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Vibrational Band Assignment and Qualitative Analysis of Benzocaine

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In the present work, the behaviour of the drug benzocaine under different storage conditions is compared. Benzocaine is an ester-linked local anesthetic. It is also used as a cutting agent in the street drugs. The Fourier transform infrared (FTIR) spectra of benzocaine have been recorded for the properly stored drug and for those exposed to direct sunlight for 4 h and to infrared radiations for a period of 4 h. The FTIR spectra have been employed for identification and assignment of the functional group in benzocaine. Some of the fundamental modes of vibration are identified in the spectra and their respective absorbance values are noted down. The ratio of absorbance among the various modes is calculated for all the three conditions. The internal standards of the drug under different storage conditions are compared with the normal storage condition. Ultraviolet visible spectroscopy is another method supporting drug research for qualitative and quantitative estimation of many drugs. The UV-Vis measurements carried out on the sample are used to identify the wavelength maxima. The adherence to Beer-Lambert's law is tested for the absorption peaks under different concentrations of the sample.

Key Words: Benzocaine, FTIR spectrum, UV-Vis spectrum, Internal standard.

INTRODUCTION

Benzocaine (*p*-amino ethyl benzoate) (Fig. 1) is an important local anesthetic sugar. It is commonly found as a cutting agent, adulterant in street drugs[1–6]. It is a weak base with amphiphilic property. An alkyl chain through an ester linkage joins a hydrophilic secondary amine on one side and a lipophilic aromatic residue on the other side. Its unique characteristic in the category of local anesthetics is that it lacks the amino group on the end of its carbon chain. It is available in the form of colourless crystals or white crystalline powder. It is odourless and freely soluble in 95% ethanol, chloroform and ether but insoluble in water. In this work, the application of FTIR and UV-Vis spectroscopy in identification of different

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groups and qualitative analysis of benzocaine will be considered. The FTIR and UV-Vis spectra of the sample have been recorded for the pure drug and for those exposed to direct sunlight for 4 h and to infrared radiation for a period of 4 h. All the spectra have been obtained in the absorbance mode and have been normalized.

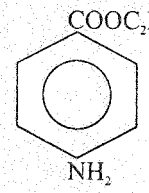

Fig. 1. Structure of Benzocaine

EXPERIMENTAL

High-grade pure sample of benzocaine was obtained from a reputed pharmaceutical company, Himedia Chemicals, Chennai and was used without further purification. FTIR spectrum was recorded in the region 4000–400 cm^{-1} in the solid state by using Bruker IFS 66 V spectrophotometer at SAIR, IIT, Chennai, India. The FTIR spectra of benzocaine under different storage conditions are presented in Fig. 2.

The UV-Vis absorbance spectra have been recorded in the range 200–400 nm on an Elico SL 159 UV-Vis spectrophotometer at Spectrophysics Research Lab in Pachaiyappa's College, Chennai, India.

Qualitative analysis of the drug: Spectrophotometric drug analysis plays a vital role in the quality control lab of any pharmaceutical firm. During the fabrication of drugs the various raw materials that are used in the fabrication should undergo a rigorous qualitative test, which can be achieved using sophisticated instruments like infrared and UV-Vis spectrophotometers. The behaviour of the drug under normal storage conditions is compared to that when it is exposed to various environmental conditions. To study this the FTIR and UV-Vis spectra of the sample have been recorded for pure drug and that exposed to sunlight and IR radiations for a period of 4 h. All the spectral measurements have been carried out in absorbance mode and have been normalized.

Vibrational band assignment: As FTIR spectrum of a compound is the superposition of absorbance bands of specific functional groups, some fundamental modes of vibration are identified in the spectrum of benzocaine and their respective absorbance values are noted down. The assignments for the fundamental modes of vibration have been made in terms of band position, shape and intensity. Work on vibrational frequencies of similar compounds like benzene, aromatic amines, aromatic ester[7–10] have been taken into consideration for this assignment and the summary of the assignments is given in Table-1.

Internal standard of benzocaine: From the internal ratio of absorbance of various bands, one arrives at the internal standards of specific modes of vibration. The sets of internal standard of the drug under different storage conditions check

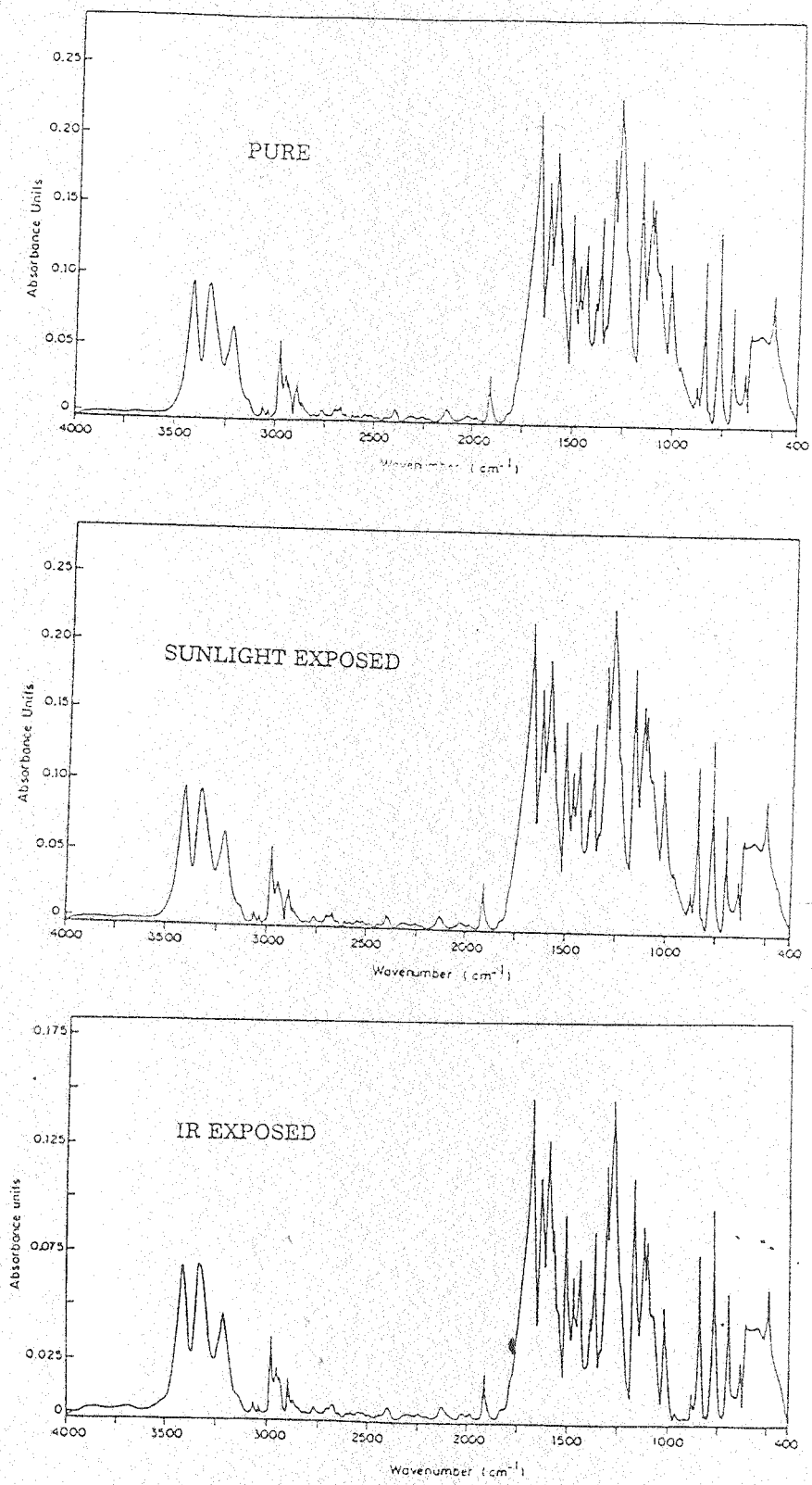

Fig. 2. FTIR spectra of benzocaine in different storage conditions

for the changes in quality of the drug exposed to different environmental conditions. Tables 2–4 are the internal standards for the specific modes of vibration of benzocaine stored at different conditions. A glance at the tables shows that the absorbance of the bands has been altered and the drug must be stored under proper conditions, *viz.*, at 25°C and away from direct sunlight.

TABLE-1
VIBRATIONAL SPECTRAL ASSIGNMENT FOR PURE BENZOCAINE

No.	FTIR vibrational frequency (cm^{-1})	Band assignments
1.	3423 m	NH_2 asymmetric stretching
2.	3000 w	CH asymmetric stretching
3.	1684 vs	C=O stretching
4.	1636 s	NH_2 bending
5.	1574 s	Ring asymmetric stretching
6.	1312 s	C—N stretching
7.	1281 vs	C—O stretching
8.	1126 s	CH asymmetric stretching
9.	846 m	CCC symmetric stretching
10.	773 m	CCC asymmetric bending

TABLE-2
INTERNAL STANDARDS AMONG SOME SELECTED SPECIFIC MODES OF VIBRATION OF PROPERLY STORED BENZOCAINE

Frequency (cm^{-1})	3423	3000	1684	1636	1574	1312	1281	1125	846	772
3423	1.000	0.553	2.342	1.789	1.434	1.974	2.395	1.658	1.211	1.395
3000	1.810	1.000	4.238	3.238	2.595	3.571	4.333	3.000	2.190	2.524
1684	0.427	0.236	1.000	0.764	0.612	0.843	1.022	0.708	0.517	0.596
1636	0.559	0.309	1.309	1.000	0.801	1.103	1.338	0.926	0.676	0.779
1574	0.697	0.385	1.633	1.248	1.000	1.376	1.670	1.156	0.844	0.972
1312	0.507	0.280	1.187	0.907	0.727	1.000	1.213	0.840	0.613	0.707
1281	0.418	0.231	0.978	0.747	0.599	0.824	1.000	0.692	0.505	0.582
1125	0.603	0.333	1.413	1.079	0.865	1.190	1.444	1.000	0.730	0.841
846	0.826	0.457	1.935	1.478	1.185	1.630	1.978	1.370	1.000	1.152
772	0.717	0.396	1.679	1.283	1.028	1.415	1.717	1.189	0.868	1.000

UV-Vis spectroscopy is another method in which the quality of the drug can be determined. The UV-Vis spectra have been recorded for properly stored, sunlight exposed and IR exposed benzocaine using ethyl alcohol as solvent as well as reference. The values of the wavelength maxima, 294 nm and 230 nm,

are found to agree well with the values reported in Indian Pharmacopoeia. The spectra have been recorded for various concentrations of the drug. It has been observed that the absorbance of wavelength maxima increases linearly with concentration and hence Beer-Lambert's law is verified. The variation of absorption with respect to concentration for the three samples is shown in Table-5.

TABLE-3
INTERNAL STANDARDS AMONG SOME SELECTED SPECIFIC MODES OF VIBRATION OF SUNLIGHT EXPOSED BENZOCAINE

Frequency (cm^{-1})	3423	3000	1684	1636	1574	1312	1281	1125	846	772
3423	1.000	0.628	2.261	1.590	1.275	1.754	2.128	1.473	1.076	1.239
3000	1.591	1.000	4.049	2.848	2.282	3.141	3.811	2.638	1.926	2.219
1684	0.442	0.247	1.000	0.703	0.564	0.776	0.941	0.652	0.476	0.548
1636	0.629	0.351	1.422	1.000	0.732	1.008	1.222	0.846	0.618	0.712
1574	0.785	0.438	1.774	1.366	1.000	1.250	1.517	1.050	0.767	0.883
1312	0.570	0.318	1.289	0.993	0.800	1.000	1.107	0.766	0.559	0.644
1281	0.470	0.262	1.062	0.818	0.659	0.904	1.000	0.616	0.450	0.518
1125	0.679	0.379	1.535	1.182	0.952	1.305	1.623	1.000	0.668	0.769
846	0.930	0.519	2.102	1.618	1.304	1.788	2.223	1.497	1.000	1.060
772	0.807	0.451	1.824	1.405	1.132	1.552	1.929	1.300	0.943	1.000

TABLE-4
INTERNAL STANDARDS AMONG SOME SELECTED SPECIFIC MODES OF VIBRATION OF INFRARED IRRADIATED BENZOCAINE

Frequency (cm^{-1})	3423	3000	1684	1636	1574	1312	1281	1125	846	772
3423	1.000	0.537	2.122	1.610	1.219	1.695	2.122	1.269	1.122	1.390
3000	1.862	1.000	3.951	2.997	2.270	3.155	3.951	2.362	2.090	2.589
1684	0.471	0.253	1.000	0.759	0.574	0.799	1.000	0.598	0.529	0.655
1636	0.621	0.334	1.318	1.000	1.239	1.705	2.068	1.432	1.045	1.205
1574	0.820	0.441	1.741	0.807	1.000	2.251	2.731	1.891	1.381	1.591
1312	0.590	0.317	1.252	0.587	0.444	1.000	1.965	1.360	0.993	1.144
1281	0.471	0.253	1.000	0.484	0.366	0.509	1.000	1.086	0.793	0.914
1125	0.788	0.423	1.672	0.698	0.529	0.735	0.921	1.000	1.326	1.528
846	0.891	0.478	1.890	0.957	0.724	1.007	1.261	0.754	1.000	1.728
772	0.719	0.386	1.526	0.830	0.629	0.874	1.094	0.654	0.579	1.000

TABLE-5
VARIATION OF UV-Vis ABSORPTION WITH RESPECT TO MOLAR CONCENTRATION OF PROPERLY STORED AND EXPOSED BENZOCAINE

Samples	Absorbance/Molarity (M)	
	λ = 294 nm	λ = 230 nm
Pure	13518.8	1598.8
Sunlight exposed	35009.3	21504.3
IR exposed	16222.6	5900.0

RESULTS AND DISCUSSION

FTIR spectra of benzocaine under different storage conditions have been recorded. A satisfactory vibrational band assignment has been made. It has been found from the spectra that the optical density of benzocaine increases when exposed to sunlight and decreases when exposed to IR radiation. The sets of internal standards of the drug indicate that the quality of the drug changes when it has not been stored under proper storage conditions. UV-Vis spectral studies reveal that there is no marked shift in the wavelength maxima of the exposed drugs to that of properly stored drug. But, the absorbance values of the sunlight-exposed drug have increased and those of IR-exposed drug have decreased, thus augmenting the IR internal standard studies.

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