



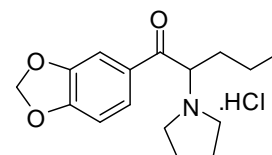
CERTIFIED REFERENCE MATERIAL CERTIFICATE OF ANALYSIS

NMIA D951b: (\pm)-3, 4-Methylenedioxyprovalerone hydrochloride

Report ID: D951b.2020.03 (Bottled 150910)

Chemical Formula: C₁₆H₂₁NO₃.HCl

Molecular Weight: 311.8 g/mol (HCl), 275.3 g/mol (base)



Certified value

Batch No.	CAS No.	Purity (mass fraction)
13-D-01	24622-62-6 (HCl) 687603-66-3 (base)	99.3 ± 0.8%

The uncertainty has been calculated according to ISO Guide 35 and is stated at the 95% confidence limit ($k = 2$).

IUPAC name: 1-(1,3-Benzodioxol-5-yl)-2-(1-pyrrolidinyl)-1-pentanone hydrochloride (1:1)

Expiration of certification: The property values are valid till 12 February 2025, i.e. five years from the date of re-certification provided the **unopened** material is handled and stored in accordance with the recommendations below. The material as issued in the unopened container and stored as recommended below should be suitable for use beyond this date, subject to confirmation of batch stability from the issuing body. The expiry date/shelf life does not apply to sample bottles that have been opened. In such cases it is recommended that the end-user conduct their own in-house stability trials.

Description: White crystalline solid prepared by synthesis, and certified for identity and purity by NMIA. Packaged in amber glass bottles with a septum and crimped aluminium cap or screw top cap.

Intended use: This certified reference material is suitable for use as a primary calibrator.

Instructions for use: Equilibrate the bottled material to room temperature before opening.

Recommended storage: When not in use this material should be stored at or below 25 °C in a closed container in a dry, dark area.

Metrological traceability: The certified purity value is traceable to the SI unit for mass (kg) through Australian national standards via balance calibration. In the mass balance approach all impurities are quantified as a mass fraction and subtracted from 100%.

Stability: This material has demonstrated stability over a minimum period of three years. The measurement uncertainty at the 95% confidence interval includes a stability component which has been estimated from annual stability trials. The long-term stability of the compound in solution has not been examined.

Homogeneity assessment: The homogeneity of the material was assessed using purity assay by GC-FID on ten randomly selected 1-2 mg sub samples of the material. The material was judged to be sufficiently homogeneous at this level of sampling as the variation in analysis results between samples was not significantly different at a 95% confidence level from that observed on repeat analysis of the same sample.

Safety: Treat as a hazardous substance. Use appropriate work practices when handling to avoid skin or eye contact, ingestion or inhalation of dust. Refer to the provided safety data sheet.

S. R. Davies

Dr Stephen R. Davies,
Team Leader,
Chemical Reference Materials, NMI.
20 September 2022

This report supersedes any issued prior to 20 September 2022.

NATA Accreditation No. 198 / Corporate Site No. 14214.

Legal notice: Terms and Conditions associated with the provision of this reference material can be found on the NMIA website.

Characterisation Report:

The identity was confirmed by a range of spectroscopic techniques, NMR, IR and MS. The certified purity value was obtained by mass balance from a combination of traditional analytical techniques, including GC-FID, thermogravimetric analysis, Karl Fischer analysis and ¹H NMR spectroscopy. The purity value is calculated as per Equation 1.

$$\text{Purity} = (100\% - I_{\text{ORG}}) \times (100\% - I_{\text{VOL}} - I_{\text{NVR}}) \quad \text{Equation 1}$$

I_{ORG} = Organic impurities of related structure, I_{VOL} = volatile impurities, I_{NVR} = non-volatile residue.

Supporting evidence is provided by HPLC-UV, qualitative headspace GC-MS analysis of occluded solvents and elemental microanalysis.

Warning: This material is sensitive to the quality of the silanised glass liner when injected at elevated temperature (~ 250 °C) into a GC instrument.

GC-FID:

Instrument:	Agilent 7890
Column:	HP-1MS, 30 m × 0.32 mm I.D. × 0.25 µm
Program:	100 °C (1 min), 20 °C/min to 220 °C (5 min), 30 °C /min to 300 °C (3 min)
Injector:	180 °C
Detector Temp:	320 °C
Carrier:	Helium
Split ratio:	20/1

Relative mass fraction of the main component as the free base:

Initial analysis:	Mean = 99.5%, s = 0.05% (10 sub samples in duplicate, March 2013)
Re-analysis:	Mean = 99.8%, s = 0.01% (5 sub samples in duplicate, February 2014)
Re-analysis:	Mean = 99.7%, s = 0.02% (5 sub samples in duplicate, February 2020)

Column: HP-5MS, 30 m × 0.32 mm I.D. × 0.25 µm

Relative mass fraction of the main component as the free base:

Initial analysis:	Mean = 99.8%, s = 0.05% (10 sub samples in duplicate, March 2013)
Re-analysis:	Mean = 99.8%, s = 0.02% (5 sub samples in duplicate, February 2017)

HPLC:

Instrument:	Waters Model 1525 Binary pump, 717 plus autosampler
Column:	X-bridge C-18, 5.0 µm (4.6 mm × 150 mm)
Column oven:	40 °C
Mobile Phase:	Acetonitrile/MilliQ water (60:40) The aqueous phase was buffered at pH 10.8 using 20mM NH ₄ OAc.
Flow rate:	1.0 mL/min
Detector:	Waters PDA 2998 operating at 229 nm

Relative mass fraction of the main component:

Initial analysis:	Mean = 99.8%, s = 0.004% (10 sub samples in duplicate, March 2013)
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Karl Fischer analysis: Moisture content 0.2% mass fraction (February 2013, February 2014 and November 2016)
 Moisture content 0.1% mass fraction (November 2019)

Thermogravimetric analysis: Thermogravimetric analysis: Non volatile residue < 0.2% mass fraction (March 2013). The volatile content (e.g. organic solvents and/or water) could not be determined because of the inherent volatility of the material and/or degradation at elevated temperatures.

Spectroscopic and other characterisation data

GC-MS:	Instrument: Agilent 6890/5973 Column: TG-1MS, 30 m × 0.25 mm I.D. × 0.25 µm Program: 100 °C (1 min), 20 °C/min to 220 °C (5 min), 30 °C/min to 300 °C (5 min) Injector: 250 °C Transfer line temp: 280 °C Carrier: Helium, 1.0 mL/min Split ratio: 20/1 The retention time of the free base is reported along with the major peaks in the mass spectrum. The latter are reported as mass/charge ratios and (in brackets) as a percentage relative to the base peak. Free base (10.9 min): 164 (2), 149 (8), 126 (100), 65 (4), 55 (4) <i>m/z</i>
ESI-MS:	Instrument: Waters Acquity UPLC/TQD Operation: Positive ion mode, direct infusion at 5 µL/min Capillary voltage: 3.5 kV Cone voltage: 30 V Peak: 276.1 (M+H ⁺) <i>m/z</i>
HS-GC-MS:	Instrument: Agilent 6890/5973/G1888 Column: DB-624, 30 m × 0.25 mm I.D. × 1.4 µm Program: 50 °C (5 min), 7 °C/min to 120 °C, 15 °C/min to 220 °C (8.3 min) Injector: 150 °C Transfer line temp: 280 °C Carrier: Helium, 1.2 mL/min Split ratio: 50/1 Solvents detected: Ethanol, diethyl ether, butanal
TLC:	Conditions: Kieselgel 60F ₂₅₄ . NH ₃ /methanol (3/200) Single spot observed, R _f = 0.73 Visualisation with UV light (254 nm).
IR:	Instrument: Biorad FTS3000MX FT-IR Range: 4000-400 cm ⁻¹ , KBr powder Peaks: 2968, 2915, 2614, 1686, 1611, 1507, 1491, 1437, 1356, 1258, 1105, 1036, 931, 869, 833, 740, 569 cm ⁻¹
¹ H NMR:	Instrument: Bruker Avance III-400 Field strength: 400 MHz Solvent: D ₂ O (4.79 ppm) Spectral data: δ 0.80 (3H, t, <i>J</i> = 7.2 Hz), 1.06-1.27 (2H, m), 1.98-2.21 (6H, bm), 2.78-3.95 (4H, bm), 5.14 (1H, t, <i>J</i> = 5.3 Hz), 6.09 (1H, d, <i>J</i> = 2.8 Hz), 6.10 (1H, d, <i>J</i> = 2.8 Hz), 6.98 (1H, d, <i>J</i> = 8.2 Hz), 7.41 (1H, d, <i>J</i> = 1.8 Hz), 7.66 (1H, dd, <i>J</i> = 1.8, 8.3 Hz) ppm Ethanol estimated at 0.4% mass fraction was observed in the ¹ H NMR. Diethyl ether and butanal were not detected in the ¹ H NMR.
¹³ C NMR:	Instrument: Bruker Avance III-400 Field strength: 101 MHz Solvent: D ₂ O Spectral data: δ 13.6, 17.5, 23.3, 32.8, 52.9, 55.3, 69.5, 103.3, 108.3, 109.1, 127.3, 128.7, 149.0, 154.4, 195.9 ppm
Melting point:	250 - 251 °C
Microanalysis:	Found: C = 61.8%; H = 7.2%; N = 4.6%; Cl = 11.2 (February, 2013) Calculated: C = 61.6%; H = 7.1%; N = 4.5%; Cl = 11.4 (Calculated for C ₁₆ H ₂₁ NO ₃ .HCl)