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Return of the lysergamides. Part I: Analytical and behavioral characterization of 1-propionyl-d-lysergic acid diethylamide (1P-LSD)

Simon D. Brandt, a,* Pierce V. Kavanagh, b Folker Westphal, c Alexander Stratford, d Simon P. Elliott, e Khoa Hoang, f Jason Wallach, g Adam L. Halberstadt, h

a School of Pharmacy and Biomolecular Sciences, Liverpool John Moores University, Byrom Street, Liverpool L3 3AF, UK

b Department of Pharmacology and Therapeutics, School of Medicine, Trinity Centre for Health Sciences, St. James Hospital, Dublin 8, Ireland

c State Bureau of Criminal Investigation Schleswig-Holstein, Section Narcotics/Toxicology, Mühlenweg 166, D-24116 Kiel, Germany

d Synex Ltd, 67-68 Hatton Garden, N13 4BS, London, UK

e ROAR Forensics, Malvern Hills Science Park, Geraldine Road, WR14 3SZ, UK

f Department of Chemistry and Biochemistry, University of the Sciences, Philadelphia, PA 19104, USA

g Department of Pharmaceutical Sciences, University of the Sciences, Philadelphia, PA 19104, USA

h Department of Psychiatry, University of California San Diego, La Jolla, CA 92093-0804, USA

* Correspondence to: Simon D. Brandt, School of Pharmacy and Biomolecular Sciences, Liverpool John Moores University, Byrom Street, Liverpool, L3 3AF, UK. E-Mail: s.brandt@ljmu.ac.uk

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* 1P-LSD = hemitartrate salt (powder); LSD = tartrate salt (powder).
GC-GC-EI ion trap MS (16.76 min)

GC-CI ion trap MS

LC-(+)-ESI-Q-MS
FrAGMENTOR VOLTAGE 50 V
LSD
m/z 324

LC-(+)-ESI-Q-MS
FrAGMENTOR VOLTAGE 50 V
1P-LSD
m/z 380

GC-MS (EI/Cl) and LC-single quadrupole MS trace of 1P-LSD
Matrix assisted ionization mass spectrum (MAI-MS) of 1P-LSD obtained from direct analysis of a 1P-LSD blotter.

**Matrix assisted ionization mass spectrometry (MAI-MS)**

A Thermo Scientific Exactive™ mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) was modified by removing the Ion Max source to expose the inlet capillary for sample introduction using glass slides. The trap fill time was set at 1000 ms to correspond with the 1 s required to achieve a resolution of 100,000 (50% FWHH, m/z 200). The sheath, auxillary, and sweep gas flow rates, as well as the electrospray ionization spray voltage, were set to zero. The inlet capillary temperature was set at 70 °C. The capillary, tube lens and skimmer voltages were optimized at 30, 60, and 18 V, respectively, and acquisition time was set to continuous mode. The higher-energy collisional dissociation (HCD) parameter was set at 35 eV to induce dissociation.

**Blotter preparation for MAI-MS analysis**

3-Nitrobenzonitrile was used as the matrix and prepared at a 0.6 mg/mL concentration with acetonitrile/water (1:1). For direct MAI-MS analysis, 1 µL of matrix solution was added onto the surface of the 1P-LSD blotter and allowed to air-dry.
Drug Testing and Analysis – Brandt et al. – Supplementary Information

HPLC-UV (1P-LSD) traces and DAD spectra (1P-LSD vs. LSD)
Incubation of 1P-LSD in human serum at 37 °C and analysis of 1P-LSD vs. LSD using LC single quadrupole MS (blank serum, 0 h and 1h)
Incubation of 1P-LSD in human serum at 37 °C and analysis of 1P-LSD vs. LSD using LC single quadrupole MS (2 h, 3 h and 24 h)
1P-LSD hemitartrate
$^1$H/$^1$H - COSY d$_6$ - DMSO (300 MHz)

TA = Tartaric acid
1P-LSD hemitartrate
$^1H \;/^1H$ - COSY $d_6$ - DMSO (300 MHz)

TA = Tartaric acid
1P-LSD hemitartrate
$^1$H/$^1$H - COSY $d_6$ - DMSO (300 MHz)

TA = Tartaric acid

$^1$H - COSY 1P-LSD hemitartrate
1P-LSD hemitartrate

$^1$H / $^1$H - COSY $d_6$ - DMSO (300 MHz)

TA = Tartaric acid
1P-LSD hemitartrate

HSQC - $d_6$ - DMSO (300 / 75 MHz)

TA = Tartaric acid
1P-LSD hemitartrate
HSQC - d\textsubscript{6} - DMSO (300 / 75 MHz)

TA = Tartaric acid
1P-LSD hemitartrate
HSQC - d₆ - DMSO (300 / 75 MHz)

TA = Tartaric acid
1P-LSD hemitartrate
HMBC - d₈ - DMSO (300 / 75 MHz)
TA = Tartaric acid
1P-LSD hemitartrate
HMBC - d$_6$ - DMSO (300 / 75 MHz)

TA = Tartaric acid
1P-LSD hemitartrate
HMBC - d_{6} - DMSO (300 / 75 MHz)
TA = Tartaric acid
1P-LSD hemitartrate
HMBC - d$_6$ - DMSO (300 / 75 MHz)
TA = Tartaric acid
LSD tartrate

$^1$H - NMR $d_6$ - DMSO (300 MHz)

TA = Tartaric acid
LSD tartrate

$^1$H-NMR $d_6$-DMSO (300 MHz)
LSD tartrate

$^1$H - NMR $d_6$ - DMSO (300 MHz)

TA = Tartaric acid
LSD tartrate

$^1H/^1H$ - COSY $d_6$ - DMSO (300 MHz)
LSD tartrate
$^1\text{H} / ^1\text{H}$ - COSY $d_6$ - DMSO (300 MHz)
TA = Tartaric acid

$\alpha$ $\beta$ $\gamma$

solvent

20 $5\alpha$

14 $\beta$

12 $\beta$

$\text{NH}$

1 $\alpha$

17 $\gamma$

$\text{O}$

$\text{N}$

$\text{H}_6$

$\text{H}_5$

$\text{H}_4$

$\text{H}_3$

$\text{H}_2$

$\text{H}_1$

$\text{H}_0$

$\text{H}_9$

$\text{H}_8$

$\text{H}_7$

$\text{H}_6$

$\text{H}_5$

$\text{H}_4$

$\text{H}_3$

$\text{H}_2$

$\text{H}_1$

$\text{H}_0$
LSD tartrate
$^1$H/$^1$H - COSY $d_6$ - DMSO (300 MHz)

TA = Tartaric acid
LSD tartrate
$^1H/^1H$ - COSY d$_6$ - DMSO (300 MHz)
TA = Tartaric acid
1P-LSD tartrate
DEPTQ - d6 - DMSO (75 MHz)
TA = Tartaric acid

LSD tartrate
DEPTQ - d6 - DMSO (75 MHz)
TA = Tartaric acid
LSD tartrate
HSQC - $d_6$ - DMSO (300 / 75 MHz)
TA = Tartaric acid
LSD tartrate
HSQC - d$_6$ - DMSO (300 / 75 MHz)
LSD tartrate
HSQC - d₆ - DMSO (300 / 75 MHz)

TA = Tartaric acid
LSD tartrate
HMBC - $d_6$ - DMSO (300 / 75 MHz)
LSD tartrate
HMBC - d$_6$ - DMSO (300 / 75 MHz)
LSD tartrate
HMBC - d₈ - DMSO (300 / 75 MHz)
TA = Tartaric acid
LSD tartrate
HMBC - $d_6$ - DMSO (300 / 75 MHz)

TA = Tartaric acid

[Diagram of the HMBC spectrum showing peak assignments and chemical shifts]
LSD tartrate
HMBC - d₆ - DMSO (300 / 75 MHz)