The Characterization of 3,4-Methylenedioxypyrovalerone (MDPV)

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ABSTRACT: The analysis and characterization of 3,4-Methylenedioxypyrovalerone (MDPV) is presented. Gas chromatography/ mass spectrometry (GC/MS), Fourier transform nuclear magnetic resonance (FTNMR) spectroscopy , solid phase Fourier transform infrared (FTIR) spectroscopy, and ultraviolet (UV) spectrophotometry data are presented.

KEYWORDS: MDPV, phenethylamines, GC/MS, FTNMR, FTIR, ultraviolet, forensic chemistry

In March 2008, police seized a small plastic bag labeled "1-(3,4-methylenedioxy-phenyl)-2-pyrrolidin-1-yl-pentan-1-one GC/MS Sample Not for Human Consumption." There was no lot number or manufacturer name on the bag. The bag contained 0.4 g of a white powdery substance that provided no match to available GC/MS libraries. The seizure was in response to a call for a vehicle off the road and stuck in the mud. The responding officer found the driver to be incoherent and confused; the driver subsequently failed a field sobriety test. The driver was requested to take a breathalyzer, which resulted in 0.00 Blood Alcohol Content. The driver declined a request for a blood test. It is not known whether the driver's condition was a direct result of MDPV intoxication. A search of the driver provided the above mentioned bag along with pharmaceutical tablets believed to be from India. The driver stated that he was a self-employed chemist and that was the reason that he was allowed to have the bag of white powder. The tablets included 98 promethazine HCl, 1 triazolam, 2 risperidine, 4 methocarbamol, 10 baclofen, 6 bromazepam, and 4 quetiapine fumarate tablets. Also recovered were a pill crusher and a prescription bottle containing residue.

MDPV and MDPK are both abbreviations for 3,4-Methylenedioxypyrovalerone (Figure 1). MDPV was first synthesized as part of a class of stimulants in 1969. MDPV is the methylenedioxy analogue of pyrovalerone, a Schedule V stimulant first synthesized in 1964. Pyrovalerone, available under the trade names Centroton and Thymergix, is used as an appetite suppressant or for the treatment of chronic fatigue.

MDPV is currently unscheduled in the United States. MDPV is found as a white or light tan powder. Users report the development of an odor when left exposed to the air. There are currently no known studies on the effects of MDPV on humans or on proper dosing. MDPV is commonly described as boosting a user's libido, however it is also associated with extreme anxiety at higher dosages. There are no known deaths due to the use of MDPV.

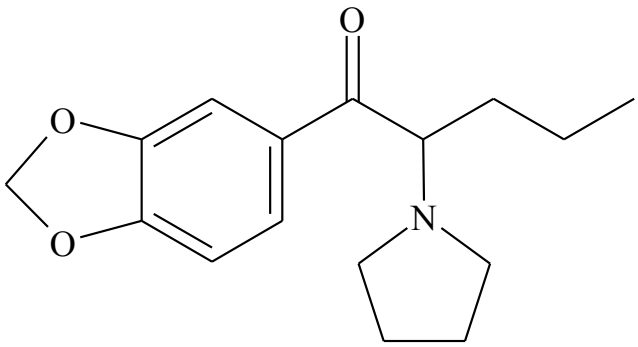

Figure 1 - 3,4-Methylenedioxypyrovalerone hydrochloride
Chemical Formula: $C_{16}H_{22}ClNO_3$
CAS Number: [24622-62-6]
Molecular Weight: 311.80 amu (as hydrochloride)
Melting Point: 238 - 239 °C with decomposition
Solubility (as hydrochloride): [Chloroform: Soluble; Methanol: Soluble; Deionized H_2O: Soluble]

Experimental

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectrum (Figure 2) was acquired using a Thermo-Nicolet Magna 560 spectrophotometer with a SensIR Durascope attenuated total reflectance (ATR) accessory. The spectrum was collected using 32 scans between 4000 cm^{-1} and 400 cm^{-1}.

Gas Chromatography/Mass Spectrometry (GC/MS)

The mass spectrum (Figures 3a-3b) was acquired using an Agilent Model 6890N GC equipped with an Agilent Model 5973 quadrupole mass-selective detector (MSD). The MSD was operated using 70 eV E.I. The GC was fitted with a 30 m x 0.25 mm I.D. fused silica capillary column coated with 0.50 µm 35% phenyl, 65% dimethyl arylene siloxane (DB-35MS), and was operated in splitless mode. The injection port was maintained at 250°C. The oven temperature program was as follows: Initial temperature 90°C (1 min), ramped to 300°C at 8°C/min (final hold 10 min). Helium was used as a purge gas at a rate of 60 mL/sec. Methanol was used as the solvent.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H- and ^{13}C-NMR spectra (see Table 1, Figures 4 and 5, respectively) were acquired at 25°C on a Varian Mercury *Plus* 400 MHz instrument using a Nalorac 5 mm indirect detect pulse field gradient (PFG) probe. (^{1}H parameters: Number of scans (nt) = 8, pulse width (pw) = 45°, relaxation delay

(d1) = 5 s, acquisition time (at) = 2.5 s; ^{13}C parameters: nt = 4098, pw = 45°, d1 = 1 s, at = 1.3 s, complete proton decoupled). Spectra were processed using ACD/Labs *SpecManager* software (Advanced Chemistry Development Inc.©, Toronto, Canada). MDPV was prepared with D_2O containing 5 mg/mL maleic acid (as internal standard) containing 0.05 wt % 3-trimethylsilyl-propionic-2,2,3,3-d_4 acid, sodium salt (TSP; Aldrich Chemical Co., Milwaukee, WI) at 16.87 mg/mL. Chemical shifts (δ) are reported in parts per million (ppm) using TSP (0.0 ppm) as the reference standard (400 MHz, D_2O).

Ultraviolet (UV) Spectrophotometry

The UV spectrum (Figure 7) was acquired using a Hewlett-Packard 845x spectrophotometer with a 1 cm cell path length. The range scanned was 220-330 nm. The sample was dissolved in methanol.

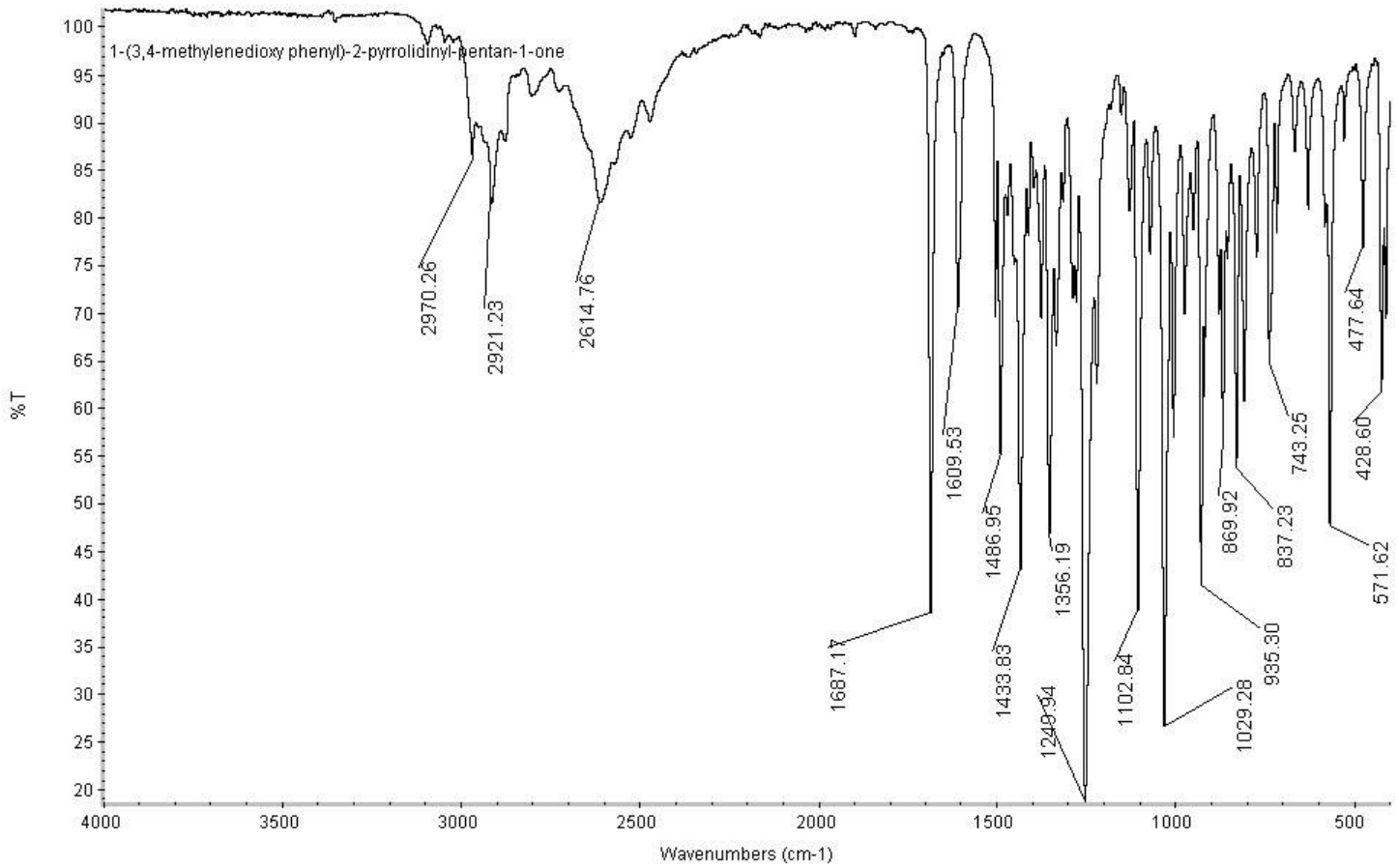

Figure 2 - FTIR-ATR spectrum of MDPV hydrochloride.

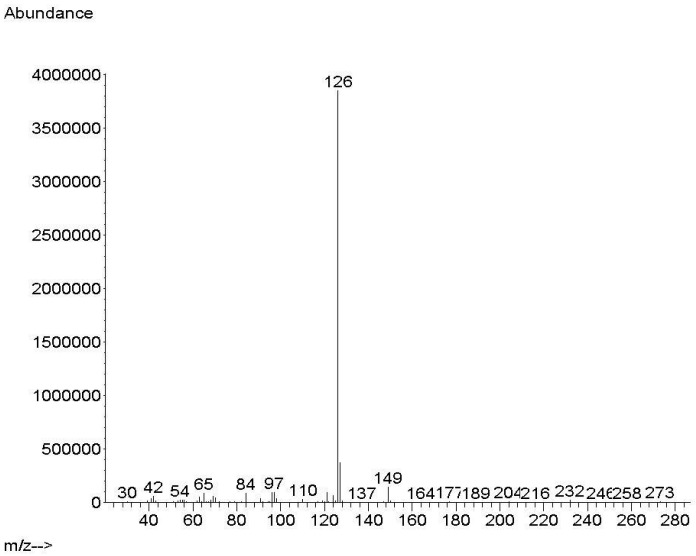

Figure 3a - E.I. mass spectrum of MDPV.

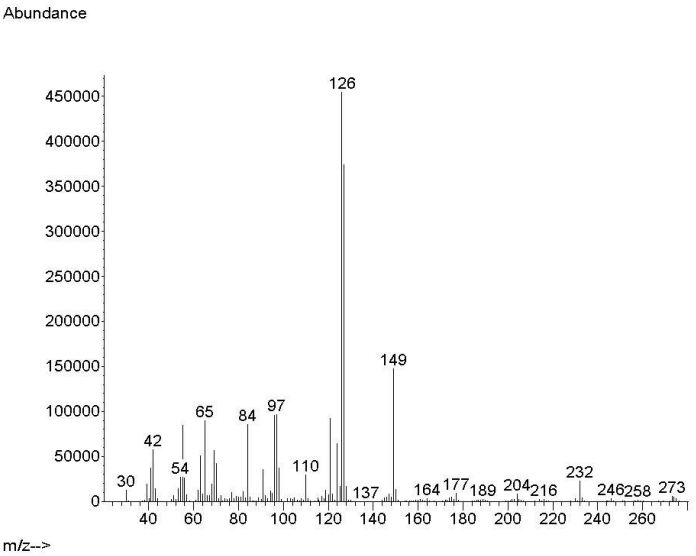

Figure 3b - Expanded E.I. mass spectrum of MDPV.

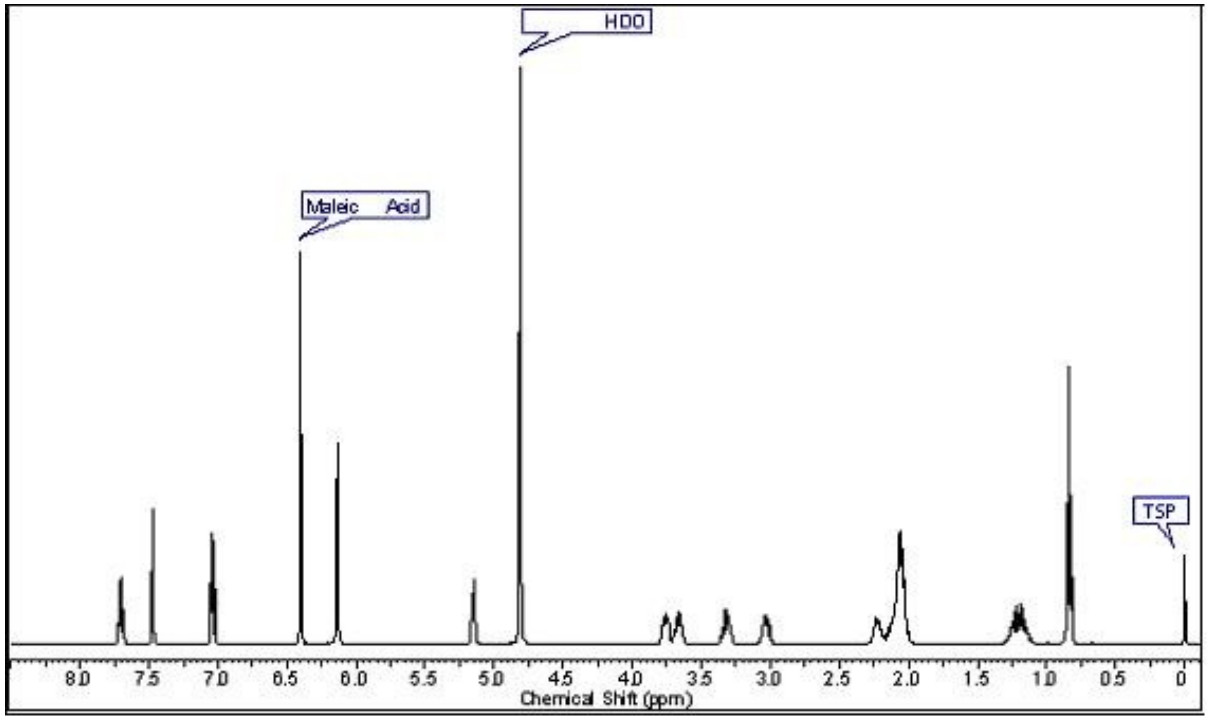

Figure 4 - 400 MHz FTNMR ^{1}H spectrum of MDPV in D_2O with maleic acid.

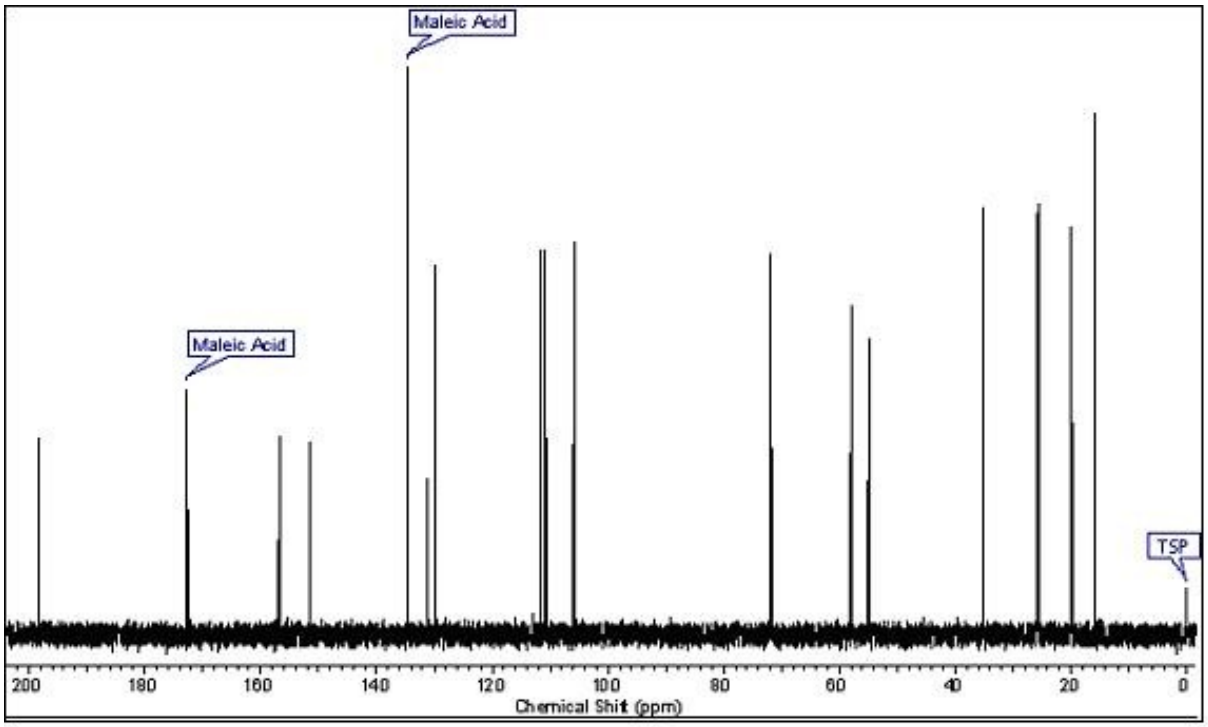

Figure 5 - 400 MHz FTNMR ^{13}C spectrum of MDPV in D_2O with maleic acid.

Results and Discussion

The MDPV mass spectrum demonstrates similarity to other amines in that it gives a low-detail mass spectral fragmentation pattern. The base ion, *m/z* 126, however, is somewhat uncommon in drug analysis, which may prove to be of value in identifying MDPV. The resultant FTIR spectrum is very detailed with a number of sharp bands in the fingerprint region that should enable relatively facile identification. Specifically, MDPV has proven to be an analyte that is easily distinguishable from other structurally related compounds.

References

1. 1-[(3,4-Methylenedioxy)phenyl]-2-pyrrolidino-1-alkanones as stimulants. (Boehringer Ingelheim Study) 1969.

Table 1 - Assignments, Multiplicities, and Coupling Constants.

Position	^{13}C (ppm)	^{1}H (ppm)	Multiplicity	*J* (Hz)
Methylenedioxyphenyl - 2	105.71	6.14	multiplet	-
Methylenedioxyphenyl - 4	110.80	7.47	doublet	1.7
Methylenedioxyphenyl - 7	111.61	7.03	doublet	8.3
Methylenedioxyphenyl - 6	129.76	7.70	dd	1.7, 8.3
Methylenedioxyphenyl - 5	131.16	-	-	-
Methylenedioxyphenyl - 7a and 3a	151.50	-	-	-
	156.84	-	-	-
Sidechain - 1	198.36	-	-	-
Sidechain - 2	71.91	5.15	triplet	5.4
Sidechain - 3	35.16	2.06	multiplet	-
Sidechain - 4	19.94	1.24	multiplet	-
		1.17	multiplet	-
Sidechain - 5	16.00	0.83	triplet	7.3
Pyrrolidine - 2 and 5	58.04	3.67	multiplet	-
		3.03	ddd	11.6, 8.0, 7.87
	54.96	3.76	multiplet	-
		3.32	multiplet*	9.5
Pyrrolidine - 3 and 4	25.80	2.22	multiplet	-
		2.06	multiplet	-
	25.63	2.06	multiplet	-

*apparent quartet

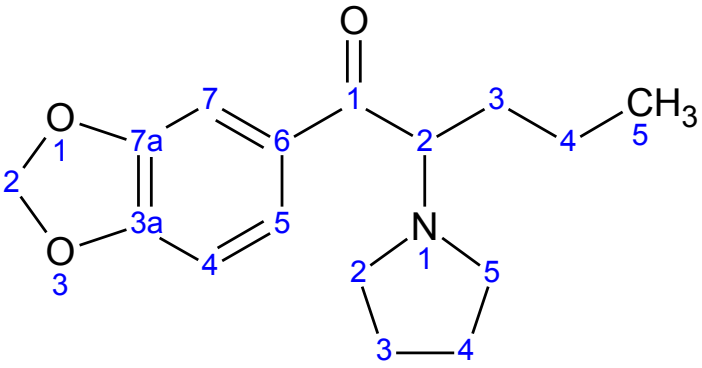

Figure 6 - Position of protons for MDPV (See Table 1).

2. Heffe, W. Die Stevens-umlagerung von allyl-phenacyl-ammoniumsalzen. Helv Chim Acta 1964;47:1289-1292.
3. Gardos G, Cole JO. Evaluation of pyrovalerone in chronically fatigued volunteers. Curr Ther Res Clin Exp. 1971;13(10):631-5.
4. http://en.wikipedia.org/wiki/MDPV (cited Feb. 5, 2009)

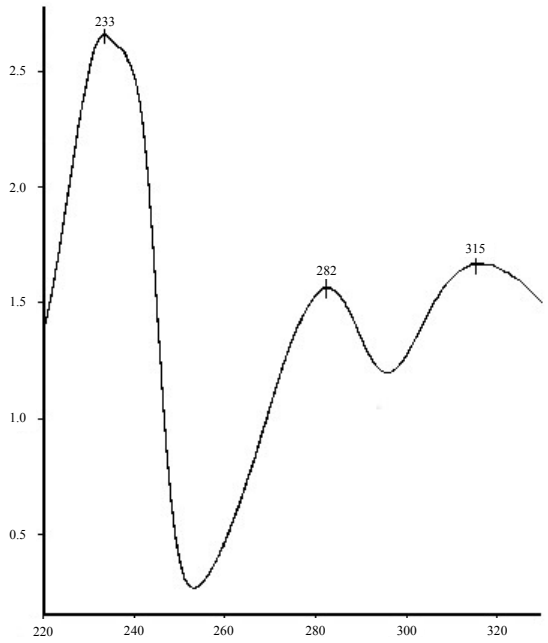

Figure 7 - Ultraviolet-visible spectrum of MDPV in methanol.