



Co-funded by the Prevention of and Fight
against Crime Programme of the European Union

Slovenia at the cutting edge of new cumyl- derivatives and some other types of synthetic cannabinoids - by chance or by choice?



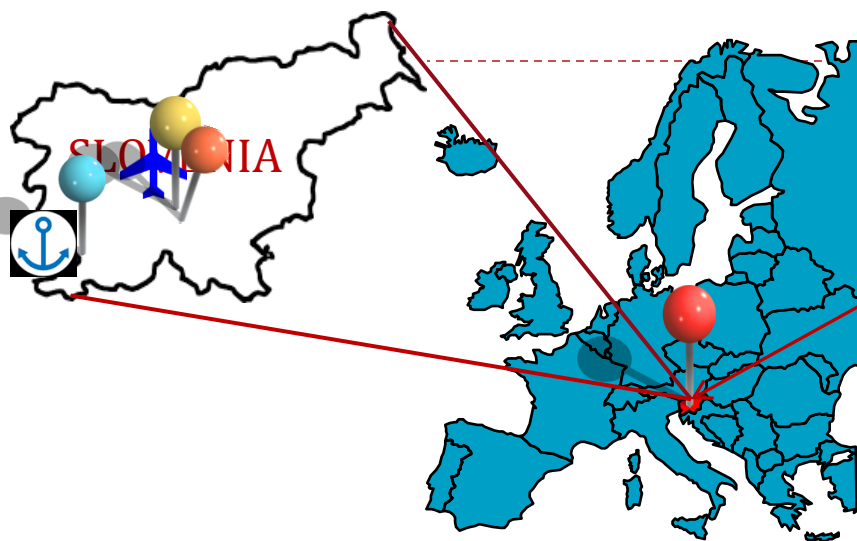
Dr. Sonja Klemenc

(sonja.klemenc@policija.si and ssklemenc@gmail.com)

MNZ GPU, National Forensic Laboratory, Vodovodna 95, 1000 Ljubljana, Slovenia

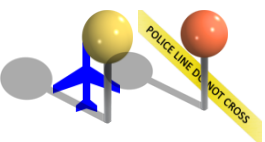
Presentation and a part of chemical characterizations have been produced with the financial support of the Prevention of and fight against crime Programme of the European Union (grant agreement number JUST/2013/ISEC/DRUGS/AG/6413). The contents of this work are the sole responsibility of the author and can in no way be taken to reflect the views of the European Commission.

“Case” at a glance

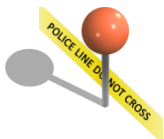


1. **Airport Ljubljana**: investigation of “dietary supplements-shipment” for a company in Ljubljana. Shipment was from Hong Kong// NFL findings: pure forms of new synthetic cannabinoids;// NFL requested supporting documentation - MSDS issued by the New Zealand’s company “STARGATE OPERATIONS LTD”. /summer 2014/
2. **Ljubljana**: investigation of the production site in Ljubljana. Investigations & analyses revealed production of “herbal highs and C-liquids” and inferred on links: China, New Zealand, Australia, Slovenia...)/ autumn 2014/
3. **Koper port**: Sizure of **herbal incenses – preparations** (cca **1500** kg) for the company in LJ. Shipment from China, invoice and cargo list from “STARGATE OPERATIONS LTD”, NZ /2014-2015/
4. **Airport Ljubljana**: Controls (customs) of 2 successive shipments (**12kg**) from China for company in **LJ** of new synthetic cannabinoid /2014 -2015/

Types of investigated materials



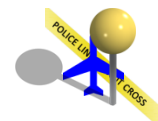
- ▶ **Pure compounds** - synthetic cannabinoids (**m ≈ 24 kg powdered forms + V ≈ 12l liquids**)
+ dimethocaine (**m ≈ 20 kg**), caffeine (**m ≈ 4 kg**)



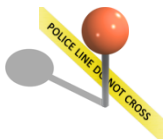
- ▶ **Liquid preparations** (C-liquids) – synthetic cannabinoid + (propylene glycol, vegetable glycerin, aromas) / (No ≈ 10000 bottles (3ml each); **V ≈ 30l**)



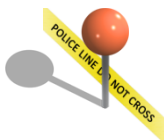
- ▶ **Herbal incenses – preparations** (smoking mixtures) (**m ≈ 1500 kg**)



- ▶ **Pills** (1 type only) (**No = 651**)

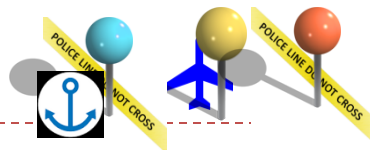


- ▶ **Other compounds** -non psychoactive /crushed plant material (m ≈ 1000 kg), aromas – flavorings (**>350 kg**), food colorants (**>150 kg**), solvents (acetone), propylene glycol, vegetable glycerin.)...



- ▶ **Equipment** (mixing, packing, label printing machines other tools), **empty packing bags, draft production guidelines, other documents..**

Chemical characterizations (NFL & FKKT)



- ▶ Analytical methods :
 - ▶ GC-MS (chromatographic separation and MS spectrum (search against different libs and literature;
 - ▶ interpretation of fragmentation pattern and crosscheck with supporting information, if available)
 - ▶ FTIR-ATR (pure compounds - search against exiting libraries)
 - ▶ GC-MS-FTIR(condensed phase – forthcoming ☺)
 - ▶ HPLC-TOF (exact monoisotopic and suggested empirical formula)
 - ▶ NMR (^1H , ^{13}C , ^1H - ^1H *gs-COSY*, ^1H - ^{13}C *gs-HSQC*, ^1H - ^{13}C *gs-HMBC*, ^1H - ^{15}N *gs-HMBC*) (*FKKT*)

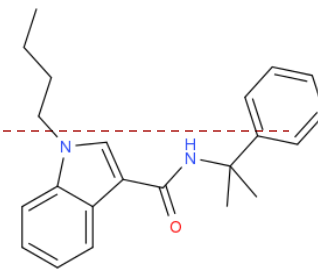
EXAMPLE

SAMPLE sized:
1645 g, white powder

MSDS ?: CAS unknown

1-butyl-*N*-(2-phenylpropan-2-yl)-1*H*-
indole-3-carboxamide

Formula: $C_{22}H_{26}N_2O$



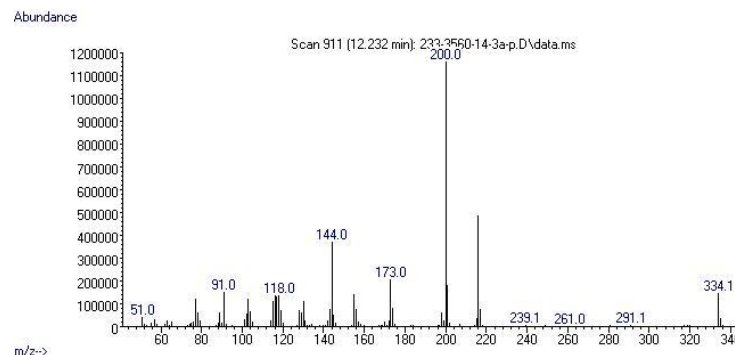
1. GC-MS

GC: single peak; MS: see below

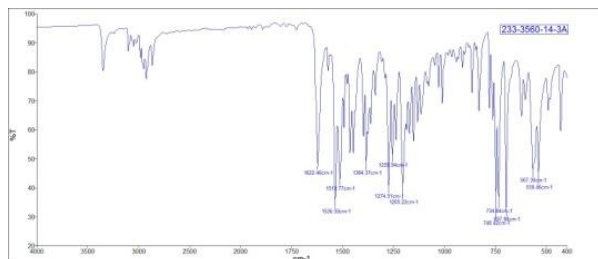
Library search: no matches

Literature search: no info

Fragmentation: pattern study (ion 216?)



2. FTIR-ATR: no matches



3. HPLC- TOF

Formula:

$C_{22}H_{26}N_2O$

Exact mass:

334.20451

TOF ($\Delta ppm = -2.09$)

4. NMR

Confirmed the proposed structure.

5. Reported:

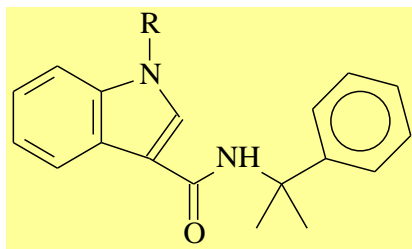
EMCDDA, SI EWS, ENFSI

6. Shared (material):

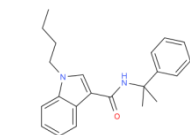
By the project partners

Compounds identified (summary)

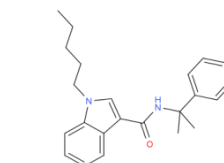
► Cumyl-carboxamides - indole (I), indazole (II), azaindole (III)



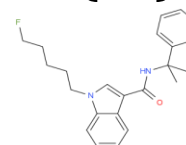
(I)



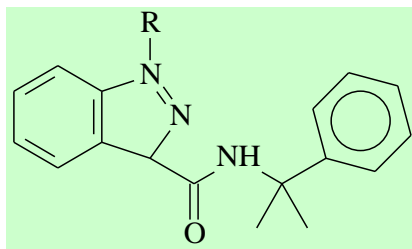
1-butyl-N-(2-phenylpropan-2-yl)-1H-indole-3-carboxamide
(CUMYL-BICA)



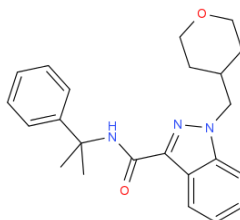
1-pentyl-N-(2-phenylpropan-2-yl)-1H-indole-3-carboxamide
(CUMYL-PICA)



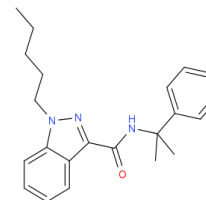
1-(5-fluoropentyl)-N-(2-phenylpropan-2-yl)-1H-indole-3-carboxamide
(CUMYL-5F-PICA)



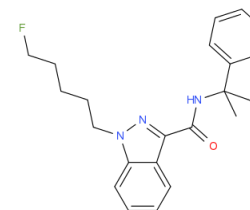
(II)



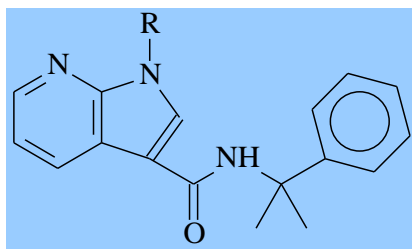
N-(2-phenylpropan-2-yl)-1-((tetrahydro-2H-pyran-4-yl)methyl)-1H-indazole-3-carboxamide
(CUMYL-THPINACA)



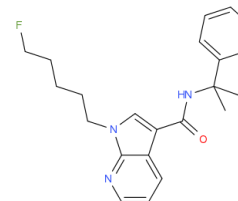
1-pentyl-N-(2-phenylpropan-2-yl)-1H-indazole-3-carboxamide
(CUMYL-PINACA)



1-(5-fluoropentyl)-N-(2-phenylpropan-2-yl)-1H-indazole-3-carboxamide
(CUMYL-5F-PINACA)



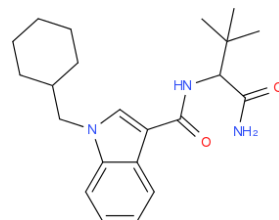
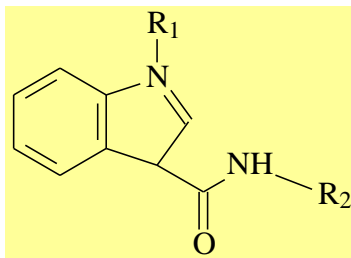
(III)



1-(5-fluoropentyl)-N-(2-phenylpropan-2-yl)-1H-(7-azaindole)-3-carboxamide
CUMYL-5F-P7AICA

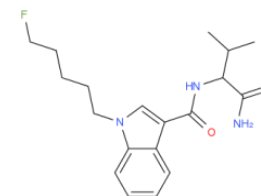
Compounds identified (summary)

► Other indole carboxamides



N-[(1-Amino-3,3-dimethyl-1-oxobutan-2-yl)-1-(cyclohexylmethyl)-1H-indol-3-yl]-carboxamide

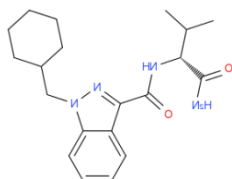
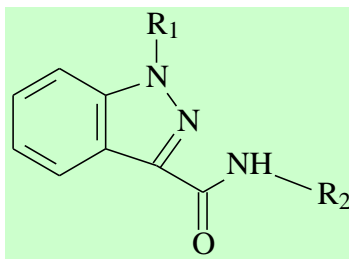
ADB-CHMICA



N-[(1-amino-3-methyl-1-oxobutan-2-yl)-1-(5-fluoropentyl)-1H-indol-3-yl]-carboxamide

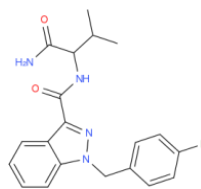
5F-AMBICA (5F-ABICA)

► Other indazole carboxamides



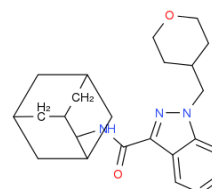
N-[1-(aminocarbonyl)-2-methylpropyl]-1-(cyclohexylmethyl)-1H-indazole-3-carboxamide

AB-CHMINACA



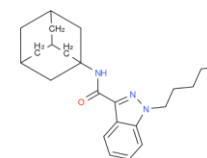
N-[(1-amino-3-methyl-1-oxobutan-2-yl)-1-(4-fluorobenzyl)-1H-indazole-3-yl]-carboxamide

AB-FUBINACA



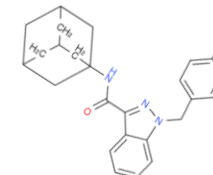
N-[(2-adamantyl)-1-(tetrahydropyran-4-ylmethyl)indazole-3-yl]-carboxamide

ADAMANTYL-THPINACA



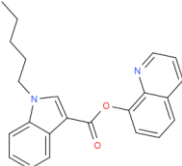
N-[(1-adamantyl)-1-pentyl-1H-indazole-3-yl]-carboxamide

AKB-48 (APINACA)



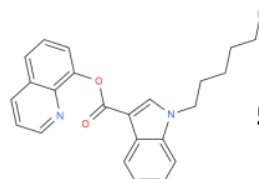
AKB48-4-fluorobenzyl analog (FUB-AKB48)

► Others

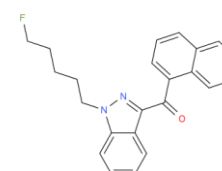


8-Quinoliny 1-pentyl-1H-indole-3-carboxylate

PB-22



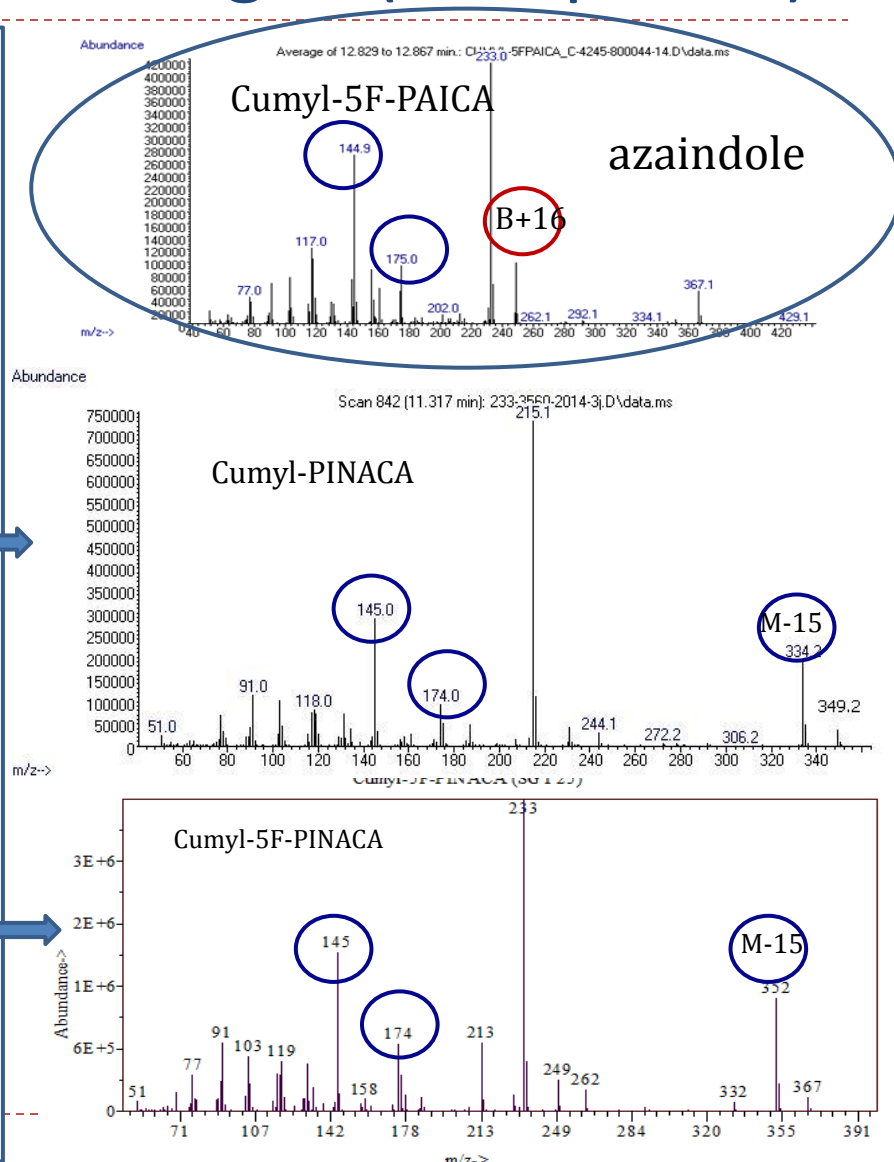
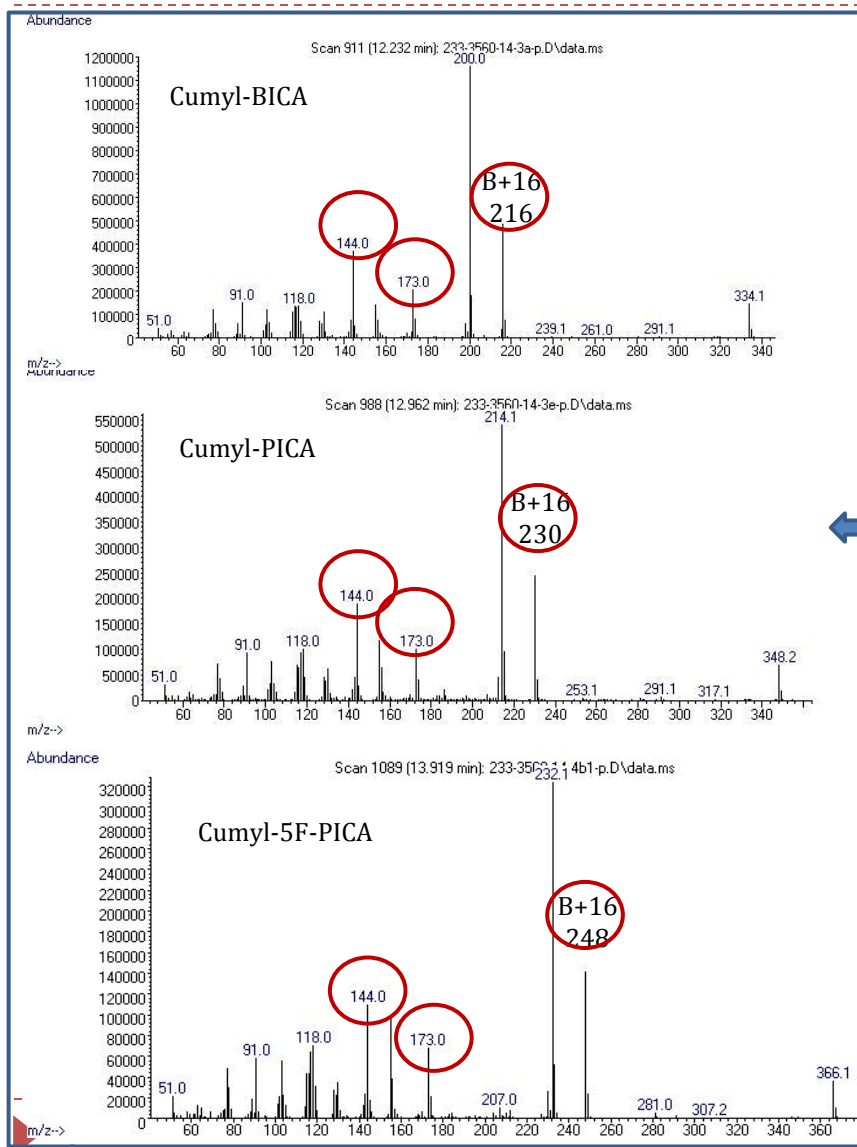
5F-PB-22



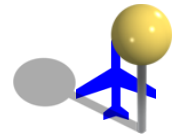
(1-(5-fluoropentyl)-1H-indazol-3-yl)(naphthalen-1-yl)methanone

THJ 2201 (AM 2202 indazole analog)

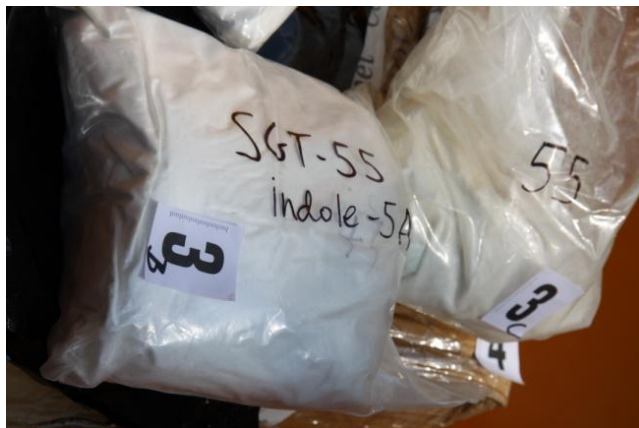
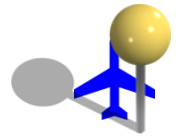
Indole, indazole, azaindole analogue (MS spectra)



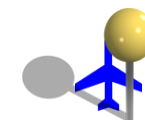
Seizure at the Ljubljana airport

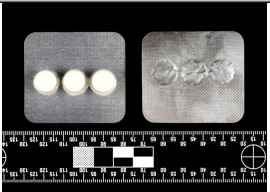


At the airport (sampling continue)



Airport Ljubljana (first seizure) - results



SUBSTANCES SEIZED AT THE AIRPORT LJUBLJANA (first seizure)				
Concentrates (pure substances)	Description	Quantity	Unit	Additional remarks
CUMYL-BICA	white powder	1645	g	3x packages (plastic bags), label: "indole-5a"
CUMYL-PICA	white powder	1269	g	2x packages (plastic bags); label: "STG-56, Indole-5b"
CUMYL-PINACA	yellowish liquid	11150	ml	13 x one-liter bottle; label: "SGT-24"
CUMYL-5F-PICA	white powder	1160	g	4x packages (plastic bags); label: "49"
CUMYL-THPINACA	white powder	3257	g	7x packages (plastic bags); label: "5F"
ADB-CHMICA	light brown	916	g	2x packages (plastic bags), label: "L-SW"
PB-22	pale white	93	g	1x package (plastic bag); label "PB22"
Pills	Description	Quantity	Unit	Additional remarks
CUMYL-THPINACA	white	651	piece	 <p>no logo or labels 217 blisters; 3 pills/blister diameter : 10.2 mm thickness: 6.1 mm</p>

Dismantling of production site in LJ (seizure II)



- ▶ Synthetic cannabinoids (pure - concentrates) and preparations (herbal and liquid)
- ▶ Non-processed herbal material : around 1000 kg of (Damiana, Marshmellow, Natural - sent mainly from Sydney, Amsterdam, one small package from Bulgaria)
- ▶ Solvents: acetone, propylene glycol, vegetable glycerine,
- ▶ Aromas – different ("Tasty Puff")
- ▶ Synthetic food colorants (green, red, blue)
- ▶ Mixing machine and packing machines
- ▶ printed foil bags (several boxes with around 150 kg of empty bags - different designs) - sent from China.
- ▶ Bags filled with herbal incenses (KRONIC, known as NZ "STARGATES `s product)
- ▶ Empty packages for tablets "Social tonic 4:20" (known NZ "STARGATES `s product) - most probably intended to be used as packaging for the tablets seized at the airport
- ▶ Document "production manual" describe composition of some preparations and advice how the production should be organized. At some parts "manual" refers to New Zealand experiences.
- ▶



Non processed herbal material, aromas, colourants..



Mixing machine: raw plant material + synthetic cannabinoid dissolved in acetone is mixed until acetone is evaporated (some preparations can be sprayed with aromas and colourants can be added as well).



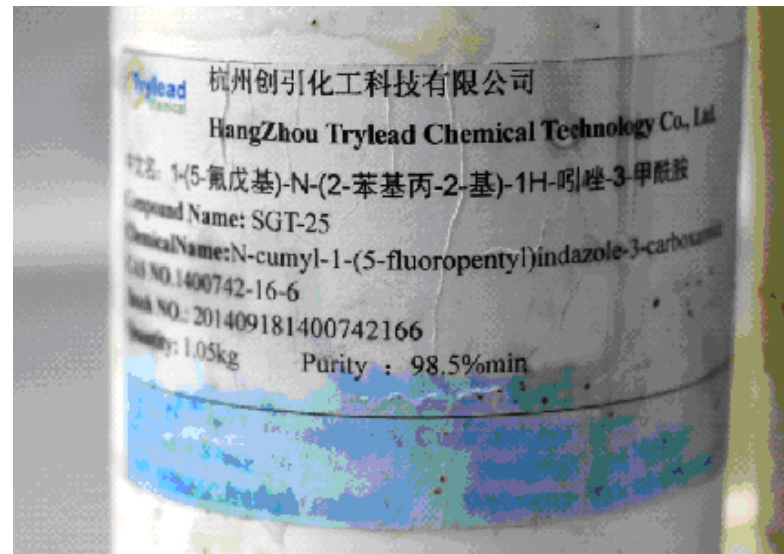
Herbal preparations

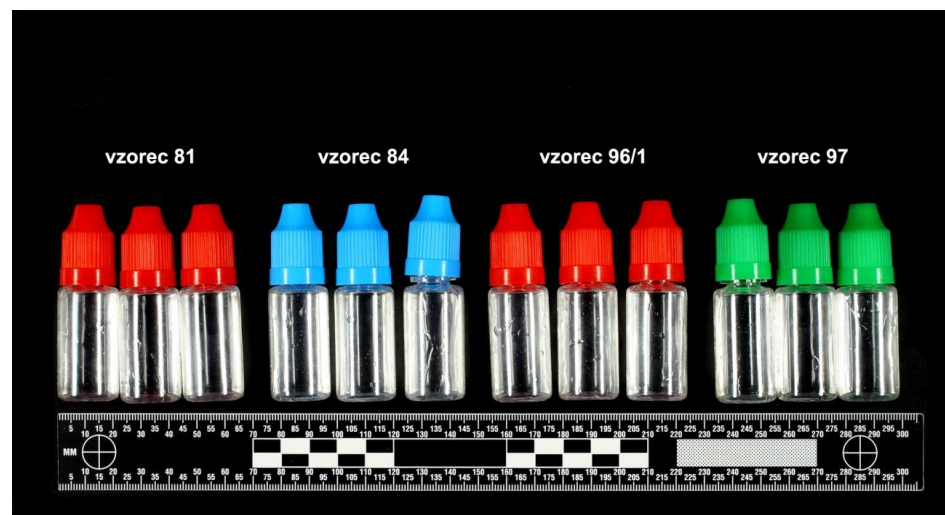






At NFL





Materials from the production site - results



SUBSTANCES SEIZED AT THE PRODUCTION SITE				
Concentrates of cannabinoids	Description	Quantity	Unit	Additional remarks
5F-ABICA	white powder	15	g	
AB-CHMINACA	white powder	4	g	
AB-FUBINACA	white powder	25	g	
ADAMANTYL-THPINACA	white	746	g	
ADB-CHMICA	light brown	2447	g	4 packages
AKB 48 + 5F-PB22	light brownish	15	g	
FUB-AKB48, AKB48 N-(4-fluorobenzyl) analogue	yellowish	101	g	
THJ 2201	white	15	g	
CUMYL-5F-PINACA	yellowish liquid	215	ml	3 plastic bottles (all opened previously) - originally labeled: 1-(5-fluoropentyl)-N-(2-phenylpropane-2-yl)-1H-indazole-3-carboxamide (SGT-25)
Liquid preparations (C-liquids)		volume (ml)		
CUMYL-5F-PINACA (preparation)	no colour, clear	2774*	ml	* laboratory sample + around 10000 x 3 ml=30l (bottles on the spot)
Herbal highs – active ingredients	Description	Quantity	Unit	Additional remarks
CUMYL-5F-PINACA (SGT-25)		15729	g	+ herbal incenses (active ingredient SGT-25) in small bags - estimated number approximately 7000 to 10000 pkg. (of different net weighs declared: 3.5g or 2g or 1.5g)
ADB-CHMICA		6680	g	
ADAMANTYL-THPINACA		2009	g	
FUB-AKB48, AKB48 N-(4-fluorobenzyl) analogue		101	g	
CUMYL-5F-PINACA+ ADB CHMICA + ADAMANTYL-THPINACA		2068	g	
CUMYL-5F-PINACA + ADB-CHMICA		2121	g	
CUMYL-5F-PINACA + ADAMANTYL-THPINACA		49	g	

Koper port - results



Seizure in Koper port (customs terminal)				
Herbal highs (active ingredients)	Description	Quantity	Unit	Additional remarks
CUMYL-PINACA	different colours and aromas	761415	g	32x packages (aluminum-plastic bags), label: "GIG" 28x packages (aluminum-plastic bags); label: "GIGGLE" 115x packages (aluminum-plastic bags); label: "Social Tonic, SGT-24" 152x packages (aluminum-plastic bags; label "DIABLO" 59x packages (aluminum-plastic bags); label: "ST"
PB-22		699829	g	155x packages (aluminum-plastic bags); label: "RED X" 195x packages (aluminum-plastic bag); label: "RAD"

From New Zealand & China to Slovenia evidence



MATERIAL SAFETY DATA SHEET

Creation Date: February, 2014
This version issued: March, 2014

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name: SGT67
Chemical name: 1-(5-fluoropentyl)-N-(1-methyl-1-phenylethyl)-1H-Indole-3-carboxamide
Catalog Codes: SGT67
CAS# 1400742-18-8
Chemical Formula: C₂₃H₂₇FN₂O

Manufacturer: Stargate Operations Ltd

Stargate Operations Ltd
PO Box 300 840
Albany, Auckland
New Zealand
Phone: 0800 78274283

2. COMPOSITION/INFORMATION ON INGREDIENTS

Components: 1-(5-fluoropentyl)-N-(1-methyl-1-phenylethyl)-1H-Indole-3-carboxamide
Percentage: 97%

3. HAZARDS IDENTIFICATION

Emergency overview: Material is a white or pale yellowish powder at room temperature. It has an acrid smell and dangerous to inhale or touch.

Route of Entry: Skin contact, eye contact, inhalation, ingestion



STARGATE OPERATIONS LTD
UNIT 1/6 ARGUS PLACE
HILLCREST, ALBANY
AUCKLAND 0632
Ph: 0800STARGATE

CONTAINER PACKING LIST

Shipment #:
CONSOL #:
Container ID:
Delivery to:

PACKING LIST SUMMARY:

Item Description:	Weights	
Potpourri:	1470	
Flavours:	294	
Colours:	40	
Total:	1804	kg

	No of Boxes	Volume / cu m
Potpourri:	77 large	7.94
Flavours:	11 large	1.25
	2 med	0.03
	1 small	0.02
Colours:	Half Pallet	0.5
	Total Volume cu m:	9.73
	Total Items:	92

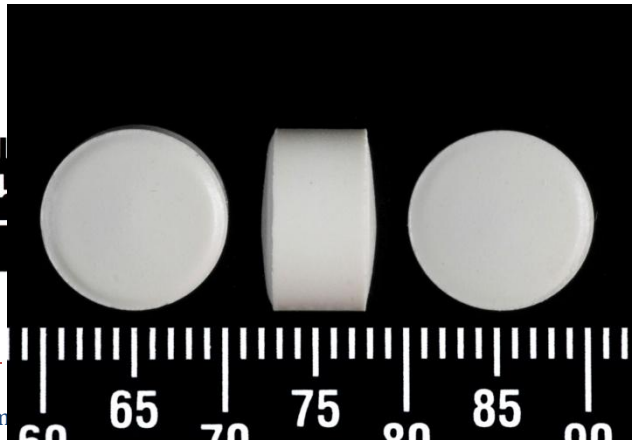
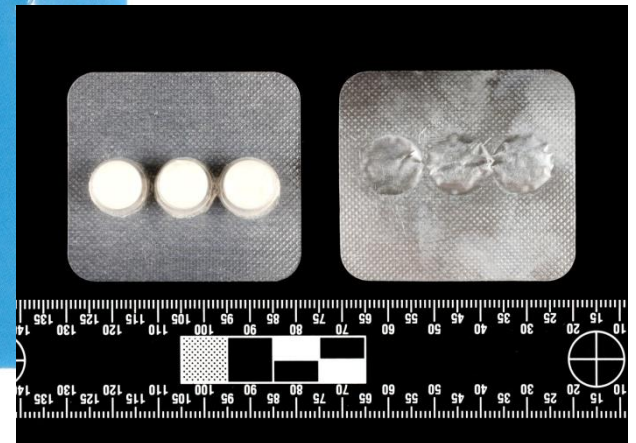
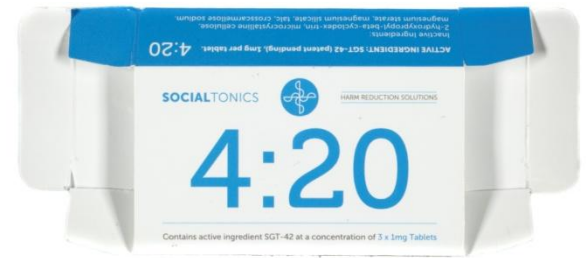
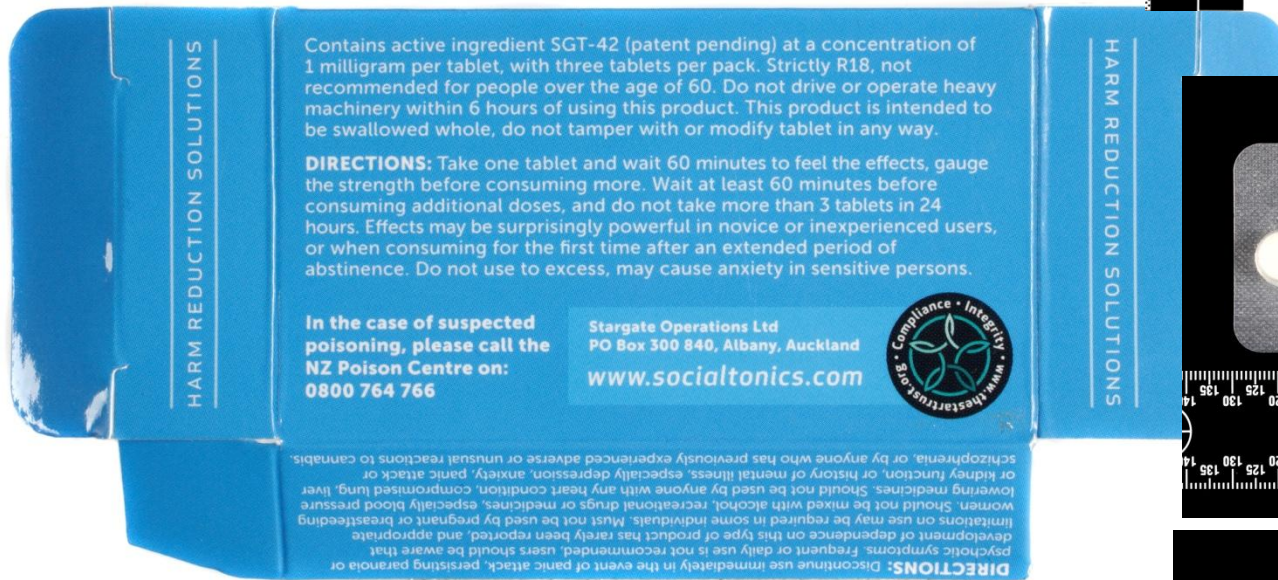
Total Weight:	1804
Total Volume cu m:	9.73
Total Number of Items:	92

From New Zealand to Slovenia - evidence

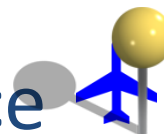


Figure 1: Empty packaging with labels of New Zealand products

From New Zealand to Slovenia evidence



From New Zealand to Slovenia - evidence

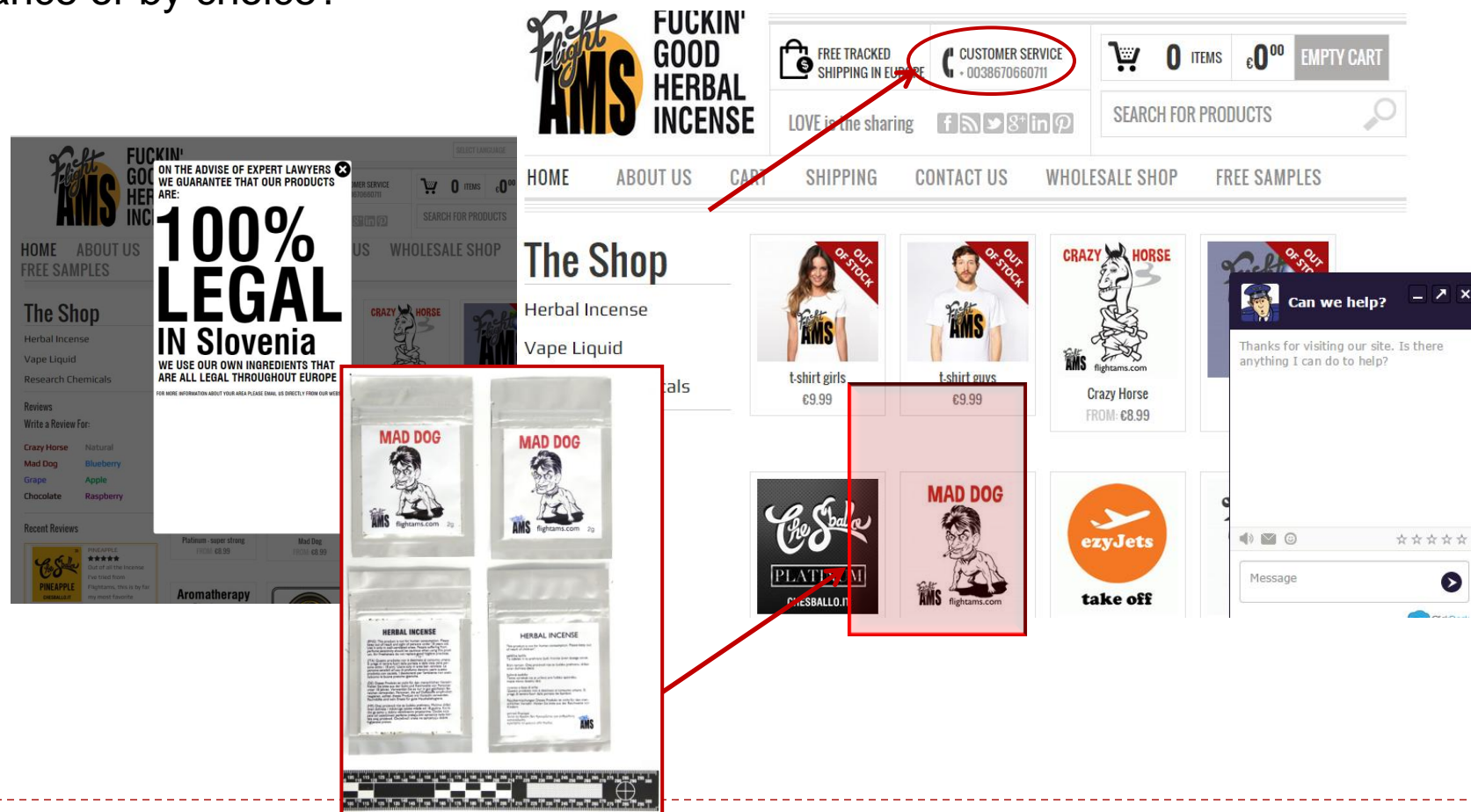


- a) Substances were imported from Hong Kong as food supplements.
- b) When NFL asked for supporting documentation, after quite some time we received MSDS for six compounds.
- c) issued by “STARGATE COMPANY”, New Zealand.
- d) Excerpt of PB-22 no analytical data were available for other compounds
- e) Not existing CAS numbers

S T A R  G A T E	
MATERIAL SAFETY DATA SHEET Creation Date: February, 2014 This version issued: March, 2014	
1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION	
Product name: SGT67 Chemical name: 1-(5-fluoropentyl)-N-(1-methyl-1-phenylethyl)-1H-Indole-3-carboxamide Catalog Codes: SGT67 CAS#: 1400742-18-8 Chemical Formula: C ₂₃ H ₂₇ FN ₂ O	
Manufacturer: Stargate Operations Ltd	
Stargate Operations Ltd PO Box 300 840 Albany, Auckland New Zealand Phone: 0800 7827 4283	
2. COMPOSITION/INFORMATION ON INGREDIENTS	
Components: 1-(5-fluoropentyl)-N-(1-methyl-1-phenylethyl)-1H-Indole-3-carboxamide Percentage: 97%	
3. HAZARDS IDENTIFICATION	
Emergency overview: Material is a white or pale yellowish powder at room temperature. It has an acrid smell and dangerous to inhale or touch. Route of Entry: Skin contact, eye contact, inhalation, ingestion	

By chance or by Choice?

It seems that the new psychoactive substance regulation introduced in New Zealand (2014) touched not only New Zealand but Slovenia as well. Was Slovenia selected by chance or by choice?



Thank you for your attention!

