398	335	14
276	524	302	384	340	11
278	538	303	355	345	9
280	545	304	326	350	7

Figure 6.

Ultraviolet absorption of (A) quinidine (B) cinchonine in n-butyl alcohol.

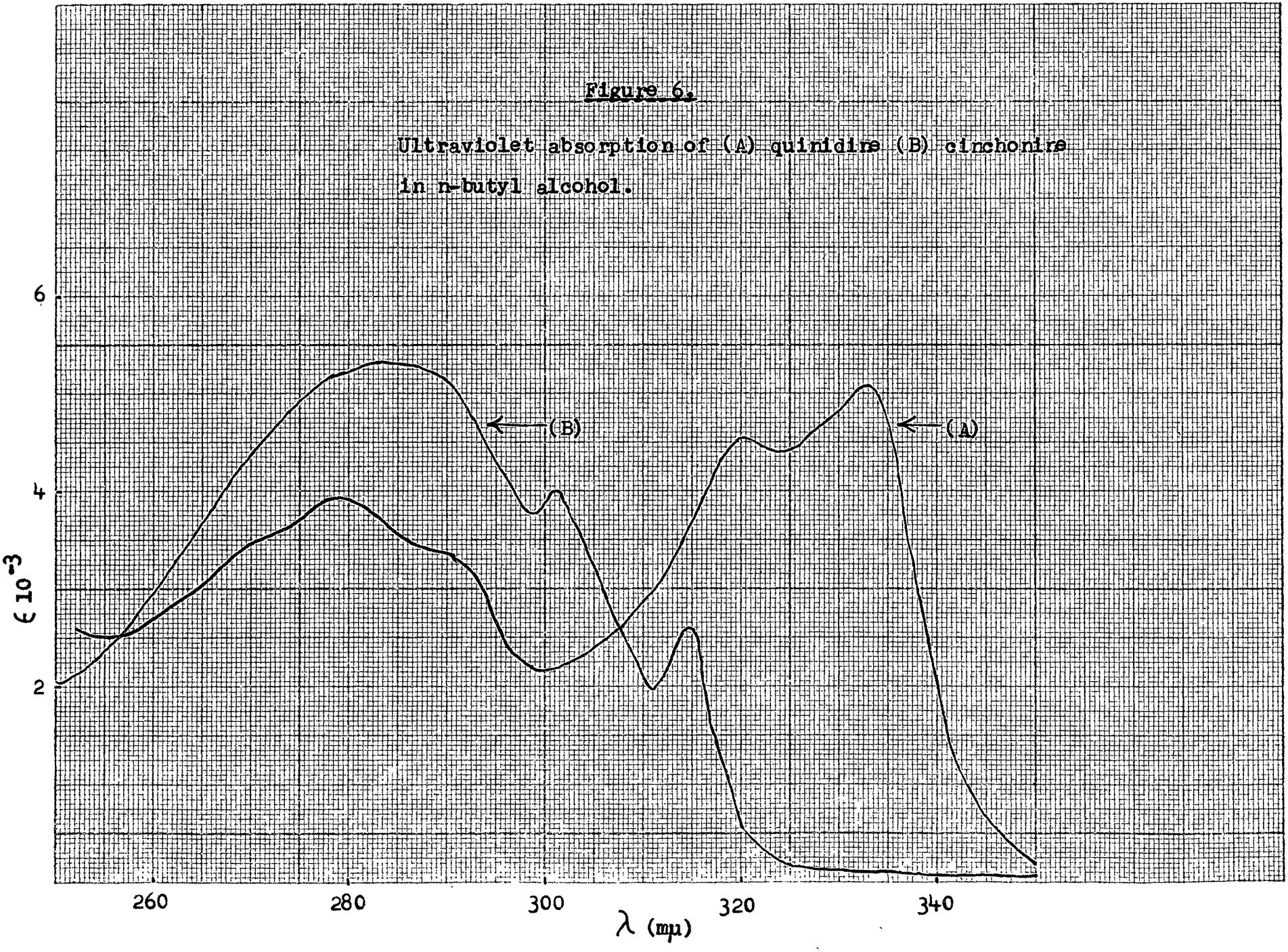

Table 3.11

Ultraviolet absroption of quinidine in n-butyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
252	260	286	349	318	432
254	251	288	343	320	453
255	251	290	340	322	447
256	254	292	325	324	441
258	260	294	288	326	447
260	270	296	242	328	470
262	282	298	224	330	478
264	297	299	218	332	502
266	312	300	216	333	508
268	334	301	217	334	490
270	346	302	221	336	416
272	347	304	233	338	303
274	364	306	248	340	211
276	380	308	263	342	132
278	392	310	288	344	86
280	392	312	309	346	55
282	383	314	349	350	17
284	364	316	392		

Table 3.12

Ultraviolet absorption of cinchonine in n-butyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
250	205	282	532	306	298
252	212	283	532	308	255
254	230	284	532	310	208
256	248	286	532	311	198
258	269	288	524	312	207
260	295	290	514	314	302
262	323	292	482	315	309
264	352	294	442	316	255
266	381	296	417	318	126
268	410	298	381	320	58
270	438	299	377	325	18
272	460	300	388	330	14
274	481	301	398	335	11
276	503	302	391	340	7
278	517	303	370	350	5
280	524	304	341		

Figure 7.

Ultraviolet absorption of (A) quinidine (B) cinchonine in iso-butyl alcohol.

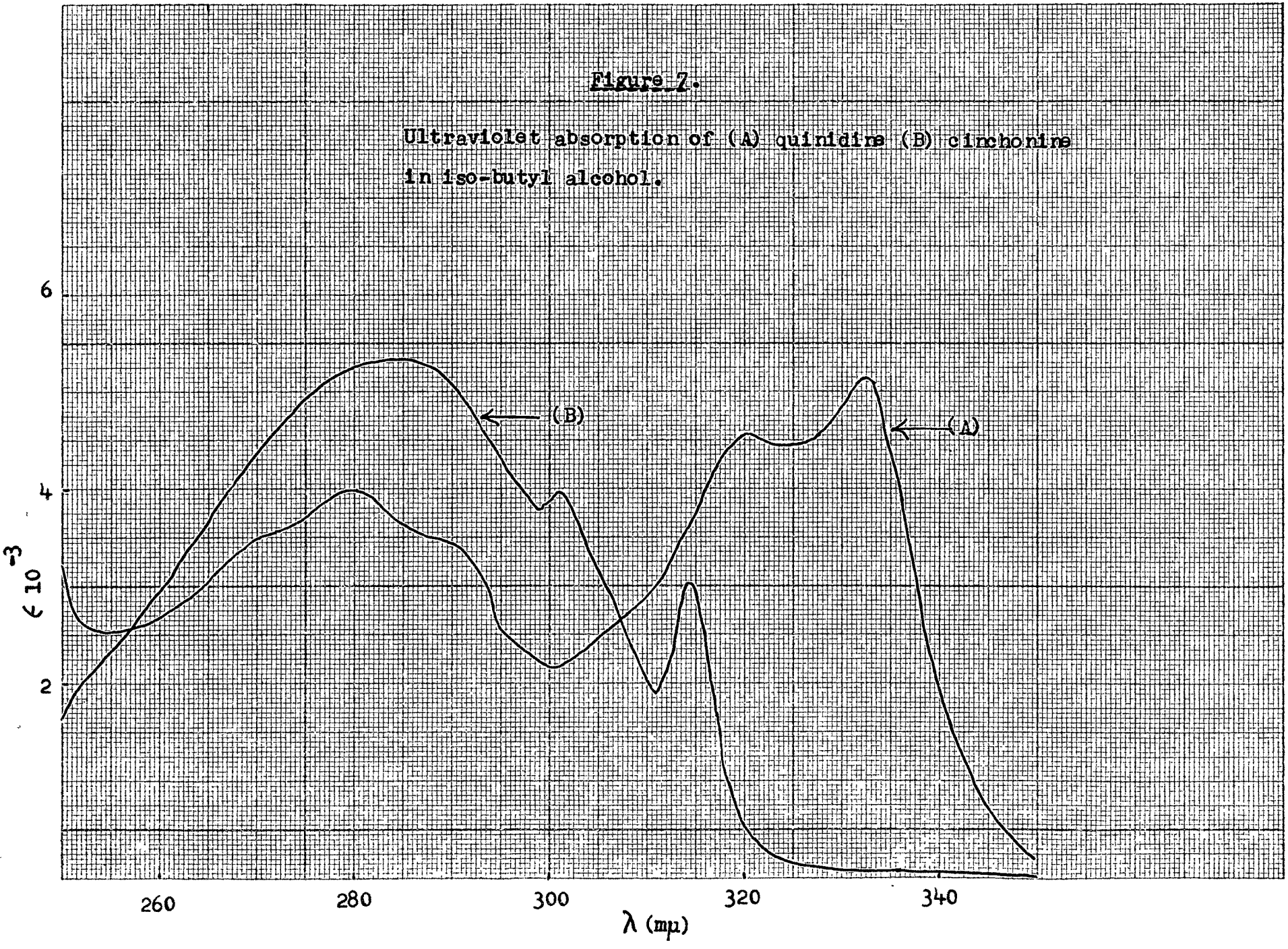

Table 3.13

Ultraviolet absorption of quinidine in iso-butyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
250	321	282	385	314	353
252	263	284	368	316	397
254	251	286	356	318	438
255	248	288	350	320	455
256	251	290	344	322	449
258	257	292	330	324	444
260	269	294	292	326	449
262	280	296	245	328	455
264	292	298	231	330	485
266	315	299	222	331	496
268	333	300	219	332	514
270	347	301	219	333	511
272	353	302	225	334	490
274	362	304	236	336	409
276	379	306	254	338	298
278	394	308	269	340	201
279	394	310	289	345	73
280	397	312	318	350	20

Table 3.14

Ultraviolet absorption of cinchonine in iso-butyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
250	181	282	529	308	252
252	200	283	532	310	203
254	218	284	532	311	192
256	240	286	529	312	207
258	266	288	525	314	296
260	292	290	510	315	303
262	318	292	477	316	252
264	348	294	440	318	122
266	377	296	414	320	56
268	407	298	385	325	15
270	436	299	377	330	11
272	459	300	388	335	7
274	481	301	396	340	7
276	521	302	388	345	4
278	518	304	334	350	4
280	521	306	296		

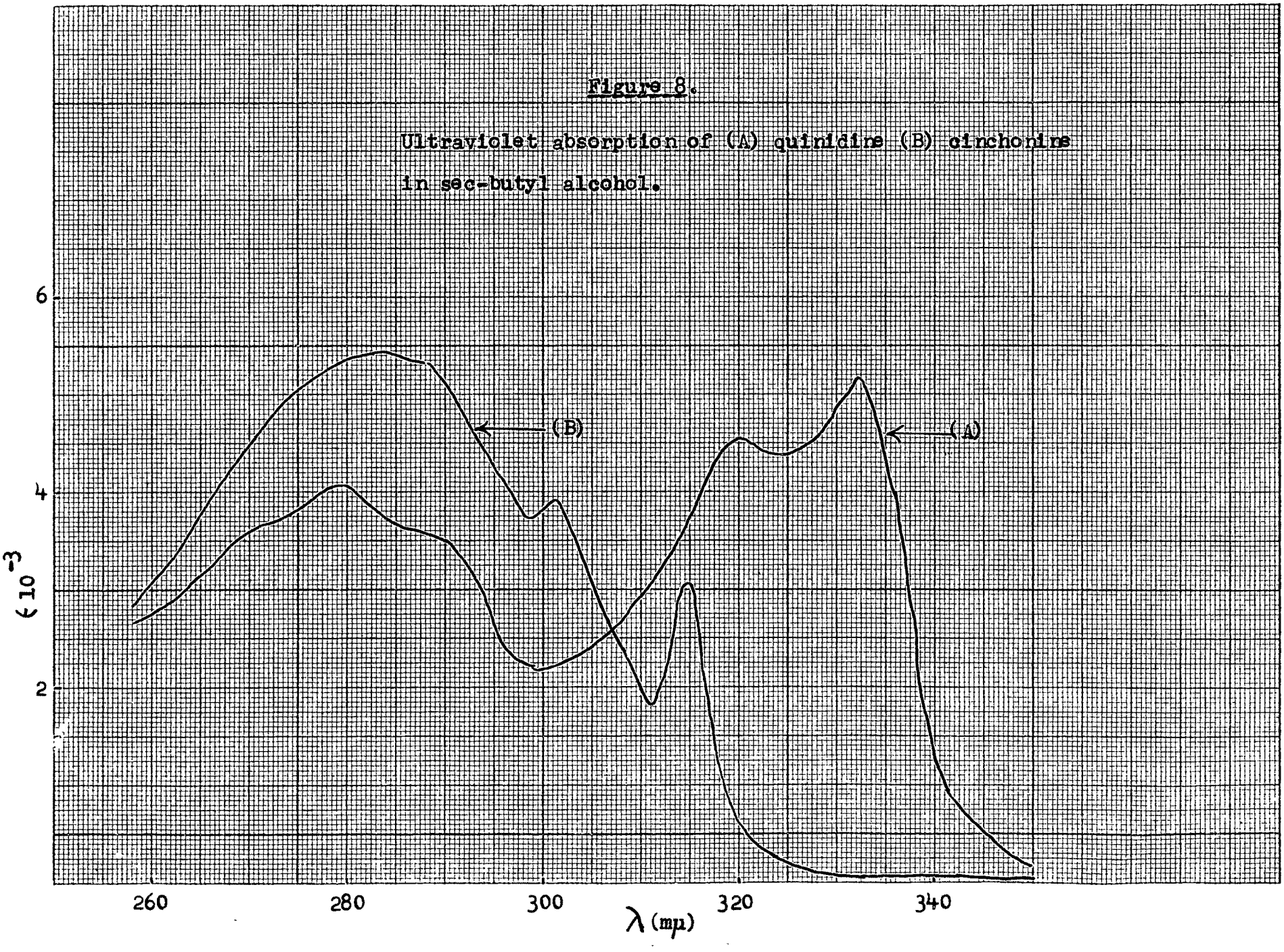

Figure 8.

Ultraviolet absorption of (A) quinidine (B) cinchonine in sec-butyl alcohol.

Table 3.15

Ultraviolet absorption of quinidine in sec-butyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
258	266	288	358	318	443
260	278	290	352	320	455
262	290	292	328	322	443
264	307	294	290	324	437
266	325	296	242	326	443
268	349	298	228	328	455
270	361	299	222	330	485
272	367	300	221	331	497
274	378	302	228	332	517
276	390	304	237	333	497
278	405	306	251	334	473
279	405	308	269	336	387
280	405	310	293	338	272
282	393	312	322	340	177
284	372	314	355	345	56
286	364	316	402	350	15

Table 3.16

Ultraviolet absorption of cinchonine in sec-butyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
258	284	286	537	310	195
260	310	288	530	311	184
262	333	290	515	312	203
264	363	292	477	313	251
266	394	294	443	314	300
268	424	296	413	315	305
270	450	298	378	316	244
272	477	299	375	318	116
274	500	300	386	320	53
276	515	301	390	325	18
278	530	302	386	330	11
280	537	303	356	335	11
282	541	304	326	340	8
283	545	306	284	345	5
284	545	308	240	350	4

Figure 9.

Ultraviolet absorption of (A) quinidine (B) cinchonine tert-butyl alcohol.

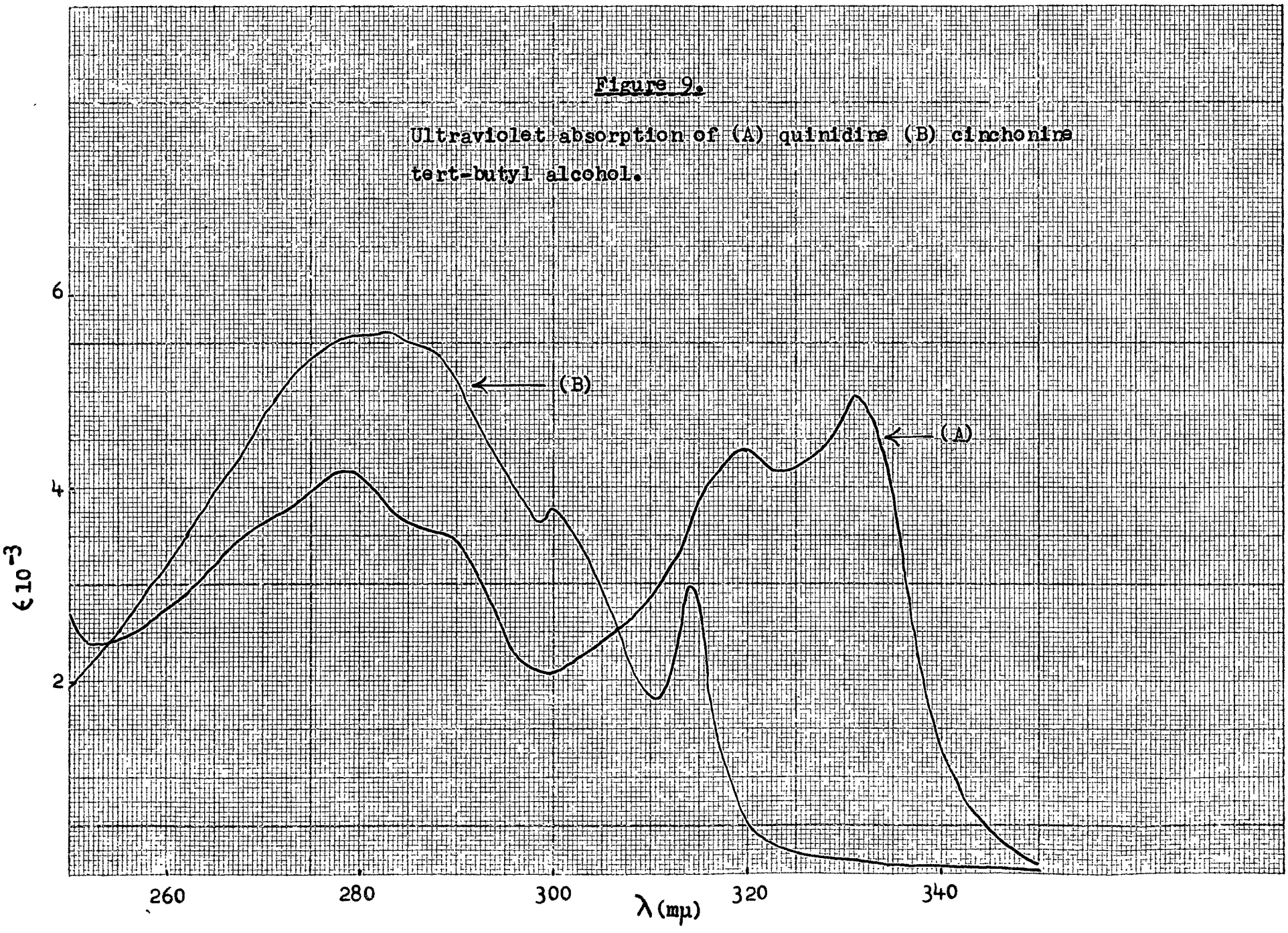

Table 3.17

Ultraviolet absorption of quinidine in tert-butyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
250	270	286	359	320	438
252	241	288	357	322	421
254	243	290	348	326	427
256	247	292	315	328	444
258	261	294	272	330	477
260	275	296	227	331	494
262	292	298	213	332	488
264	309	299	211	333	466
266	331	300	208	334	438
268	348	301	211	336	337
270	365	302	219	338	225
272	371	304	230	340	140
274	387	306	247	342	87
276	404	308	264	344	56
278	416	310	286	346	34
279	416	312	315	348	20
280	413	314	359	350	11
282	393	316	404		
284	371	318	432		

Table 3.18

Ultraviolet absorption of cinchonine in tert-butyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
250	192	282	558	308	231
252	217	283	561	310	185
254	238	284	554	311	181
256	263	286	547	312	199
258	295	288	540	314	298
260	320	290	511	315	284
262	348	292	469	316	217
264	384	294	433	318	107
266	412	296	405	320	53
268	440	298	369	325	21
270	476	299	369	330	18
272	504	300	376	335	14
274	533	301	369	340	9
276	540	302	362	345	7
278	554	304	313	350	7
280	555	306	270		

Figure 10.

Ultraviolet absorption of (A) quinidine (B) cinchonine in n-amyl alcohol.

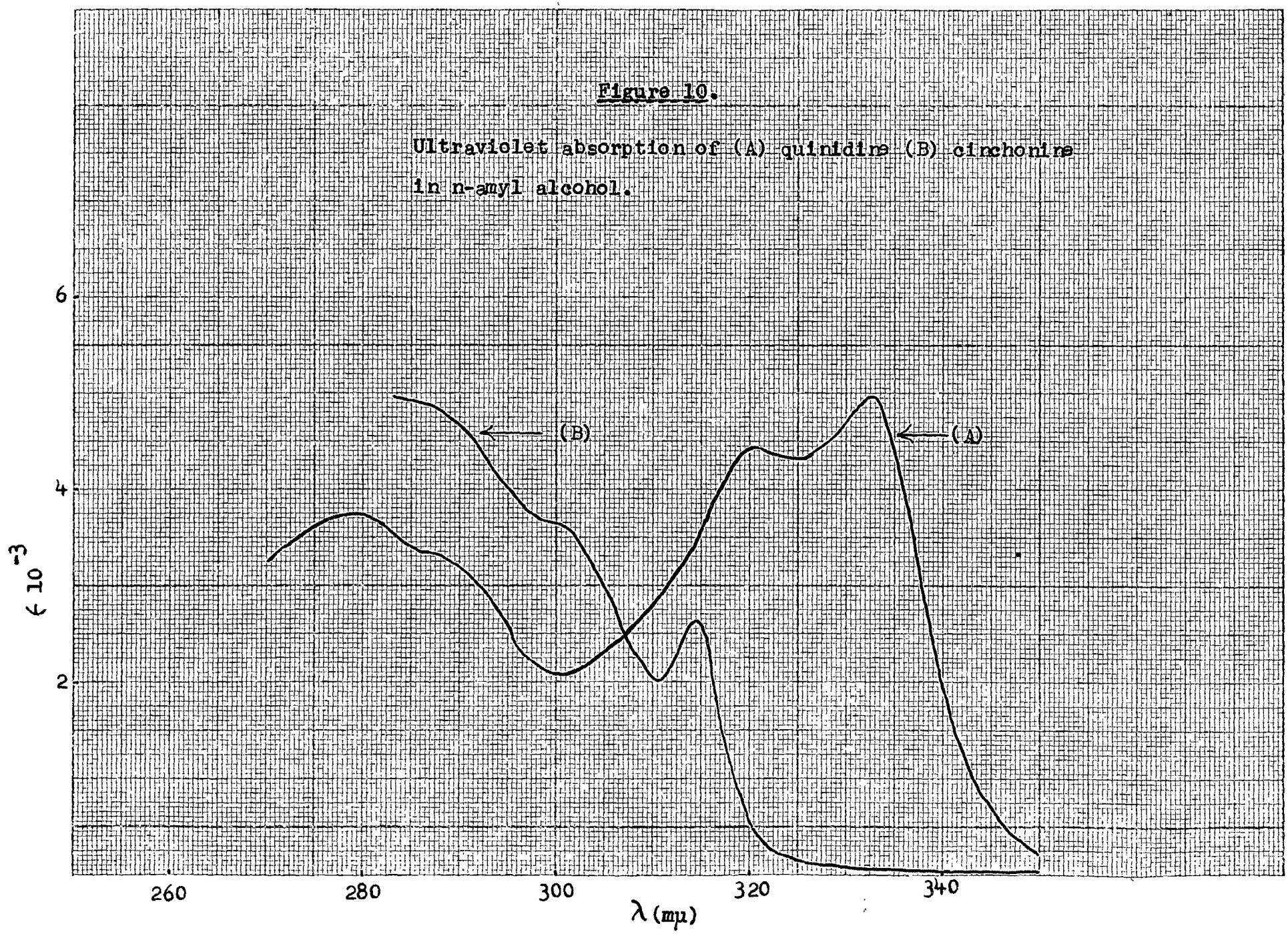

Table 3.19

Ultraviolet absorption of quinidine in n-amyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
270	326	298	218	326	433
272	341	300	212	328	449
274	357	301	209	330	467
276	366	302	212	332	492
278	375	304	224	333	495
279	375	306	243	334	480
280	375	308	258	336	406
282	363	310	280	338	295
284	350	312	304	340	194
286	338	314	338	342	132
288	335	316	381	344	86
290	323	318	424	346	52
292	301	320	443	348	34
294	277	322	437	350	22
296	238	324	430		

Table 3.20

Ultraviolet absorption of cinchonine in n-amyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
283	497	300	365	315	261
284	497	301	361	316	229
286	497	302	358	318	125
288	486	304	322	320	57
290	469	306	275	325	14
292	444	308	236	330	7
294	415	310	204	335	7
296	393	311	200	340	4
298	372	312	215	345	4
299	368	314	261	350	2

Figure 11.

Ultraviolet absorption of (A) quinidine (B) cinchonine in iso-amyl alcohol.

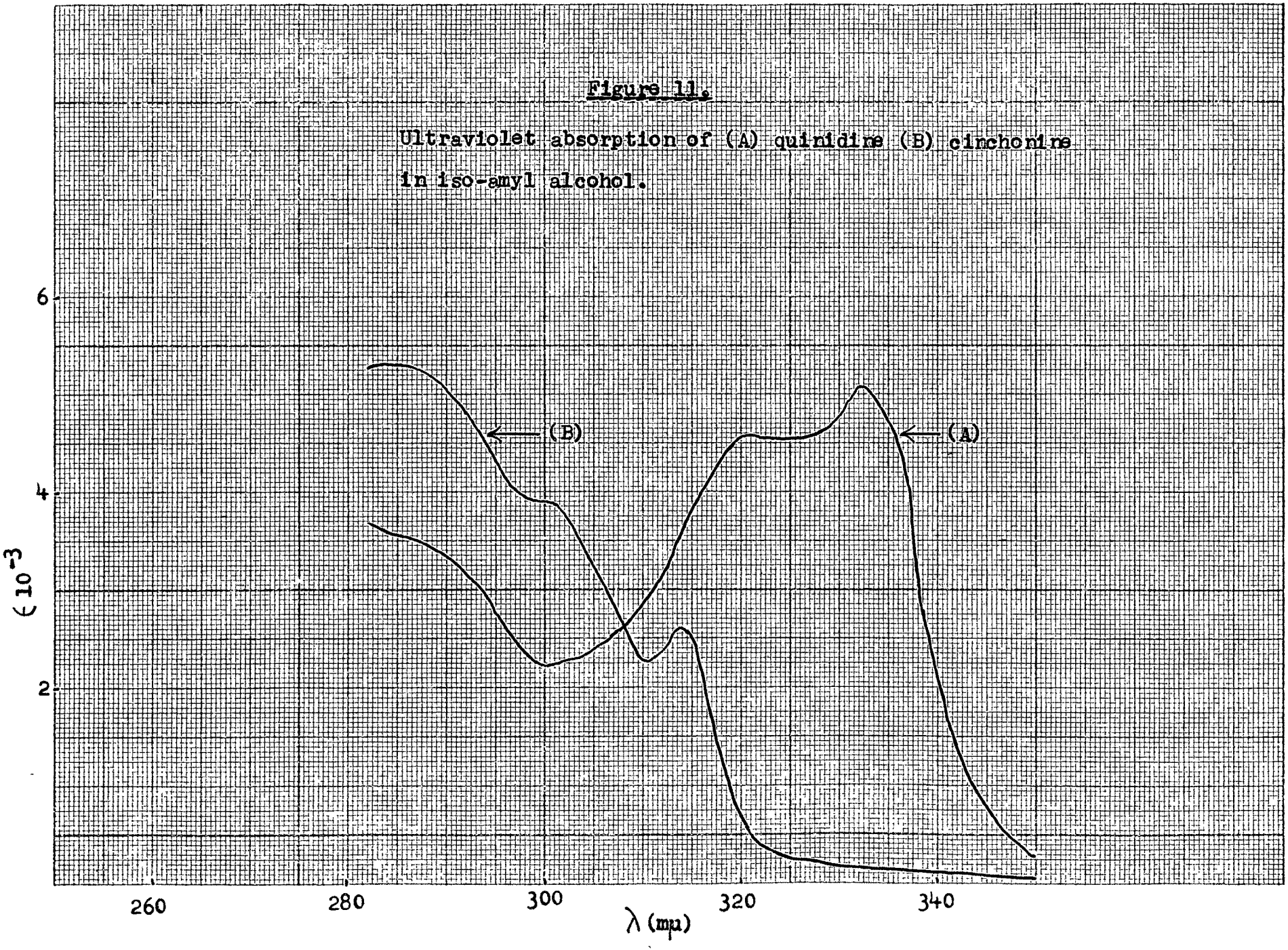

Table 3.21

Ultraviolet absorption of quinidine in iso-amyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
282	367	303	229	324	456
283	364	304	234	326	456
284	359	305	239	328	463
285	357	306	244	330	483
286	354	307	255	331	497
287	351	308	262	332	507
288	346	309	270	333	504
290	336	310	283	334	490
292	321	312	311	336	415
294	290	314	359	338	317
296	260	316	402	339	269
298	234	318	436	340	218
300	223	320	456	345	82
301	222	321	459	350	30
302	224	322	457		

Table 3.22

Ultraviolet absorption of cinchonine in iso-amyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
282	528	301	388	314	261
283	531	302	376	315	252
284	531	303	365	316	227
285	531	304	344	317	179
286	531	305	322	318	135
287	531	306	305	319	92
288	524	307	279	320	71
290	510	308	258	325	225
292	482	309	238	330	18
294	453	310	228	335	17
296	422	311	230	340	13
298	397	312	235	345	10
300	390	313	251	350	9

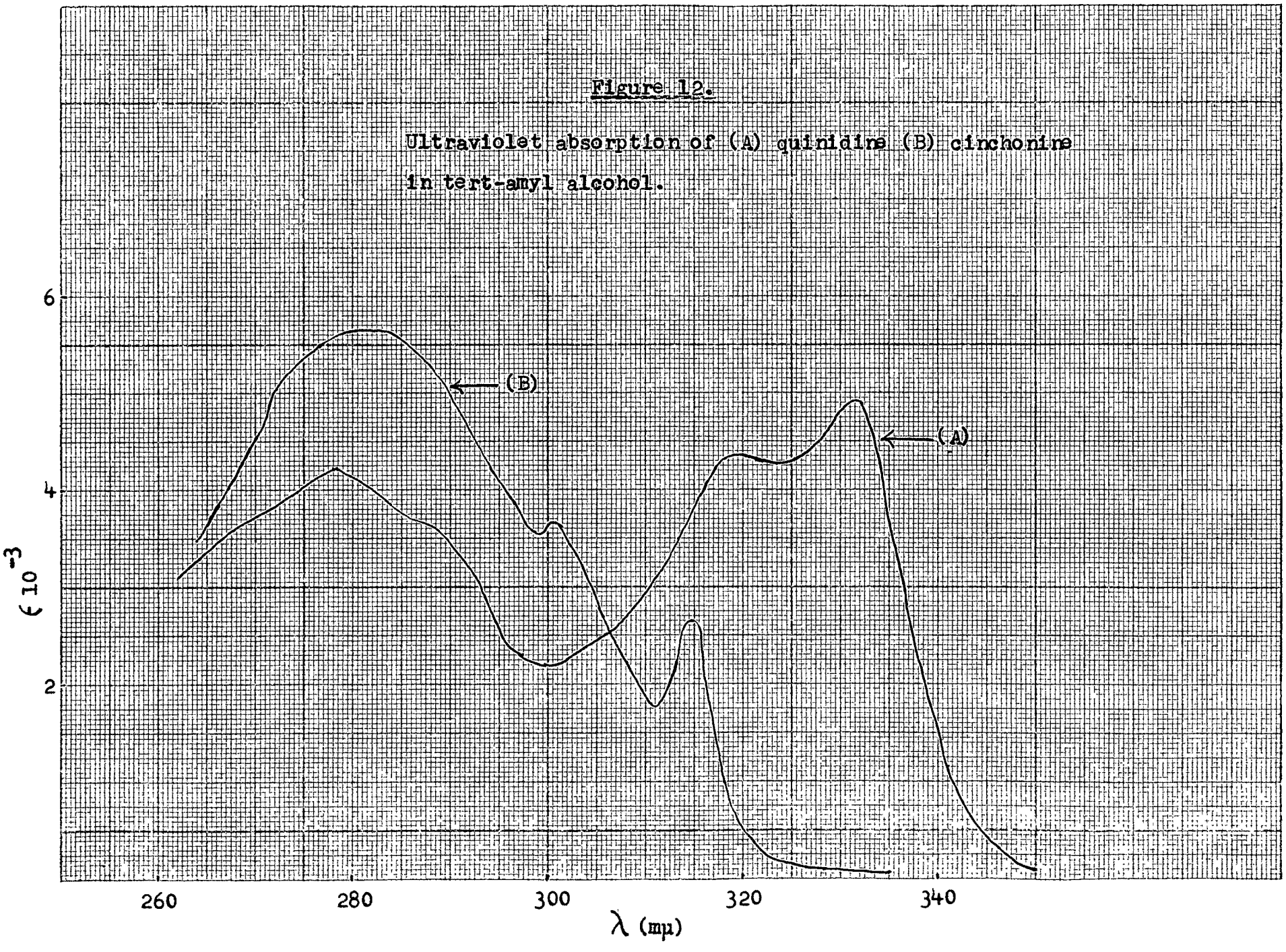
Figure 12.
Ultraviolet absorption of (A) quinidine (B) cinchonine in tert-amyl alcohol.
6
4
2
ϵ 10^{-3}
(B)
(A)
260
280
300
320
340
λ (mμ)

Table 3.23

Ultraviolet absorption of quinidine in tert-amyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
262	306	292	321	322	430
264	324	294	282	324	427
266	345	296	239	326	436
268	360	298	224	328	451
270	372	300	218	330	478
272	382	301	218	331	487
274	394	302	224	332	487
276	409	304	236	333	466
278	418	306	248	334	436
279	415	308	267	336	333
280	412	310	288	338	230
282	400	312	318	340	151
284	382	314	357	345	42
286	369	316	400	350	12
288	363	318	430		
290	348	320	436		

Table 3.24

Ultraviolet absorption of cinchonine in tert-amyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
264	346	288	540	308	220
266	382	290	496	310	180
268	418	292	461	311	176
270	453	294	419	312	187
272	503	296	389	314	259
274	525	298	360	315	263
276	540	299	353	316	223
278	555	300	360	318	108
280	563	301	364	320	50
282	563	302	353	325	11
283	563	303	331	330	5
284	563	304	309	335	3
286	548	306	256		

Figure 13.

Ultraviolet absorption of (A) quinidine (B) cinchonine in n-hexyl alcohol.

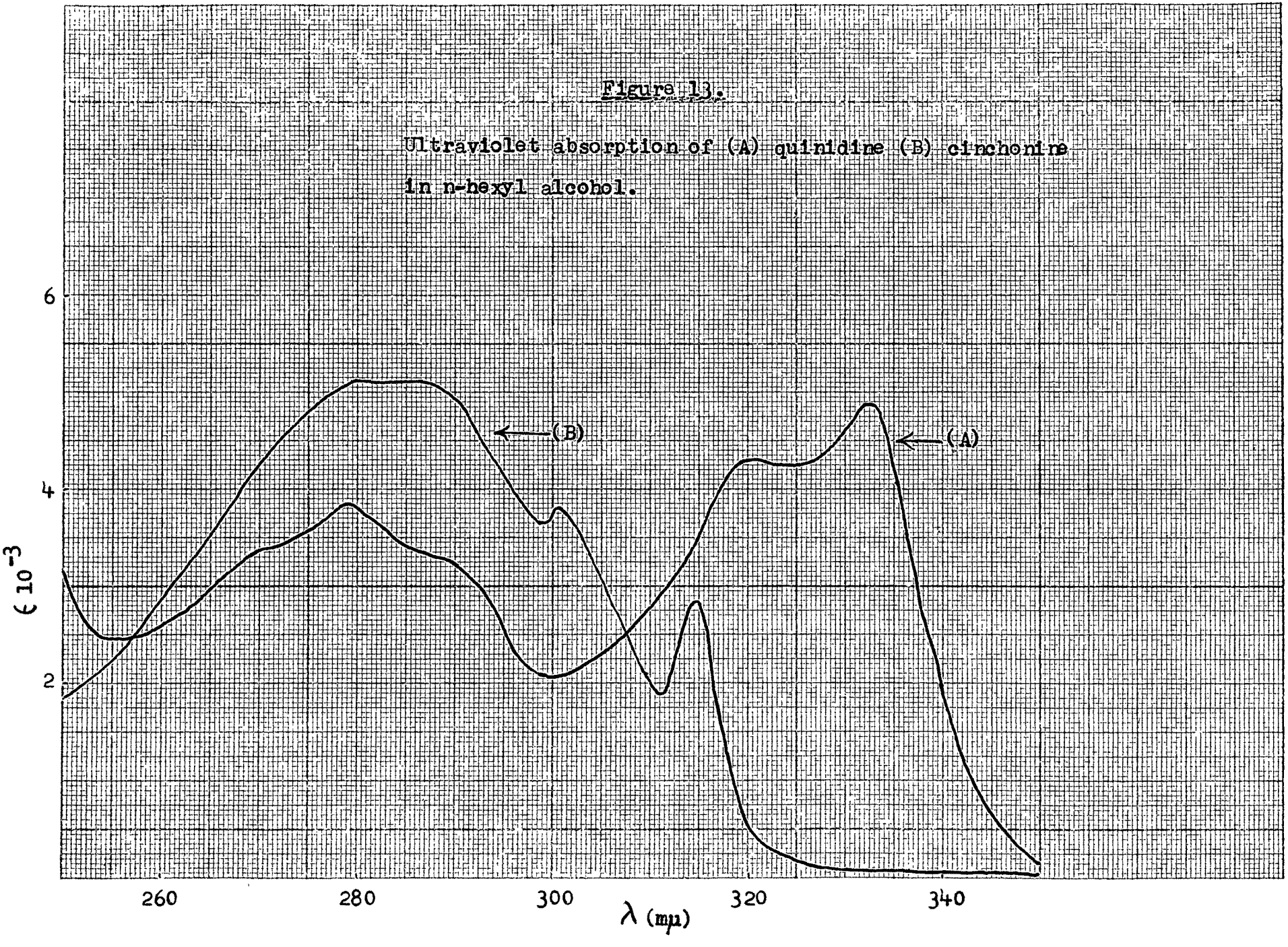

Table 3.25

Ultraviolet absorption of quinidine in n-hexyl alcohol.

λ (mμ)	ε/10	λ (mμ)	ε/10	λ (mμ)	ε/10
250	318	282	368	318	413
252	267	284	349	320	432
253	254	286	337	322	429
254	248	288	330	324	422
255	245	290	324	326	426
256	245	292	308	328	432
258	251	294	280	330	457
260	260	296	234	331	470
262	273	298	216	332	489
264	286	300	207	333	489
266	305	301	207	334	476
268	321	302	210	336	394
270	337	304	224	338	302
272	343	306	235	340	210
274	353	308	254	342	130
276	362	310	275	344	83
278	378	312	299	346	54
279	381	314	330	348	35
280	378	316	375	350	16

Table 3.26

Ultraviolet absorption of cinchonine in n-hexyl alcohol.

λ (mμ)	ϵ/10	λ (mμ)	ϵ/10	λ (mμ)	ϵ/10
250	185	283	511	310	196
252	195	284	511	311	188
254	213	286	508	312	196
256	234	288	508	314	274
258	259	290	497	315	284
260	284	292	462	316	252
262	313	294	426	318	128
264	337	296	398	320	57
266	369	298	369	322	32
268	398	299	366	324	21
270	426	300	369	326	14
272	447	301	380	328	11
274	469	302	368	330	11
276	490	303	348	335	9
278	497	304	327	340	6
280	511	306	271	345	6
282	511	308	244	350	4

Table 3.27

Ultraviolet absorption data for cinchona alkaloids.

alcohol	ε/10 for quinidine at λ_N, 255	λ_X, 279	λ_N, 300	λ_X, 332	ε/10 for cinchonine at λ_X, 284	λ_N, 299	λ_X, 301	λ_N, 311	λ_X, 314
methyl alcohol	257	399	237	528	527	378	386	211	302
ethyl alcohol (distilled)	240	380	212	481	523	370	385	200	290
ethyl alcohol (absolute)	259	405	227	512	518	368	384	194	296
n-propyl alcohol	266	414	233	509	547	391	409	214	314
iso-propyl alcohol	260	413	224	513	549	380	398	194	305
n-butyl alcohol	251	392	216	508	532	377	398	198	309
iso-butyl alcohol	248	397	219	514	532	377	396	192	303
sec-butyl alcohol	-	405	221	517	545	375	390	184	300
tert-butyl alcohol	240	416	208	494	561	369	369	181	298
n-amyl alcohol	-	375	209	495	497	-	361	200	261
iso-amyl alcohol	-	-	222	507	-	-	390	228	261
n-hexyl alcohol	245	381	207	489	511	366	380	188	284

Table 3.28

Analysis of some binary mixtures.

Mixture containing	Solvent	amount of the alkaloids in mgs. present	calculated
quinidine	ethyl	51.2	51.2
cinchonine	alcohol	81.0	81.0
quinidine	methyl	50.5	51.0
cinchonine	alcohol	81.0	81.4

Discussion :

The results indicate that the ultraviolet absorption spectra of quinidine are distinctly different from those of cinchonine. Figures 3.01 - 3.13 give the type of spectra obtained. The maxima and minima Table (3.27) are not significantly affected by the alcohols but the value of the extinction coefficient, ϵ , is, in some cases, affected to some extent. From the study of spectra it is seen that ϵ for cinchonine at 332 mμ is quite small, about 2 - 4 %, of the ϵ for quinidine at the same wavelength. Hence in a mixture of quinidine with cinchonine, the absorption at 332 mμ should enable the estimation of quinidine in the presence of cinchonine in aliphatic alcohols. Table (3.28) gives two examples to illustrate the type of results obtained for the analysis of mixtures of quinidine and cinchonine.

Conclusion :

The maxima and minima for ultraviolet absorption of quinidine and cinchonine are not significantly affected by the change of alcohols but the value of ϵ is affected, to some extent, in some cases. The ultraviolet absorption at 332 mμ may be used for the analysis of the mixtures of quinidine and cinchonine.

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