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FTIR Analysis of Some Pills of Forensic Interest

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ABSTRACT

This paper deals with the use of modern Fourier Transform Infrared (FTIR) spectroscopy with quick and easy Diamond Attenuated Total Reflectance (ATR) technique for generating a spectral library of some benzodiazepines of forensic interest. These types of drugs can be seized as bulk street drugs as well as traces found at the scene of crime. There can be legal queries regarding identification of these drugs which a forensic expert has to answer. In these cases, the standard reference database is required for comparison. The modern FTIR systems with diamond ATR proves to be a rapid, sensitive and non-destructive analysis of samples with very little effort. This spectral library can be used as a reference library when an unknown sample is suspected of being benzodiazepine.

Key words: Forensic, Infrared, FTIR- ATR and benzodiazepines

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INTRODUCTION

Benzodiazepines are a group of drugs with wide application as tranquillizers, hypnotics, muscle relaxants and anticonvulsants. Primary use of benzodiazepines is to induce sleep but accidentally or intentionally these drugs can also induce an endless sleep when overdosed. Benzodiazepines are usuallu prescribed in anxiety, stress and insomnia. Diazepam, Nitrazepam and Temazepam are amongst the common types of benzodiazepines. They are controlled under the Misuse of Drugs Act. It's illegal to possess benzodiazepines without a prescription. When people without prescriptions take these drugs for their sedating or intoxicating effects, then use turns into abuse. Nowadays, benzodiazepines are being abused as a common fashion because of their low-cost, easy availability and failure of many pharmacies to conform to prescribed requirements. In addition to their misuse, they have also been frequently detected in criminal cases, such as homicide and burglary [1]. Complaints of theft of the belongings of pilgrims in an outskirt area of the holy places were also reported when the travelers were offered eatables, and drinks premixed with sleep inducing drugs [2]. Abusers of stimulants such as cocaine, amphetamines and even ecstasy, can also use benzodiazepines as "downers" to overcome the effects of their "uppers." Benzodiazepines have also been used as a "date rape" drug. Some street users have moved on to take large amounts of oral benzodiazepines in combination with injected opiates such as buprenorphine [3]. Benzodiazepines are also involved in many death cases due to overdose [4]. Various authors have noted the age-standardized benzodiazepine associated mortality rates [5,6,7,8]. Death cases associated with toxic concentrations of benzodiazepines have been discussed and reported by [9,10,11]. Therefore, conviction of people illegally involved in this practice may be noticed.
Several methods have been used to identify the intact samples suspected of being benzodiazepines. Use of infrared spectroscopy has been made many times in forensic science for chemical fingerprinting of benzodiazepines [1,12-21]. In spite of these efforts, an attempt in the present study has been made to obtain chemical fingerprinting of some commonly encountered sleeping pills using a non-destructive FTIR- Diamond ATR method. Reason behind generating FTIR-ATR spectra database of some closely related sleeping pills was the lack of the reference spectrograms of these samples. This investigation is a valuable addition as a reference spectral library of benzodiazepines for any forensic chemist.

MATERIALS AND METHOD

Samples

Diazepam, Tranax, Normozin, Tensyn-Plus, Libropar and Dizeral of pharmaceutical grade were obtained for research purpose.

Procedure

Transmittance spectra were acquired using an FTIR spectrophotometer (Alpha Model, Bruker) on Diamond -Attenuated Total Reflectance (ATR) accessory. Opus software was used for spectra acquisition. The sample of interest was crushed to powder form and then it was placed in direct contact with the internal reflecting diamond crystal. Once in contact with the crystal, multiple scans were obtained. All the spectra was baseline

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corrected. The spectral range was made set from 4000cm^{-1} up to 500cm^{-1}, at a resolution of 4cm^{-1}.

RESULTS

Six closely related samples of benzodiazepines were subjected to analysis with FTIR. The IUPAC name for the benzodiazepine group is 2,3-diazabicyclo[5.4.0]undeca-3,5,7,9,11pentaene. The core chemical structure is the fusion of a benzene ring and a diazepine ring (**Fig. 1**).

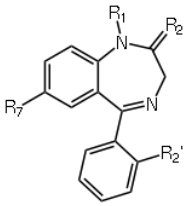

Fig. 1: Basic structure of Benzodiazepines

The different drugs have been varying substituents on this basic skeleton, and the spectrum selected samples have been shown in Fig. 2-7. It is evident from Figure-2 that Diazepam ($C_{16}H_{13}ClN_2O$), chemically known as 7-Chloro–1,3–dihydro–1–methyl–5–phenyl–2H-1,4–benzodiazepin–2–one is one has shown most of the characteristic peaks at wavenumber 550cm^{-1}, 705cm^{-1}, 840cm^{-1}, 875cm^{-1}, 1057cm^{-1}, 1120cm^{-1}, 1144^{-1}, 1201cm^{-1}, 1201cm^{-1}, 1340cm^{-1}, 1420cm^{-1}, 1653cm^{-1} and 1684cm^{-1}. Tensyn Plus is a mixture of Diazepam and Propranolol Hydrochloride ($C_{16}H_{21}NO_2HCl$). The principal peaks of Tensyn Plus have been noticed at wavenumber 571cm^{-1}, 667cm^{-1}, 769cm^{-1}, 1073cm^{-1}, 1142cm^{-1}, 1240cm^{-1}, 1270cm^{-1} and 1579cm-^{1}. Diazeral is another mixture of Diazepam and Propranolol Hydrochloride. Spectrum of Diazeral is similar to the spectrum of Tensyn Plus in terms of spectral range and principal peaks. Tranax contains alprazolam ($C_{17}H_{13}ClN_4$). The principal peaks of Tranax have been noticed at 600cm^{-1}, 667cm^{-1}, 758cm^{-1}, 875cm^{-1}, 899cm^{-1}, 1070cm^{-1}, 1201cm^{-1}, 1259cm^{-1}, 1339cm^{-1} and 1423cm^{-1}. Libropar is a mixture of Chlordiazepoxide ($C_{16}H_{14}ClN_3O$) and Trifluoperazine salt ($C_{21}H_{24}F_3N_3S$, 2HCl). Libropar has shown principal peaks at wavenumber 667cm^{-1}, 761cm^{-1}, 872cm^{-1}, 1000cm^{-1}, 1076cm^{-1}, 1262cm^{-1}, 1417cm^{-1} and 1622cm^{-1}. Normozin is another mixture of Chlordiazepoxide & Trifluoperazine. Interpretation of the spectrum of Normozin has revealed the characteristic peaks in range of 1700cm^{-1} to 500cm^{-1} comparable to Libropar.

Since all these drugs are derivatives of benzodiazepines and most of these samples have similar constituents, hence alike spectral images have been noticed. Most of the principal peaks of the selected drugs have been observed between a range of 1700cm^{-1} to 500cm^{-1} while somewhere, some peaks have been noticed near 2500cm^{-1}. As per as samples are concerned, Tensyn Plus and Diazeral have same salt, therefore spectrum of these samples has been noticed with a like spectral range i.e. 1700cm^{-1} to 500cm^{-1} while Libropar and Normozin with alike composition, have also shown similar spectra images. Tranax and Diazepam have shown some differences in their spectral images.

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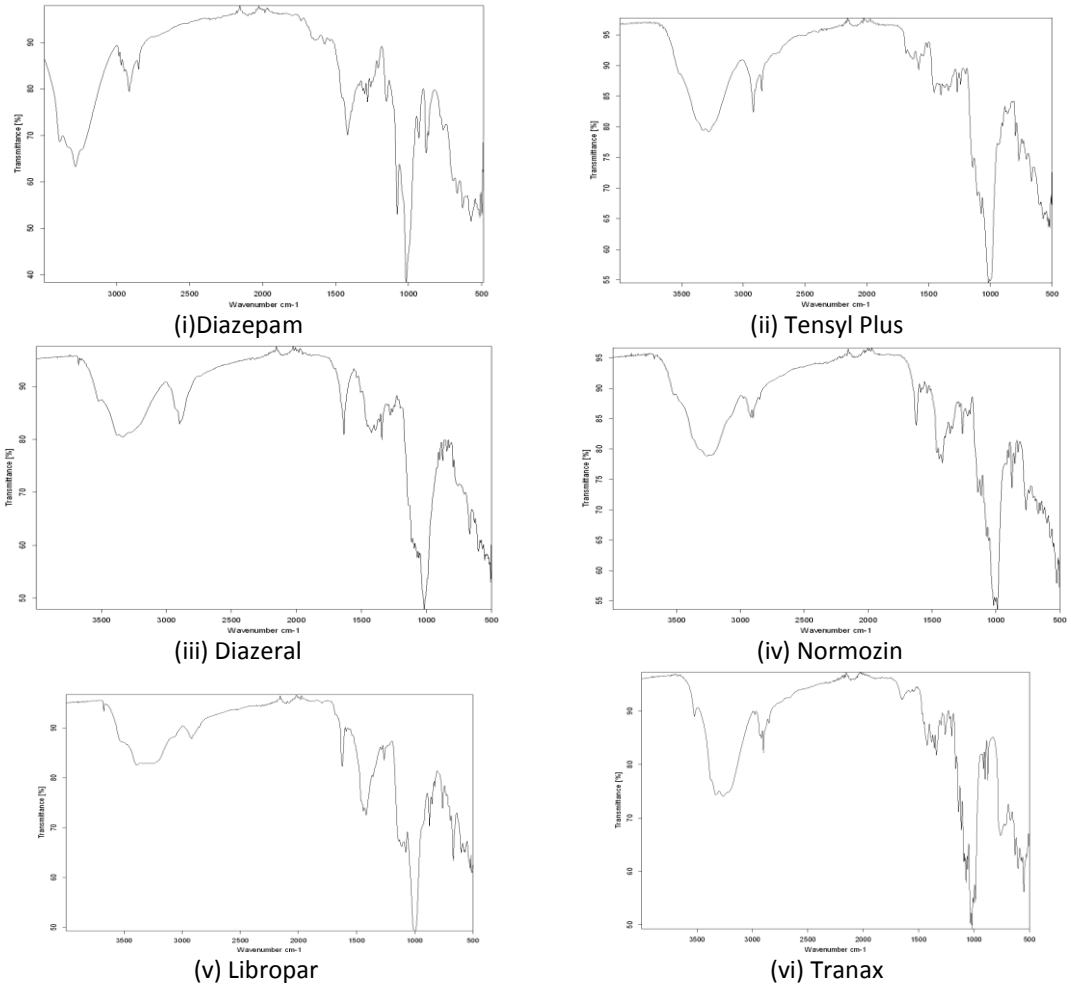

Fig. 2: FTIR-ATR spectrum of (i) Diazepam, (ii) Tensyn Plus, (iii) Diazeral, (iv) Normozin, (v) Libropar and (iv) Tranax.

CONCLUSION

Some of the closely related structures may have spectra very similar to that of a particular substance, especially for benzodiazepines. It is thus imperative that appropriate techniques should be used by the forensic chemist to ensure that optimal spectral data are obtained to get a feel for the discriminating features of a spectrum. Screening with FTIR is particularly convenient because of both its speed and its ability to use accessories with no sample preparation. It is quite possible to screen certain intact tablets with FTIR-ATR, simply by powdering them directly. The present work may provide a potential positive contribution to discriminate unknown benzodiazepines.

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