Asian Journal of Chemistry Vol. 19, No. 1 (2007), 335–346

FTIR, FT Raman and UV-Visible Spectral Measurements and Analysis on Atorvastatin Calcium

S. GUNASEKARAN*, T.S. RENUGA DEVI and P.S. SAKTHIVEL
Postgraduate and Research Department of Physics
Pachaiyappa's College, Chennai-600 030, India

Atorvastatin calcium is the drug of choice in allopathic medicine for the treatment of hyperlipidemia and mixed dyslipidemia. In the present study, the infrared, Raman and UV-Vis spectroscopic measurements are employed for the qualitative analysis of atorvastatin calcium. The different functional group vibrations present in the compound are identified and assigned satisfactorily using the FTIR and FT Raman spectra. The UV-Vis spectral measurements carried out on the compound identify the wavelength maxima λ_{max}. By exposing the drug to various environmental conditions, the qualitative change in the behaviour of the drug is tested by employing internal standard calculations. The interaction of the compound with some trace elemental constituents such as sodium, potassium, calcium, iron and lead have been analysed by employing UV-Vis spectral measurements.

Key Words: Atorvastatin calcium, UV-Visible, FTIR and FT Raman spectra, Qualitative analysis, Trace elements-drug interaction.

INTRODUCTION

Atorvastatin calcium is a lipid lowering agent, it lowers the low density cholestrol (LDL) by inhibiting the HMG–CoA reductase, which is otherwise known as 3-hydoxy-3-methyl-glutaryl-coenzyme-A. Atorvastatin calcium has the chemical name [R-(R*,R*)]2-(4-fluorophenyl)-b,d-dihydroxy-5-(1-methylethyl)-3-phenyl-4[(phenylamino)carbonyl]-1H-pyrrole-1-heptanoic acid, calcium salt (2 : 1) trihydrate. The empirical formula of atorvastatin calcium is $(C_{33}H_{34}FN_2O_5)_2Ca\cdot 3H_2O$ (m.w. 1209.42) (Fig. 1). Karalis *et al.*[1] compared the efficacy and safety of atorvastatin with simuvastatin in patients with dyslipidemia, with and without coronary heart disease. The ability of atorvastatin and simuvastatin to reduce LDL-C and TG concentrations was studied by Olsson and his group[2]. Castano and his co workers[3] compared the efficacy and tolerability of policosanol with atorvastatin in older patients with Type-II hypercholesterolaemia. Stein *et al.*[4] studied the efficacy and safety of ezetimibe co-administrated with atorvastatin. Though investigations on atorvastatin have been made by many, not much work is done on atorvastatin calcium, spectroscopically.

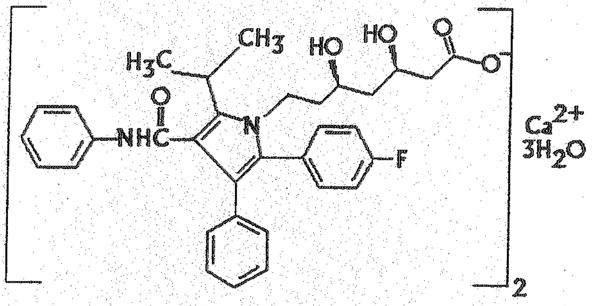


Fig. 1. Chemical structure of atorvastatin calcium

In this work the basic functional groups of atorvastatin calcium are identified and assigned by employing the FT-IR and FT Raman spectra of the compound. UV-Vis spectral measurements are carried out to determine the absorption characteristic of the compound and to check whether there is any change in the behaviour of the drug when it is exposed to different environmental conditions. Also, the behaviour of the drug under the influence of some trace elemental constituents such as sodium, potassium, calcium, iron and lead have also been analysed using UV-Vis spectroscopic measurements.

EXPERIMENTAL

The spectroscopically pure sample of atorvastatin calcium has been procured from Syn Fine Inc., Canada and used as such. The FT-IR and FT Raman spectra of atorvastatin calcium have been recorded using Bruker IFS 66 V spectrophotometer over the regions 4000–4000 cm^{-1} and 4000–50 cm^{-1} respectively at Sophisticated Analytical Instrumentation Facility (SAIF), IIT, Chennai, India. Transmitted light samples are prepared for FT-IR and FT Raman spectra by mixing the sample powder with spectral grade KBr powder, grinding to mix and then pressing to form a semi-transparent disk of KBr containing the suspended sample powder. Both the spectra have been recorded at 303 K. The frequencies of all the sharp bands are accurate to ± 1 cm^{-1}. A spectral width of 4.29 cm^{-1} was used and spectra were measured with a scanning speed of 1.87 cm^{-1} per min. The UV–Vis spectral measurements are carried out using Elico SL–159 UV–Vis spectrophotometer of readability 0.1 nm, repeatability 0.2 nm and drive speed 900 nm/min. The UV–Vis spectra are recorded over the region 200–400 nm at Spectrophysics Research Laboratory, Pachaiyappa's College, Chennai, India.

RESULTS AND DISCUSSION

Vibrational spectral analysis

The FTIR and FT Raman spectra of atorvastatin calcium are given in Fig. 2 (Table-1). By observing the position, shape and relative intensities of the vibrational bands in FTIR and FT Raman spectra of atorvastatin calcium a satisfactory vibrational band assignment has been made.

TABLE-1
VIBRATIONAL SPECTRAL ASSIGNMENT OF ATORVASTATIN CALCIUM

Frequency (cm^{-1})		Assignment
FT-IR	FT Raman	
3365 s	3352 (vvw	N—H stretching
3250 w	—	O—H stretching (asym)
3072 w	3063 (s	O—H stretching (sym)
2971 w	2972 (w	CH_3/CH_2 /C—H stretching
935 vw	2944 (s	CH_3/CH_2 /C—H stretching
2910 vw	2921 (s	CH_3/CH_2 /C—H stretching
1651 ms	1651 (s	C═O stretching
1579 s	1576 vvw	C═O stretching
1552 s	1550 vw	C═C Ring stretching
1524 ms	1524 ms	C═C Ring stretching
1510 ms	1512 s	C═C Ring stretching
1470 w	1470 w	C═C Ring stretching
1436 ms	1416 s	CH_3 deformation
1381 vvw	1398 w	CH_3 deformation
1368 vw	1370 w	CH_3 deformation
1346 w	—	CH_3/CH_2 deformation
1322 vvw	—	CH_3/CH_2 deformation (sym)
1317 s	1319 vw	CH_3/CH_2 deformation (sym)
1304 vvw	1299 vvw	O—H in plane deformation
—	1276 vvw	O—H in plane deformation
1254 w	1259 w	C—C stretching
1242 vw	1224 w	C—N stretching
1216 s	1215 w	C—N stretching/C-O stretching
11 76 vvw	1180 vw	C—C—H in plane deformation
1159 w	1160 w	C—C—H in plane deformation/O-H in plane deformation
1108 vw	1108 vw	C—C—H in plane deformation
1069 vw	1055 vw	C—F stretching
1031 vvw	1034 w	C—C—H in plane deformation
994 ww	999 s	C—C—H in plane deformation
975 ww	969 vvw	C—C—H in plane deformation
925 ww	918 vvw	C—C—H in plane deformation
884 vw	898 w	C—H out of plane deformation
843 s	858 w	C—H out of plane deformation
810 w	825 s	C—H out of plane deformation
746 s	747 vw	C—H out of plane deformation
665 w	670 vvw	O—H out of plane deformation
635 ww	643 vw	O—H out of plane deformation
624 w	617 vw	C—C—C deformation
582 ww	592 vvw	C—C—C deformation
534 vw	531 vvw	C—C—C deformation
505 w	498 vw	C—C—C deformation

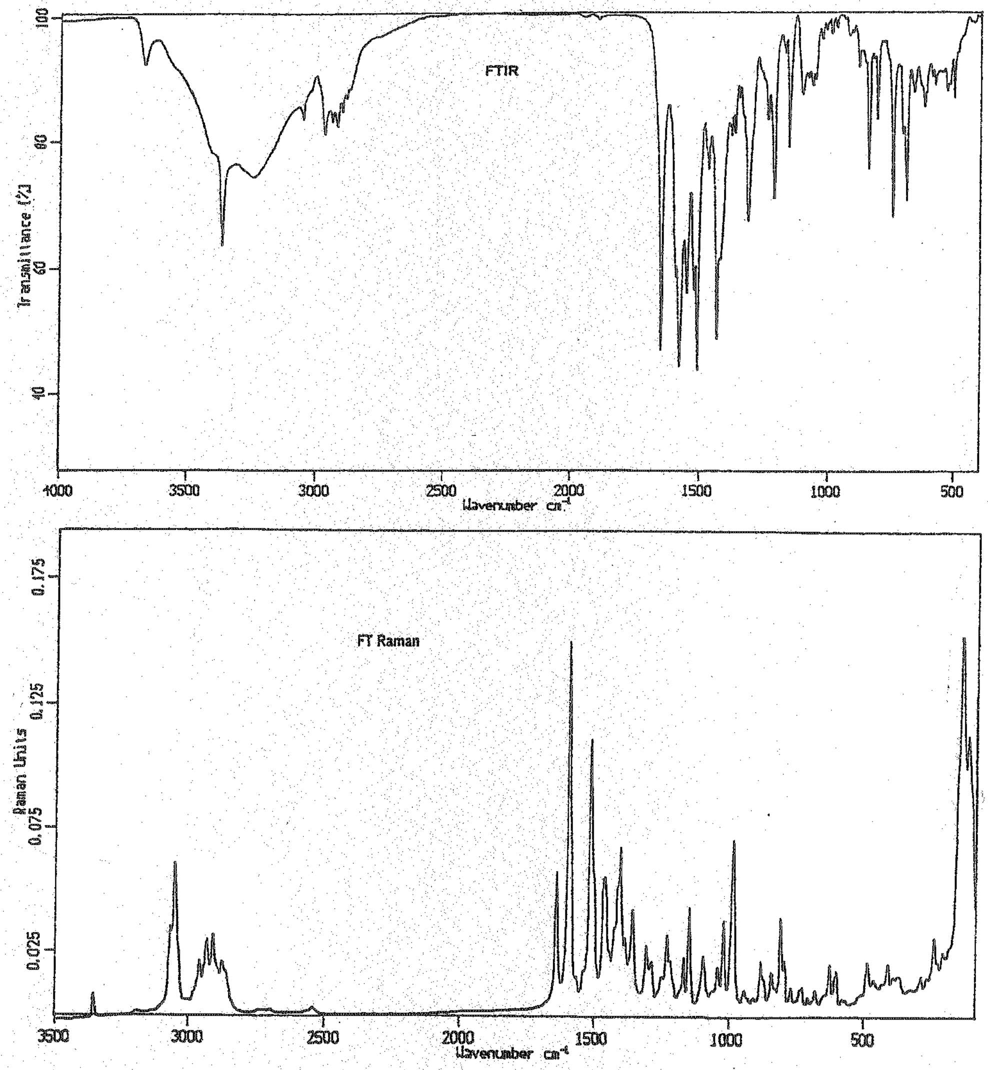


Fig. 2. Vibrational spectra of atrovastatin calcium

N—H vibrations

As solids or liquids, primary aliphatic amines absorb in the region 3450–3250 cm^{-1} and exhibit a broad band of medium intensity. In dilute solution in non-polar solvents, two bands are observed for primary amines due to N—H asymmetric and symmetric vibrations in the range 3550–3250 cm^{-1}. In aromatic compounds medium intensity bands are observed, one at 3520–3450 cm^{-1} and the other at 3420–3350 cm^{-1}. For primary amines in the solid phase the bands are usually observed at 100 cm^{-1} lower than for dilute solutions.

The bands due to N—H stretching vibrations are sharper and weaker than those due to O—H stretching vibrations. Symmetry and asymmetry bands of the N—H vibrations of aminobenzene occur at 3230 and 3461 cm^{-1} respetively[5]. The appearance of the sharp vibrational bands present at 3377 cm^{-1} is allotted as N—H stretching due to the imidazole ring in theophylline. In theobromine the corresponding band is due to the pyrimidine ring of the compound which is allotted to be 3114 cm^{-1} from FTIR spectrum[7]. The assignment of these vibrations has been checked by the presence of these bands in the FT Raman spectrum. Keeping this consideration, the sharp and weak intensity band observed at 3365 cm^{-1} in the FTIR spectrum and the band at 3352 cm^{-1} in FT Raman spectrum of the compound have been assigned to N—H stretching vibration of atorvastatin calcium.

O—H vibrations

Phenols have a broad absorption band at 3620–3590 cm^{-1} due to O—H stretching in the absence of intramolecular hydrogen. The relative intensity of the band due to the hydroxyl stretching vibration decreases with the increase in concentration with additional broader bands appearing at lower frequencies 3580–3200 cm^{-1}. In the present compound the hydroxyl stretching occurs at 3364 cm^{-1} in FTIR and 3363 cm^{-1} in FT Raman spectra respectively[5]. As a result of the presence of hydrogen bonding, carboxylic acids in the liquid and solid phase exhibit a broad band at 3300–2500 cm^{-1} due to O—H stretching vibrations, which sometimes in the lower half of the frequency range has two or three weak bands superimposed on it[6]. A band at 2487 cm^{-1} has been assigned for the carboxylic acid O—H stretching vibrations of nalidixic acid[11]. The broad band absorbed at 3250 cm^{-1} and at 3072 cm^{-1} in the FTIR spectrum and the band at 3063 cm^{-1} in the FT Raman spectrum are allotted as O—H stretching vibrations of atorvastatin calcium. The in-plane O—H deformation generally gives rise to strong band at 1440–1260 cm^{-1}, while out-of-plane deformation results at 700–600 cm^{-1}. The bands at 1299, 1276, 670, 643 cm^{-1} in the FT Raman spectrum are assigned to O—H deformation vibrations of the compound.

C—N vibrations

C—N stretching absorption of primary aliphatic amines is weak and occurs in the region 1090–1020 cm^{-1}. Secondary aliphatic amines have bands of medium intensity at 1190–1170 cm^{-1} and 1145–1130 cm^{-1}. For aromatic and unsaturated amines, two bands are observed at 1360–1250 cm^{-1} and at 1280–1180 cm^{-1}. The identification of the C—N stretching frequency in the side chain is a rather difficult task since there are problems for identifying from the other vibrations. Pandey *et al.*[8] assigned C—N stretching band at 1368 cm^{-1} in benzamides. Silverstein *et al.*[9] assigned C—N stretching absorption in the region 1342–1266 cm^{-1}. The spectra of benzene and pyridyl substituted compounds exhibit a band in the region 1220–1210 cm^{-1}. The band in the region 1222 cm^{-1} in IR and 1226 cm^{-1} in Raman have been assigned to C—N symmetry stretching of the compound fluorouracil[10]. Similarly, the bands observed at 1275 cm^{-1} in IR and 1280 cm^{-1} in Raman have been assigned to C—N asymmetry stretching. In analogy with this the bands observed at 1216 and 1242 cm^{-1} in the FTIR spectrum and the bands at 1224 and 1215 cm^{-1} in the FT Raman spectrum of atorvastatin calcium are assigned due to C—N stretching vibrations.

C—F vibrations

The band due to the C—F stretching vibrations may be found over a wide frequency range, 1360–1000 cm^{-1}. Since the vibration is easily influenced by adjacent atoms or groups, monofluorinated compounds have a strong band at

1110–1000 cm^{-1} due to C—F stretching vibration. With further fluorine substitution, two bands are observed due to asymmetric and symmetric stretching vibrations, those occurring at higher frequencies.

Due to the strong coupling of the C—F and C—C stretching vibrations, polyfluorinated compounds have a series of very intense bands in the region 1360–1090 cm^{-1}. In fluorouracil, the band observed at 1046 cm^{-1} in IR and at 1048 cm^{-1} in Raman have been assigned to C—F stretching[10]. Thus the band observed at 1216 cm^{-1} in the FTIR spectrum and at 1215 cm^{-1} in the FT Raman spectrum of this compound are assigned to C—F stretching vibrations.

C—O and C═O vibrations

Saturated aliphatic ketones absorb strongly in the range 1700–1680 cm^{-1} and this band is shifted from its expected position by a number of parameters due to the adjacent position. The bands due to C—O stretching vibrations are strong and occur in the region 1260–1000 cm^{-1}. In the present compound the strong bands near 1071 cm^{-1} in the IR and 1070 cm^{-1} in Raman are assigned to C—O stretching vibrations[5]. In fluorouracil, the bands observed at 1621 cm^{-1} in IR and at 1617 cm^{-1} in Raman are assigned to C═O symmetry stretching. The bands observed at 1657 cm^{-1} in IR and at 1660 cm^{-1} in Raman are assigned to C═O asymmetry stretching vibration[10]. A strong absorption band due to C═O stretching occurs in the region 1850–1550 cm^{-1}. Because of high intensity and relative interference free region in which it occurs, this band is reasonably easy to recognize. A strong band at 1712 cm^{-1} is assigned for C═O carbonyl stretching of nalidixic acid[11]. The band at 1684 cm^{-1}, which is close to the literature range with due characteristics is assigned for C═O stretching[12] in benzocaine. The C—O bond in the carbonyls is stiffer than the other single bonds due to resonance which leads to localize the high vibration in the C—O bond. Esters conjugated with aromatic ring such as benzoate usually have a strong band near 1280 cm^{-1}. In benzocaine, the very strong and sharp peak at 1281 cm^{-1} has been assigned to the C—O stretching[12]. Keeping this in mind, the sharp band present in the expected region being at 1651, 1579 cm^{-1} in the FTIR spectrum are allotted to be due to C═O stretching vibrations of atorvastatin calcium. A band of medium strong intensity may be found in the region 1325–1115 cm^{-1} for aliphatic ketones. Hence the band at 1216 cm^{-1} in FTIR spectrum and the band at 1215 cm^{-1} in the FT Raman spectrum are allotted to C—O stretching vibration.

Ring vibrations

The bands exhibited in the region around 3000 cm^{-1} can be immediately assigned to be due to aromatic C—H stretchings. The vibrational bands present at 2825, 2954, 3001 and 3057 cm^{-1} in FTIR spectra and the bands found at 2797, 2963, 2980 and 3007 cm^{-1} in the FT Raman spectra are assigned to be due to the C—H stretching of xanthine, caffine, theophylline and theobromine respectively. The bands observed at 862 and 800 cm^{-1} correspond to the vibrations in caffine, 970 and 915 cm^{-1} in theophylline and 889 and 865 cm^{-1} in theobromine in FTIR spectra[7]. The C—C ring stretching vibrations occur in the region 1625–1530 cm^{-1}. For aromatic six member rings, there are 2 or 3 bands in this region due to skeletal vibrations, the strongest usually being about 1500 cm^{-1}. In aminobenzoesaeure, the bands of strong intensity at 1600 and 1422 cm^{-1} are assigned to asymmetric and symmetric vibrations of ring C—C stretching vibrations. The ring symmetry and asymmetry bending vibrations result in bands at 698 and 770 cm^{-1} in FTIR, 700 and 768 cm^{-1} in FT Raman[5]. A sharp band observed at 1442 cm^{-1} in the spectrum of benzocaine has been analysed to C—C symmetry stretching and bands at 1574, 1514, 1453 and 1433 cm^{-1} to C—C asymmetry stretching vibrations. Aromatic ring deformation vibrations occur below 700 cm^{-1}. The ring asymmetry bending results in the bands at 615, 464 and 443 cm^{-1}.[12] In view of this, the vibrational frequencies exhibited at 2971, 2935 and 2910 cm^{-1} in the FTIR spectrum are considered to be due to C—H stretching vibrations of the compound.

The spectral region 1290–1000 cm^{-1} is occupied by a number of C—H in-plane deformation vibrations which are sharp and of weak to medium intensity. Apart from these, this region also contains vibrations due to C—C and C—O stretchings. The sharp bands present at 1176, 1159, 1108, 1069, 994, 975, 925 cm^{-1} are allotted as C—H in-plane deformations. The C—H out-of-plane deformations occur in the range 900–675 cm^{-1} and the bands exhibited at 884, 843, 810 and 746 cm^{-1} in the FTIR spectrum are allotted as C—H out-of-plane deformations.

The symmetrical deformation of the hydrogen atoms of a methyl group results in an absorption band in the range 1385–1370 cm^{-1} which is stable in position. The asymmetrical CH_3/CH_2 deformation gives rise to absorption bands close to 1465 cm^{-1}. In the present case the bands observed at 1346, 1322 and 1317 cm^{-1} in the FTIR spectrum are allotted to be due to CH_3/CH_2 deformations, and the bands at 1368, 1381 and 1436 cm^{-1} are assigned due to deformation vibrations of methyl group and they are confirmed by FT Raman bands.

The fundamental studies on benzene vibrations having the characteristic skeletal stretching modes of the semi–unsaturated carbon–carbon bond lead to the appearance of a group of four bands between 1650 and 1450 cm^{-1}.The bands observed at 1552, 1524, 1510 and 1470 cm^{-1} are allotted as aromatic ring stretching vibrations which are present in both FTIR and FT Raman spectra. Aromatic ring deformation vibrations occur below 700 cm^{-1} and normally the in-plane deformation vibration is at a higher frequency than the out-of-plane deformations. With this note, the bands observed at 624, 582, 534 and 505 cm^{-1} in the FTIR spectrum are allotted as ring deformations. Thus a satisfactory vibrational band assignment has been made available for atorvastatin calcium through infrared and Raman spectroscopy. The remaining bands observed in the spectra may be due to overtones and combinations of fundamental vibrations.

Internal standard calculation and qualitative analysis

The stability of the drug under different storage conditions is one of the quality assurance methods undertaken in the pharmaceutical laboratory. The FTIR spectra have been recorded for pure drug kept in suitable storage condition (airtight container) and for that exposed to sunlight. All the spectral measurements have been normalised. Fig. 3 represents the FTIR spectra of atorvastatin calcium kept under suitable storage conditions and exposed to sunlight. Some specific modes of vibration are identified and the absorbance values are noted under these conditions of exposure.

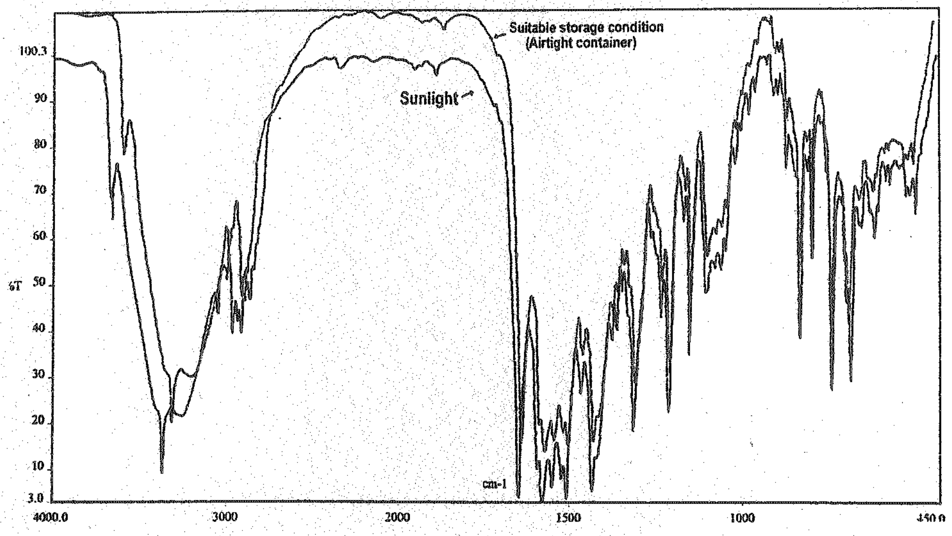


Fig.3. Comparative FTIR spectra of atorvastatin calcium exposed to different storage conditions

The ratios of absorbance among the various modes are calculated, which represents the internal standards. The sets of internal standards of the drug are compared with suitable storage conditions[13, 14] to check whether any change has taken place due to exposure to sunlight. Table-2 summarizes the values of some internal standards of specific modes of vibration under different conditions. A glance at the table shows the internal standard values vary due to exposure and hence the quality and action of the drug are altered and the drugs must always be stored under the proper prescribed conditions.

TABLE-2
INTERNAL STANDARDS CALCULATION UNDER
DIFFERENT STORAGE CONDITIONS

Condtions	3250/ 3365	1579/ 3365	1579/ 1510	3365/ 843	1579/ 843	1552/ 843	1510/ 843	1216/ 843	3365/ 691	3250/ 691	1579/ 691
Airtight container	0.660	1.892	0.981	1.504	2.845	1.977	2.884	1.194	1.169	0.771	2.211
Sunlight	0.233	0.412	0.290	2.401	0.990	2.844	3.411	1.584	1.816	0.424	0.749

UV-Vis spectral measurements

The UV-Vis spectral measurements are carried out on atorvastatin calcium and by checking the sample obeying Beer's law the absorption peaks are identified. The sample is dissolved in methanol and a solution of 3% concentration is prepared and a smooth spectrum is obtained. The spectral recordings show two peaks at 215 and 249 nm. The experiment is repeated for other concentrations. As expected theoretically the absorption level of the peaks increases as the concentration is increased, thus verifying Beer's law[15, 16]. Hence the absorption peak observed at 249 nm is identified as λ_{max}. Fig. 4 shows the UV-Vis spectrum of atorvastatin calcium.

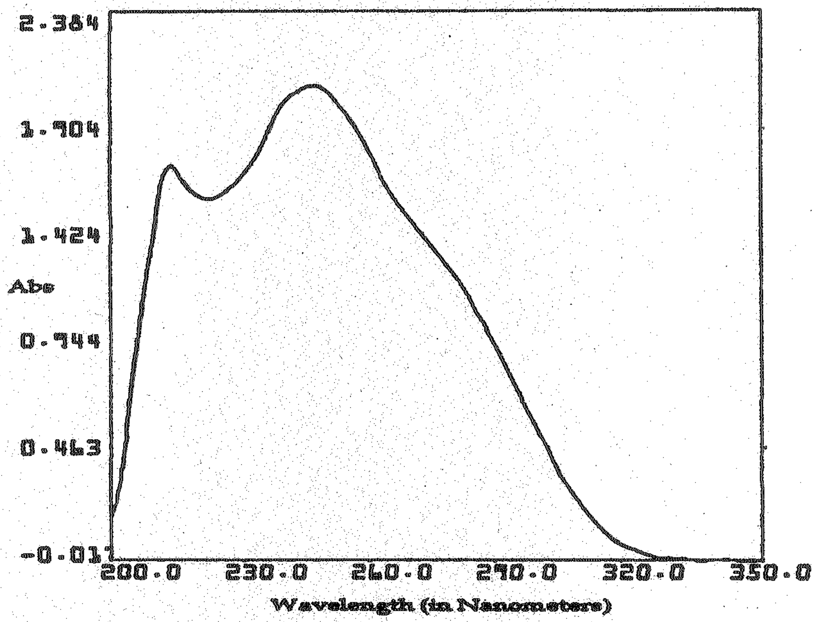


Fig. 4. UV-Vis spectrum of atorvastatin calcium

To investigate whether there is an alteration in the light absorption characteristics, the sample is exposed to sunlight, for a stipulated period and the UV-Vis spectral reording is made. The absorption band was observed around 250 nm, as expected but the amount of absorption has been altered. The slope values of the concentration *vs.* absorbance curves obtained for the drug, atorvastatin calcium kept in suitable storage condition (airtight container) and sun radiation are found to be 0.38 and 0.29 respectively. The variation of absorbance of λ_{max} with concentration under different conditions is given in Fig. 5. It is observed that the drug activity changes more significantly due to improper storage of the drug.

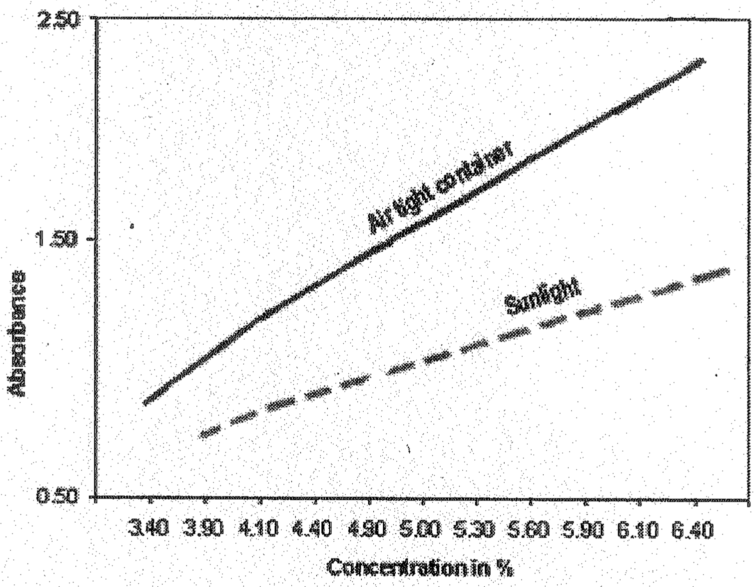


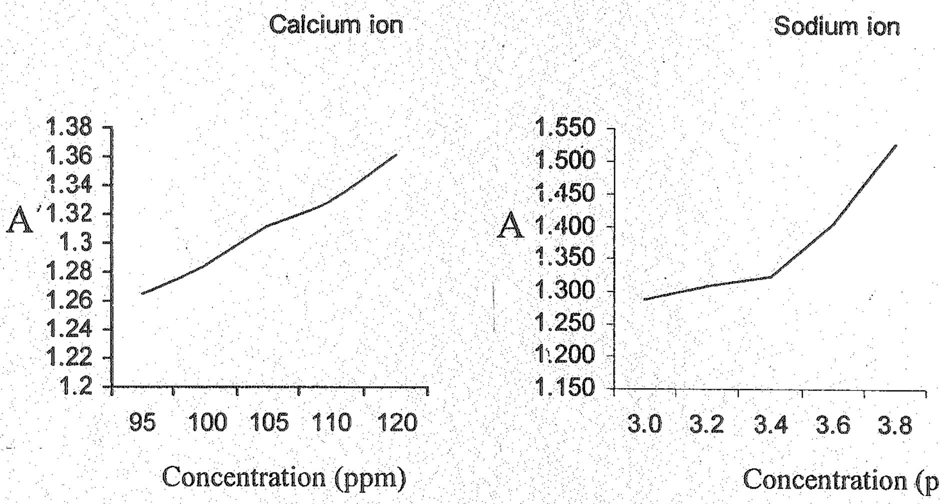
Fig. 5. Variation of absorbance of λ_{max} with concentration under different conditions

TABLE-3
VARIATION OF ABSORBANCE OF λ_{max} OF ATORVASTATIN CALCIUM WITH TRACE ELEMENTAL CONSTITUENTS

Ca^{2+}		Na^{2+}		Pb^{2+}		K^+		Fe^{2+}	
Conc. (ppm)	Absorb.	Conc. (ppm)	Absorb.	Conc. (ppm)	Absorb.	Conc. (ppm)	Absorb.	Conc. (ppm)	Absorb.
95	1.266	3.0	1.290	0.010	2.57	44	1.125	1.300	2.477
100	1.285	3.2	1.311	0.015	2.49	45	1.134	1.350	2.277
105	1.312	3.4	1.326	0.020	2.34	46	1.153	1.400	2.031
110	1.329	3.6	1.406	0.025	2.24	47	1.177	1.450	1.941
120	1.361	3.8	1.527	0.030	2.13	48	1.202	1.500	1.853

The biological activity of the drugs can be considerably reduced or abolished by introducing a chemical change in the drug molecule. Some drugs are chelating agents which are capable of combining with certain metallic ions like lead, mercury, arsenic, copper or iron.

The influence of the drug atorvastatin calcium in the presence of metallic ions like calcium, sodium, lead, potassium and iron are studied using UV-Vis spectroscopy in the present study. The trace elemental constituents of normal human blood contain the metallic ions namely Ca, Na, K, Fe and Pb with permissible ranges 99–120, 3.18–3.8, 45–48, 1.28–1.5 and 0.010–0.028 ppm respectively[17]. The solutions containing these metallic ions are prepared in the characteristic concentration level (ppm) and for each ppm level the spectrum is recorded. The variations of the absorbance level of the drug are noted with various concentrations and the values are summarized in Table 3. The variation in the absorption level of atorvastatin calcium with trace elemental constituents is represented graphically in Fig. 6. It is observed that the activity of the drug is very much influenced by the trace elemental interactions in the body.


Calcium ion

Sodium ion

Fig. 6. Variation of absorbance of λ_{max} of astorvastatin calcium with trace elemental constituents (*Contd.*)

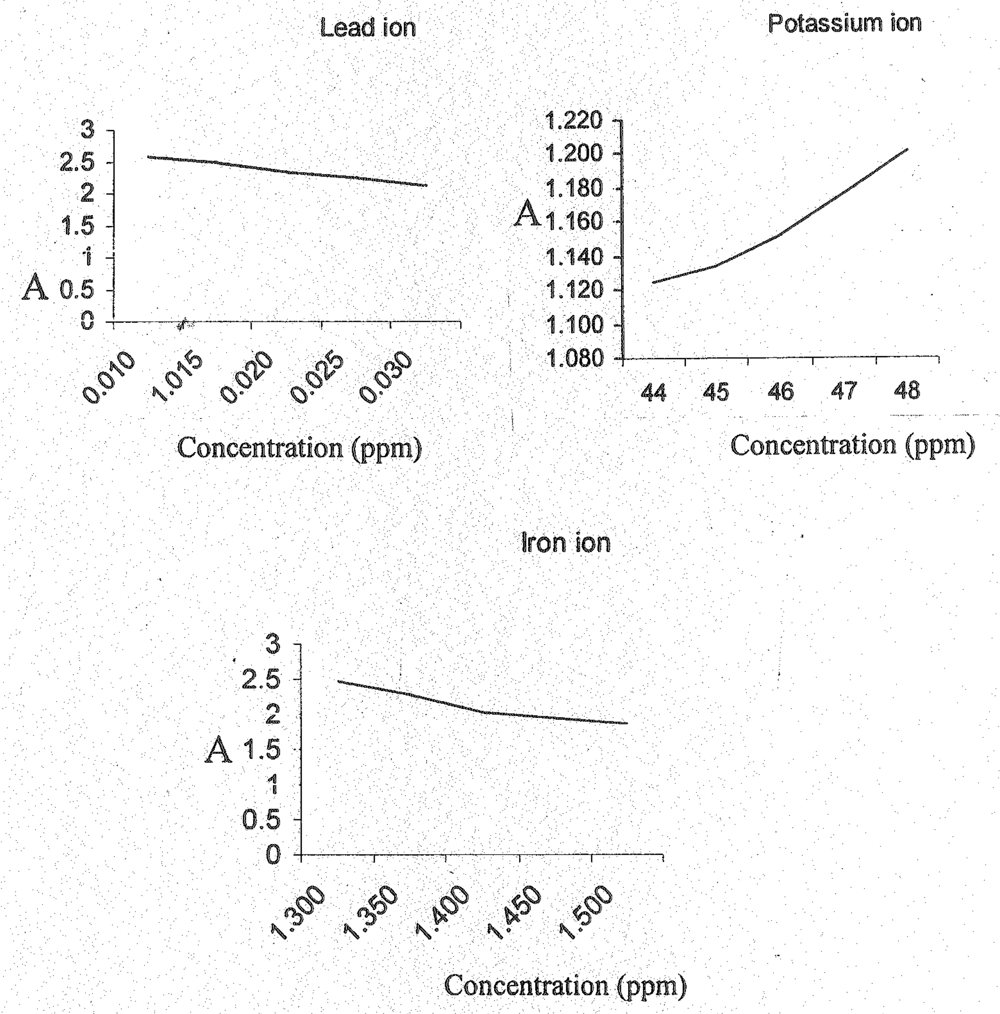


Fig. 6. Variation of absorbance of λ_{max} of astorvastatin calcium with trace elemental constituents

Conclusion

A satisfactory vibrational band analysis has been made for the drug atorvastatin calcium using FT-IR and FT Raman spectroscopy. The drug is exposed to sunlight and FT-IR spectrum shows significant changes in the absorption level of the peaks, hence confirming the quality change in the drug due to the environmental exposures. The internal standard calculations among the specific modes of vibration clearly shows that the light absorption activity of the drug altered more due to sun exposure. It is observed that the behaviour of the drug is notably altered with different nature and amount of the trace elemental constituents of human blood. It has been studied that a particular drug of standard strength behaves in a different way for different concentrations of the trace elemental constituents.

REFERENCES

1. D. Karalis, A.M. Ross, R. Vacari, H. Zarren and R. Scott, *Am. J. Cardiol.*, **89**, 667 (2002).
2. A.G. Olsson, M. Eriksson, O. Johnson, T. Kjellstran, J. Lanke, M.L. Larsen, T. Pedersen, M.J. Tikkanen and O. Wklund, *Clin. Theor.*, **25**, 119 (2003).
3. G. Castano, R. Mas, L. Fernandez, L.J. Illnai, M. Mesa, E. Alvarez and M. Lezcay, *Drugs Aging*, **20**, 153 (2003).
4. E. Stein, S. Stender, P. Mata, P. Sager, D. Ponsonnet, L. Melani, L. Lipka, R. Suresh, P. Maccubbin and E. Veltri, *Am. Heart J.*, **148**, 447 (2004).
5. S. Gunasekaran and P. Abitha, *Indian J. Pure Appl. Phys.*, **43**, 329 (2005).
6. S. Gunasekaran and R. Rathika, *Indian J. Pure Appl. Phys.*, **41**, 503 (2003).
7. S. Gunasekaran, G. Sankari and S. Ponnuswamy, *Spectrochim. Acta*, **61A**, 117 (2005).
8. K.S. Pandey, B.P. Asthaman and P.C. Mishra, *Spectrochim. Acta*, **49A**, 53 (1993).
9. R.M. Silverstein, G.C. Oesslor and T. Morril, Spectrometric Identification of Organic Compounds 4E, John Wiley, New York (1981).
10. S. Gunasekaran, U. Ponnambalam, S. Muthu and S. Kumaresan, *Indian J. Phys.*, **78**, 1141 (2004).
11. S. Gunasekaran, R.K. Natrajan, R. Rathika and D. Syamala, *Indian J. Phys.*, **79**, 503 (2005).
12. S. Gunasekaran, R.K. Natrajan, R. Rathika and D. Syamala, *Indian J. Phys.*, **79**, 509 (2005).
13. S. Gunasekaran and P. Abitha, *Asian J. Chem.*, **15**, 1764 (2003).
14. S. Gunasekaran, R.K. Natrajan and K. Santhosam, *Asian J. Chem.*, **15**, 1347 (2003).
15. Venkata Ramana Rao, P. and G. Ramana Rao, *Spectrochim. Acta*, **58A**, 3205 (2002).
16. S. Gunasekaran and G. Sankari, *Acta Ciencia Ind.*, **31**, 1061 (2005).
17. Website: www.UPS.edu

(*Received*: 30 September 2005; *Accepted*: 5 June 2006) AJC-4944
