

SLOVENIA AT THE CUTTING EDGE OF NEW CUMYL- DERIVATIVES AND SOME OTHER TYPES OF SYNTHETIC CANNABINOIDS

15th Annual meeting of the Reitox Early Warning System Network, 8–9 June 2015, Lisbon, Portugal



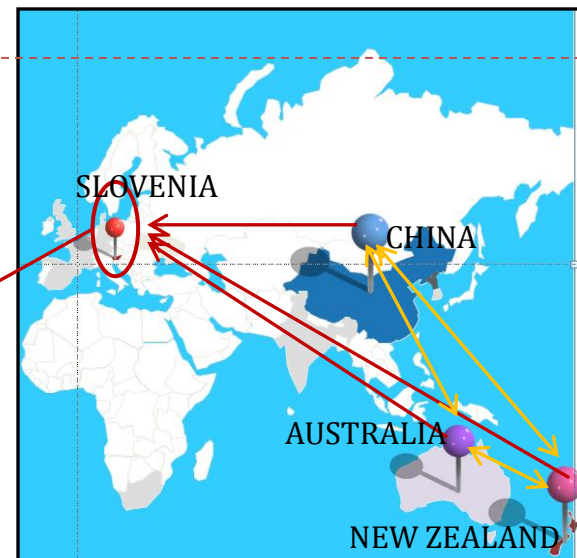
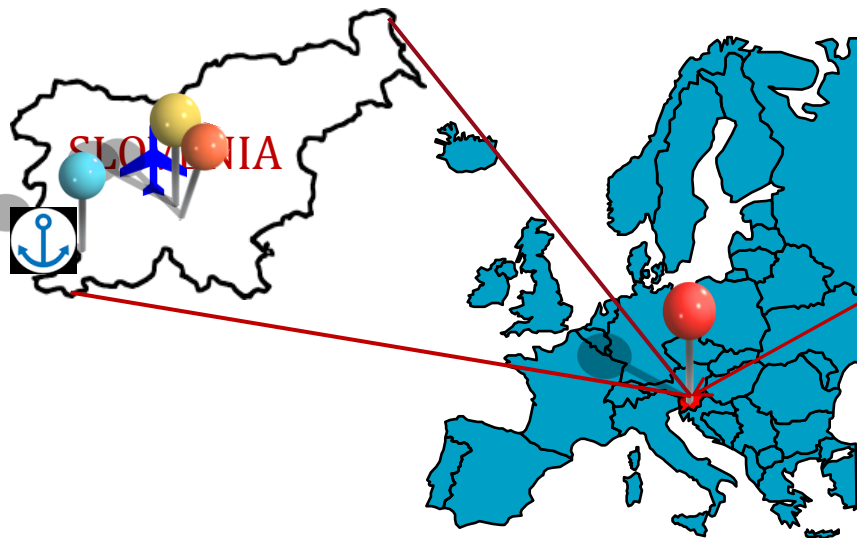
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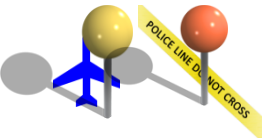
A part of chemical characterizations have been produced with the financial support of the Prevention of and fight against crime Programme of the European Union (grant agreement number JUST/2013/ISEC/DRUGS/AG/6413). The contents of this work are the sole responsibility of the author and can in no way 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 **A** 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– company **A (+ B)**. Investigations & analyses revealed production of “herbal highs and C-liquids” and inferred on links: China, New Zealand, Australia, Slovenia...)/ late autumn 2014/
3. **Koper port**: Sizure of **herbal incenses – preparations** (cca **1500** kg) for the company “**A+B**”. 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 “**A +B**” – **pure form** of new synthetic cannabinoid /REQUEST for identification and structure confiramation from Customs lab./2014-2015/

Types of investigated materials



- ▶ **Pure compounds** - synthetic cannabinoids (**m ≈ 24 kg powdered forms + V ≈ 12l liquids**) – 6 compounds completely new – not reported previously
- ▶ + dimethocaine (**m ≈ 20 kg**), caffeine (**m ≈ 4 kg**)



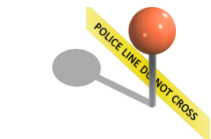
- ▶ **Liquid preparations** (C-liquids) – synthetic cannabinoid + (propylene glycol, vegetable glycerin, aromas) / (No ≈ 10000 bottles (3ml each); **V ≈ 30l**)



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



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

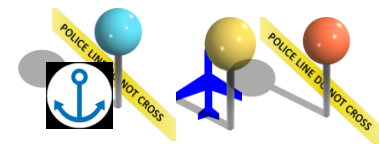


- ▶ **Other compounds** -non psychoactive /crushed plant material (m ≈ 1000 kg), aromas – flavorings (**>350 kg**), food colorants (**>150 kg**), solvents (acetone), propylene glycol, vegetable glycerin.)...



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

Chemical characterizations

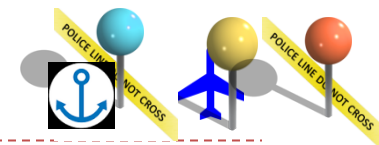


Detection of NPS “unknowns” is mostly not a problem. However, identification of these “unknowns” is a big challenge and joy!!!

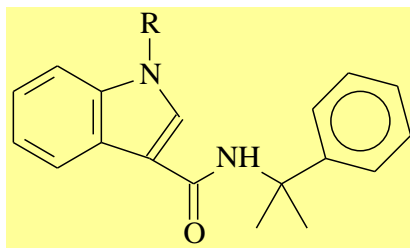
- ▶ Analytical methods applied, so far :
 - ▶ GC-MS (chromatographic separation and MS spectrum (search against different libs and literature));
 - ▶ interpretation of fragmentation pattern and crosschecking with supporting information, if available)
 - ▶ FTIR-ATR (for pure compounds - search against exiting libraries)
 - ▶ GC-MS-FTIR (condensed phase) – (IR spectra of compounds in mixtures)
 - ▶ HPLC-TOF (exact monoisotopic mass 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*)

Compounds identified

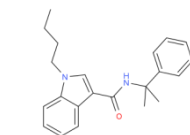
(summary/ only synthetic cannabinoids are shown)



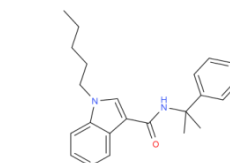
► Cumyl-carboxamides - indole (I), indazole (II), azaindole (III)



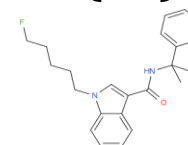
(I)



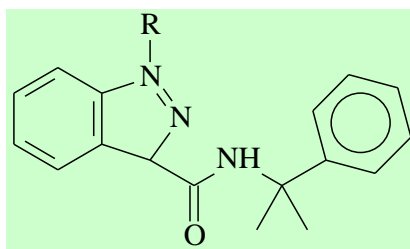
1-butyl-N-(2-phenylpropan-2-yl)-1H-indole-3-carboxamide
(CUMYL-BICA)



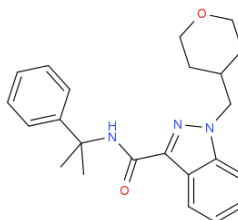
1-pentyl-N-(2-phenylpropan-2-yl)-1H-indole-3-carboxamide
(CUMYL-PICA)



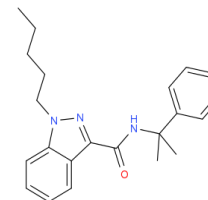
1-(5-fluoropentyl)-N-(2-phenylpropan-2-yl)-1H-indole-3-carboxamide
(CUMYL-5F-PICA)



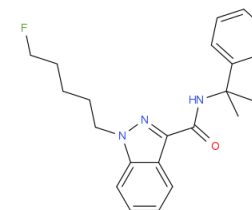
(II)



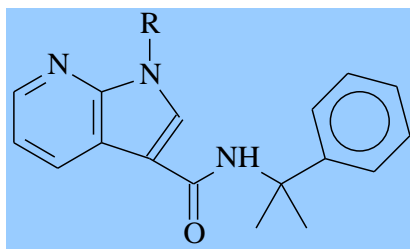
N-(2-phenylpropan-2-yl)-1-((tetrahydro-2H-pyran-4-yl)methyl)-1H-indazole-3-carboxamide
(CUMYL-THPINACA)



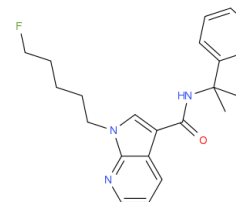
1-pentyl-N-(2-phenylpropan-2-yl)-1H-indazole-3-carboxamide
(CUMYL-PINACA)



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



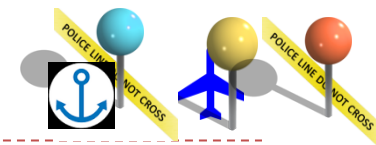
(III)



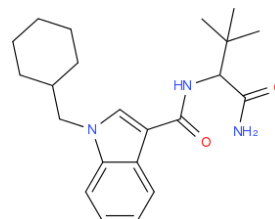
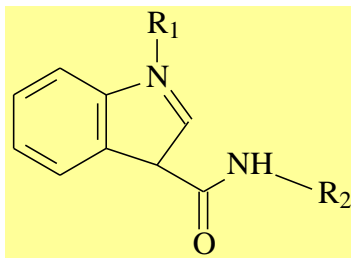
1-(5-fluoropentyl)-N-(2-phenylpropan-2-yl)-1H-(7-azaindole)-3-carboxamide
CUMYL-5F-P7AICA

Compounds identified

(summary/ only synthetic cannabinoids are shown)

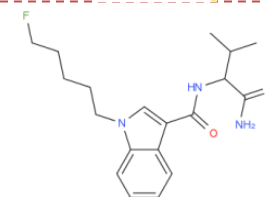


► Other indole carboxamides



N-(1-Amino-3,3-dimethyl-1-oxobutan-2-yl)-1-(cyclohexylmethyl)-1H-indole-3-carboxamide

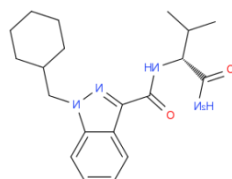
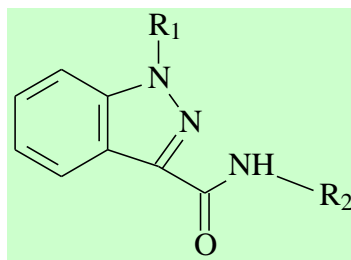
ADB-CHMICA



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

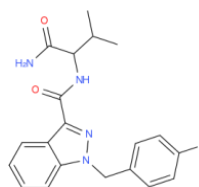
5F-AMBICA (5F-ABICA)

► Other indazole carboxamides



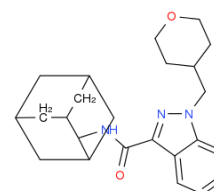
N-[1-(aminocarbonyl)-2-methylpropyl]-1-(cyclohexylmethyl)-1H-indazole-3-carboxamide

AB-CHMINACA



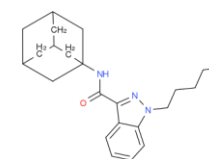
N-(1-amino-3-methyl-1-oxobutan-2-yl)-1-(4-fluorobenzyl)-1H-indazole-3-carboxamide

AB-FUBINACA



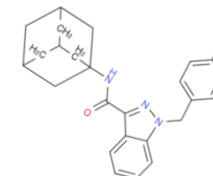
N-(2-adamantyl)-1-(tetrahydropyran-4-ylmethyl)indazole-3-carboxamide

ADAMANTYL-THPINACA



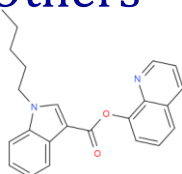
N-(1-adamantyl)-1-pentyl-1H-indazole-3-carboxamide

AKB-48 (APINACA)



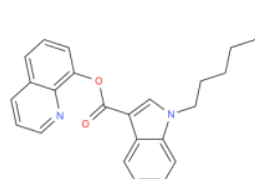
AKB48-4-fluorobenzyl analog (FUB-AKB48)

► Others

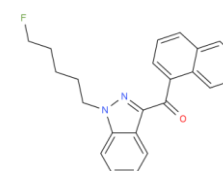


8-Quinoliny 1-pentyl-1H-indole-3-carboxylate

PB-22



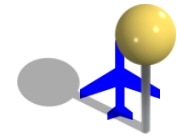
5F-PB-22



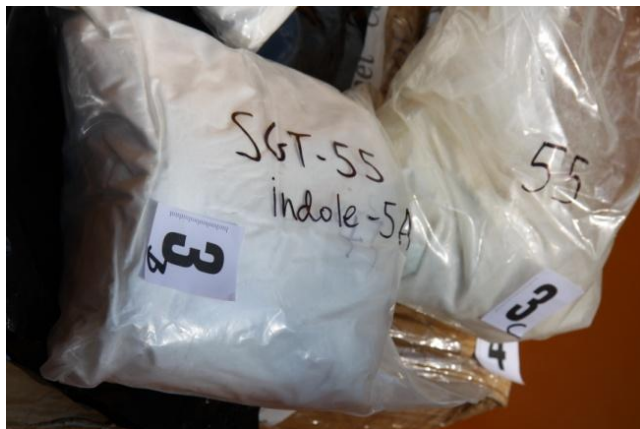
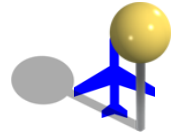
(1-(5-fluoropentyl)-1H-indazol-3-yl)(naphthalen-1-yl)methanone

THJ 2201 (AM 2202 indazole analog)

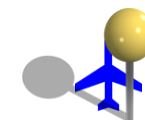
Seizure at the Ljubljana airport

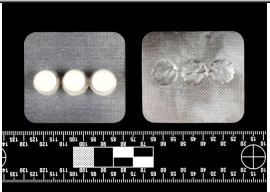


At the airport (sampling continue)



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" describes composition of some preparations and advices how the production should be organized. At some parts "manual" refers to New Zealand experiences.
- ▶

“Dismantling” of the production site in LJ (seizure II)



Non processed herbal material, aromas, colorants..



Mixing machine: raw plant material + synthetic cannabinoid dissolved in acetone is mixed until acetone is evaporated



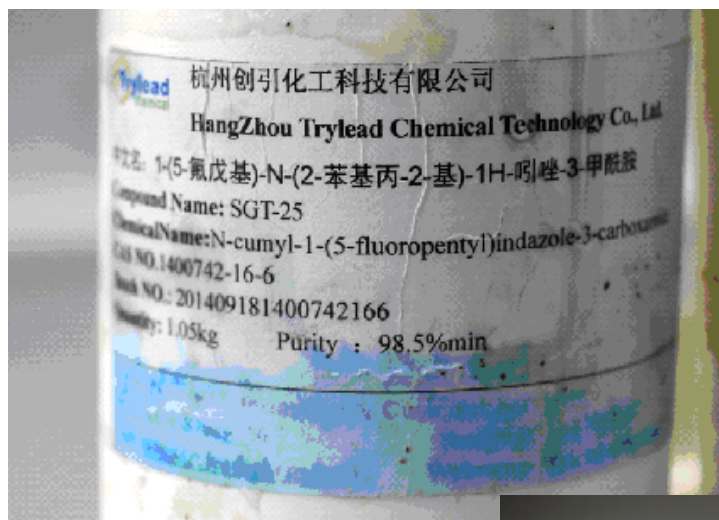
Herbal preparations (smoking mixtures)



“Dismantling “of the production site in LJ (seizure II) - pure compounds (from CHINA)



Pure compounds (shipped from CHINA)



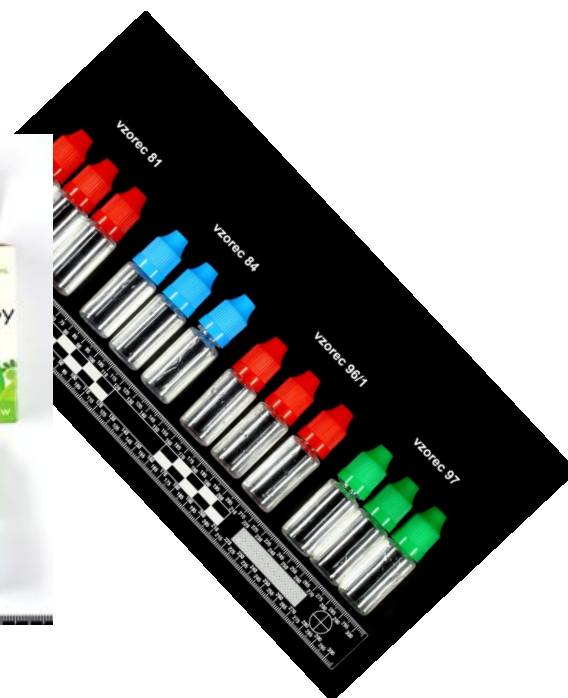
Packing bags(shiped from CHINA)



Parcels with empty packing bags (from China)



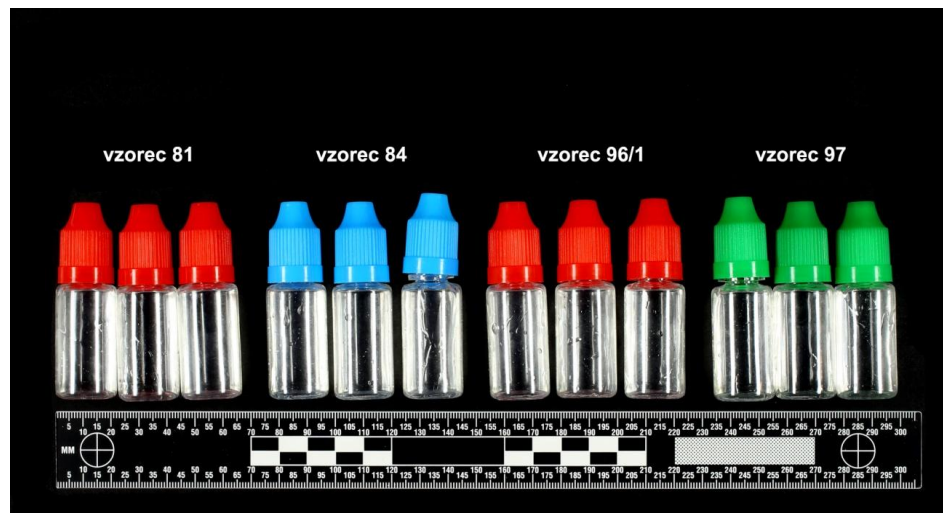
C-liquids (produced on the spot)



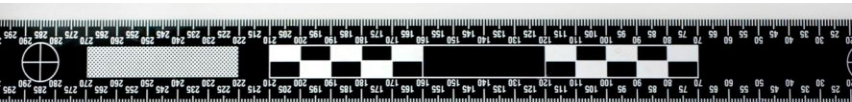
“Packing machines and “Kronic” product just beeing packed on the spot



Laboratory investigations (examples of seized materials)



Miscellaneous



Document “production manual” (excerpt)

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Master Manufacturing document draft

List of ingredients according to products.

Social Tonic – 125g of SGT-24 + 10l of acetone + 20kg of damiana + 5kg of Marshmellow

Giggle – 125g of SGT-24 + 10L of acetone + 0.75L of grape flavour + 0.75L of blueberry flavour + Blue colouring (check weight). + 20kg of damiana + 5kg of Marshmellow

Diablo – 125g of SGT-24 + 10L of acetone + 1.5L of Chumpy Chocolate + Red colouring + Yellow Colouring + Blue colouring (again check weight) + 20kg of damiana + 5kg of Marshmellow

RedX – 1kg of PB-22 + 10L of acetone + 20kg of damiana

Radiation – 800g of PB-22 + 10L of acetone + 20kg of damiana

bucket, until fully dissolved. Full PPE gear is required for operators involving at least full coveralls, double nitrile gloves, arm sleeve protectors, filter masks and hair nets. If any active lands on skin or PPE gear wash thoroughly or replace gear involved immediately.

Colouring

Colouring of product is performed when mixing active ingredient into acetone, after this step the appropriate colours are added at a standard weight of ----- . This is then mixed into the acetone until dissolved before mixing of ingredients begins. For Diablo this involves ----- of Blue -----, the same amounts of Yellow -----, and Red -----.

Preparation of excipients

Damiana should be prepared in large trays once opened from packaging, separate out 20kg of plant material through a screen into large clean dustbins per run. 2 full size dustbins are needed 10kg in each per run. Marshmellow should also be prepared in large trays once opened from packaging as above, and 5kg separated out through a screen into large clean dustbins per run. 1 Dustbin is required to hold 5kg per run.

Mixing of ingredients

Mixing should be done in an isolated room with ventilation and filtering. The mixer used in New Zealand is ----- . 20kg of Damiana and 5kg of Marshmellow are deposited in the top of the machine as per run requirements. The acetone with the active dissolved in it is then added and the machine turned on to run for 15 minutes. When product starts "dusting" then it is ready for drying (large amounts of dust being produced from the top of the machine. Remove from the bottom of machine using a clean wheelbarrow to deposit into large drying trays generally three trays to a run. These are then stacking in a ventilated room for drying until there is no scent of acetone. Full PPE gear is required for operators involving at least full coveralls, double nitrile gloves, arm sleeve protectors, filter masks and hair nets.

If any active lands on skin or PPE gear wash thoroughly or replace gear involved immediately, as this can cause intoxicating effects.

Drying of product

If any active lands on skin or PPE gear wash thoroughly or replace gear involved immediately, as this can cause intoxicating effects.

Drying of product

The drying room and production booth needs to be well ventilated due to the volatility of the ingredients being used and because of the amount of dust being generated. System in New Zealand has two large intake fans into a spray booth with 200mm thick filtering, and an outtake fan. Filters need to be cleaned regularly and exchanged every month. The 3 trays from each production are stacked in order of production to know which batch run is which. These are stacked within the well ventilated drying room and stored there for at least 1 day. Move on to next process once scent of acetone has disappeared from product.

Flavouring of product

Flavouring requires its own mixer the model in New Zealand is this -----, first one run is deposited into the clean machine and lid is put on. A clean chemical sprayer is used to deliver the 1.5L of Chumpy Chocolate flavouring under the lid. The run is then left to dry and mix for 5 minutes and then taken out of the machine into a drying tray to be packaged immediately.

Packaging of product

Need scales and large standalone bags (3kg in size) scoops used must be specific to the product being packaged to prevent cross-contamination. Runs are then deposited into bags with 2.01kg inside them. From each batch run, 2 samples must be taken of around 2g each one is reserve sample for records and the other sample is for contaminants and potency testing to be done both in house and at contracted labs. Labels are then added with each label stating date of manufacture, date of packaging, batch number and product name. Then are then boxed up and stored until sold.

RedX

Mixing of active

1kg of PB-22 is prepared by mixing a premeasured amount of the solid chemical into a bucket containing 10L of acetone, this is then mixed in a heated water bath (set to 75°C) until fully dissolved. Full PPE gear is required for operators involving at least full coveralls, double nitrile gloves, arm sleeve protectors, filter masks and hair nets. If any active lands on skin or PPE gear wash thoroughly or replace gear involved immediately, as this can cause intoxicating effects.

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	

Seizure from Koper port – material shipped from China, container packing list and invoice from New Zealand



STAR GATE

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

CONTAINER PACKING LIST

Shipment #:
CONSOL #:
Container ID
Delivery to:

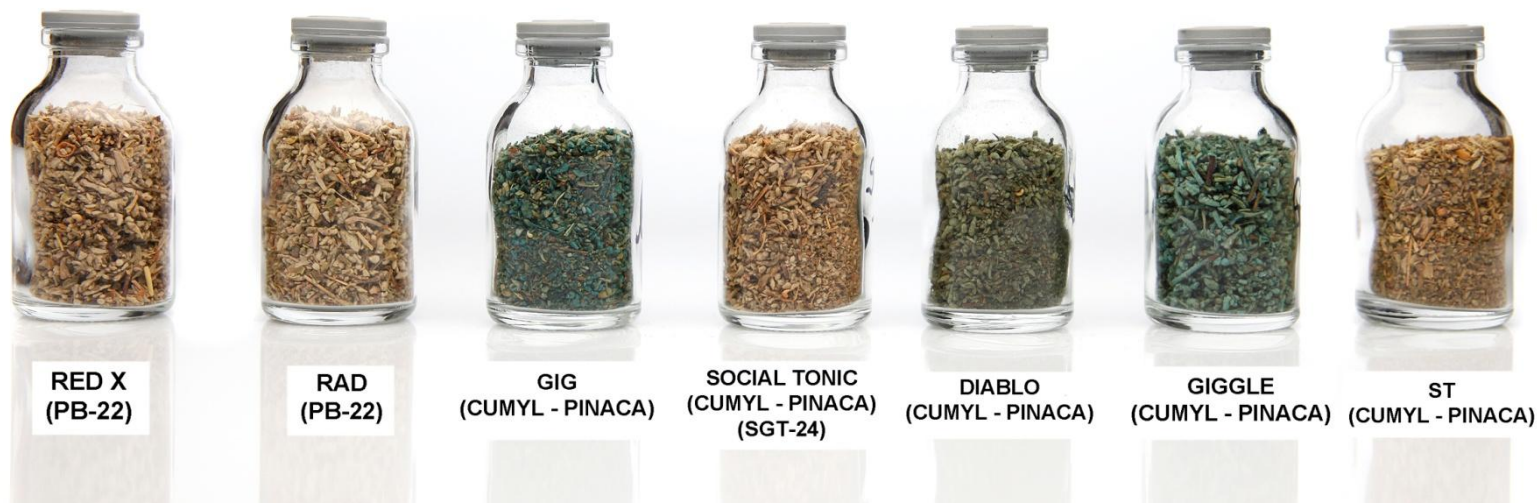
PACKING LIST SUMMARY:

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

Koper port - results



Seizure in Koper port (cus			
Herbal highs (active ingredients)	Description	Quantity	Unit
CUMYL-PINACA	different colours and aromas	761415	g
PB-22		699829	g

Master Manufacturing document draft

List of ingredients according to products.

Social Tonic – 125g of SGT-24 + 10l of acetone + 20kg of damiana + 5kg of Marshmellow

Giggle – 125g of SGT-24 + 10L of acetone + 0.75L of grape flavour + 0.75L of blueberry flavour + Blue colouring (check weight). + 20kg of damiana + 5kg of Marshmellow

Diablo – 125g of SGT-24 + 10L of acetone + 1.5L of Chumpy Chocolate + Red colouring + Yellow Colouring + Blue colouring (again check weight) + 20kg of damiana + 5kg of Marshmellow

RedX – 1kg of PB-22 + 10L of acetone + 20kg of damiana

Radiation – 800g of PB-22 + 10L of acetone + 20kg of damiana

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Airport Ljubljana (2014,2015) - two successive shipments from China - results

NPS identified: Cumyl-5F-P7AICA - **pure compound 12kg**

Compound: Cumyl-5FPAICA (C22H26FN3O)

ANALYTICAL REPORT: Cumyl-5FPAICA (C22H26FN3O) 1-(5-fluoropentyl)-N-(2-phenylpropan-2-yl)-7-azaindole-3-carboxamide

Sample ID:	C 4245-800044/2014
Sample description:	White powder
Report date:	14/02/2015
Other:	/
Sample type	Seizure

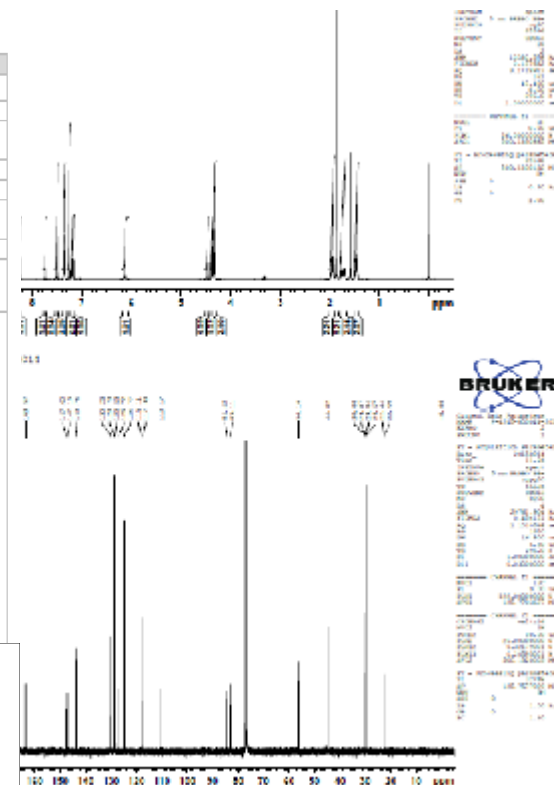
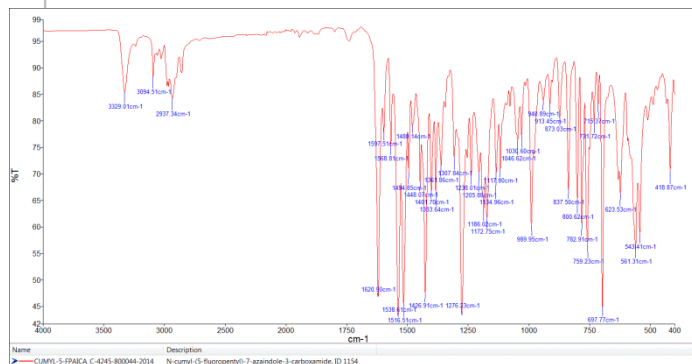
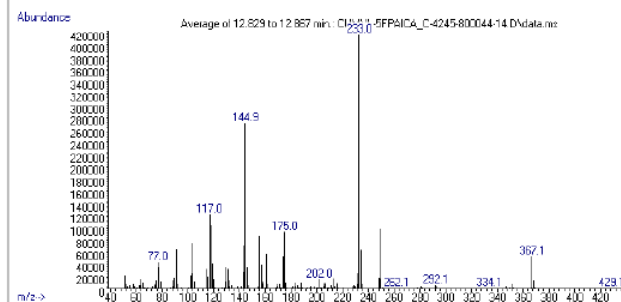
Substance identified- Structure	
Systematic name	<ul style="list-style-type: none"> 1-(5-fluoropentyl)-N-(2-phenylpropan-2-yl)-7-azaindole-3-carboxamide 1-(5-fluoropentyl)-N-(2-phenylpropan-2-yl)-1H-pyrrolo[2,3-b]pyridine-3-carboxamide
Other names	N-cumyl-(5-fluoropentyl)-7-azaindole-3-carboxamide; CUMYL-5FPAICA (suggested); SGT-263
Formula (per base form)	C ₂₂ H ₂₆ FN ₃ O
M _w [g/mol]	367.46
Exact mass (monoisotopic)	367.2071
Salt form	base
Other compounds detected	none
Smiles	CCCCCN1C=C(C2=CC=CC=C12)C(=O)N(C3C)C4=C(C=CC=C4)N=C5C=C(C=C5)F
Compound Class	Cannabinoids

This report has been produced with the financial support of the Prevention of and fight against crime Programme of the European Union (grant agreement number JUST/2013/SEC/DRUGS/AG/6413). The contents of this report are the sole responsibility of the National Forensic Laboratory and can in no way be taken to reflect the views of the European

Supporting information

Analytical techniques:	remarks
GC-MS	+ sample extracted in CH ₂ Cl ₂
FTIR-ATR	+ direct measurement
GC-MS-FTIR (condensed phase)	/
HPLC-TOF	+ sample extracted in MeOH
NMR-confirmed	yes Faculty of Chemistry and Chemical technology (FKKT); University Ljubljana
Validation - other	/ along our knowledge at the time of this report, reference material and/or reference FTIR and MS spectra are not yet available
other	

MS spectrum (EI)



There was something strange in all those cases!



- ▶ Shipments from China and supporting documentation from New Zealand
- ▶ Production site in Slovenia and some packing materials labeled as New Zealand's products
- ▶ Packaging of well known product from NZ company (Kronic Pinnacle) and "Social tonic" tablets took place in Ljubljana
- ▶ Companies (A + B) in Ljubljana :
 - ▶ At the same address and in the same premises, director of A and B is the same person from Australia, share holders from New Zealand

It seems that the new psychoactive substance regulation introduced in New Zealand (2014) caused big movements of NZ "legal" highs production, i.e. from New Zealand to another part of the world (unfortunately Slovenia).

From New Zealand & China to Slovenia: evidence



MATERIAL SAFETY DATA SHEET

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

1. IDENTIFY PRODUCT AND COMPANY IDENTIFICATION

Product name: SGT55
Chemical name: 1-butyl-N-(1-methyl-1-phenylethyl)-1H-Indole-3-carboxamide
Catalog Codes: SGT55
CAS# 1400742-22-4
Chemical Formula: $C_{22}H_{26}N_2O$

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-butyl-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 a inhale or touch.

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



STARGATE OPERATIONS LTD
UNIT 1/5 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

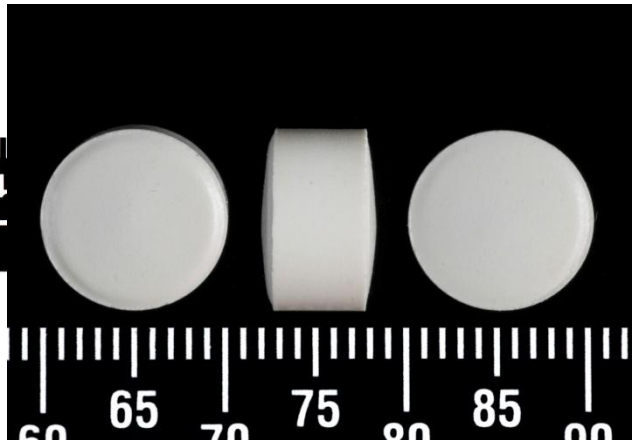
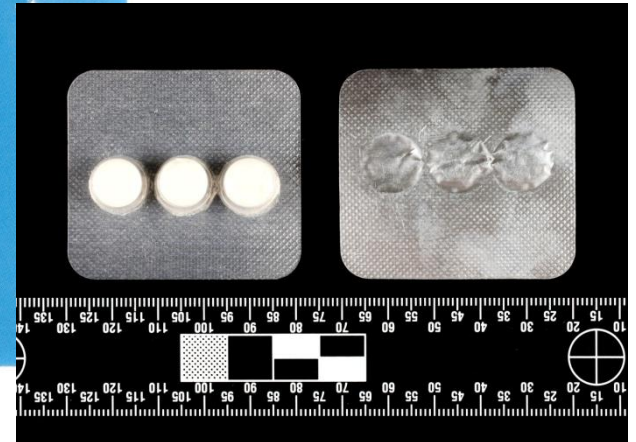
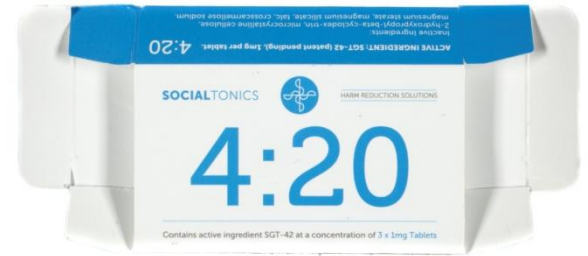
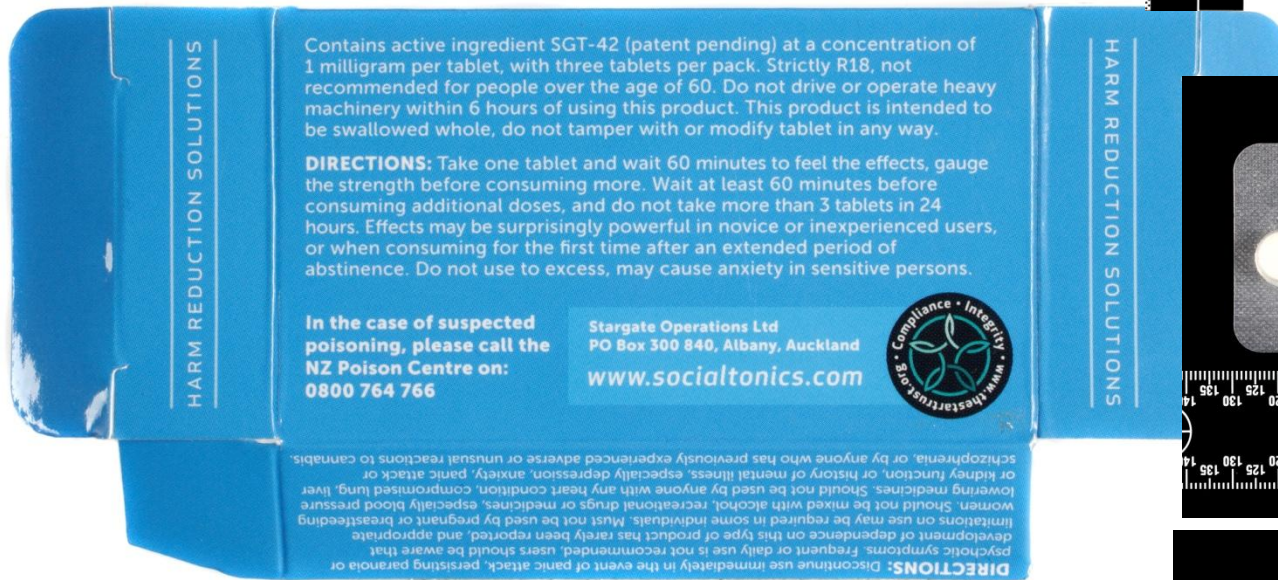
Total Weight:	1804
Total Volume cu m:	9.73
Total Number of Items:	92

From New Zealand to Slovenia - evidence



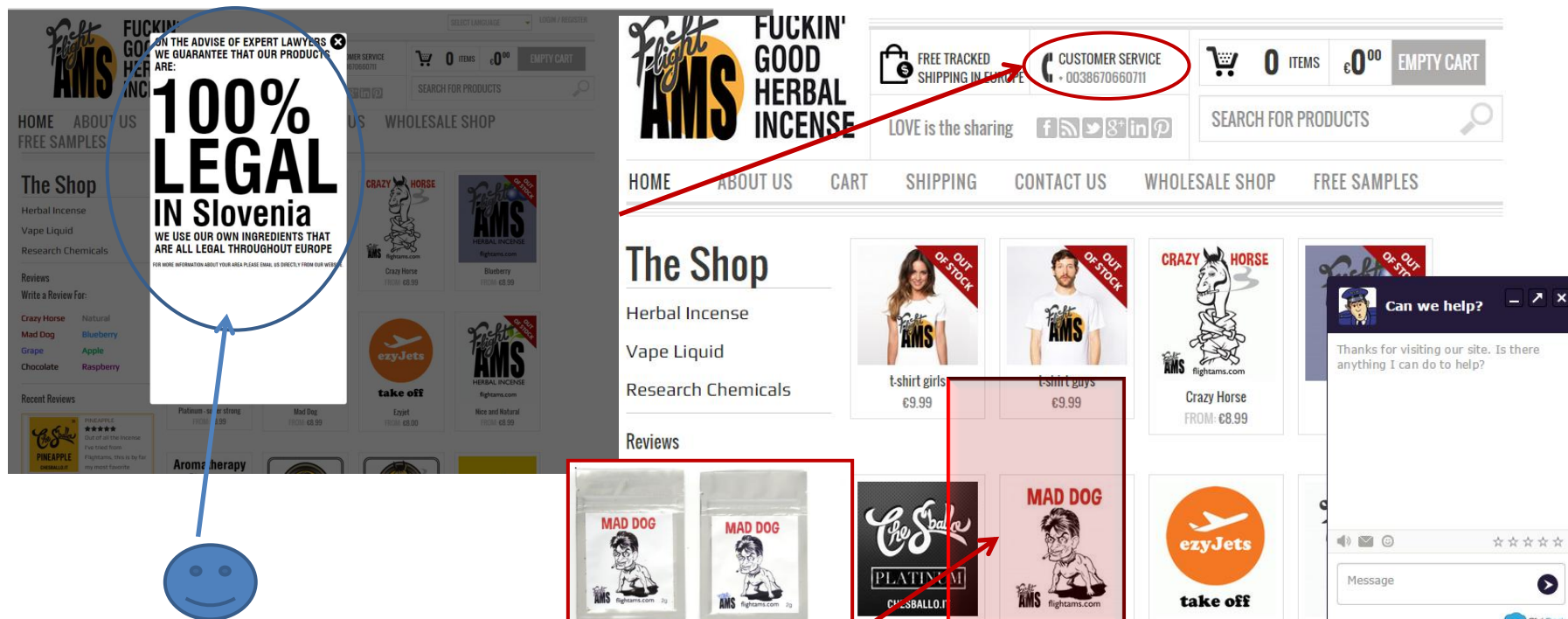
Figure 1: Empty packaging with labels of New Zealand products

From New Zealand to Slovenia evidence



Was Slovenia selected by chance or by choice?

It seems that someone studied Slovenian legislation on drugs....but...



SI forensic chemists respond:
In our opinion the statement
is not 100% correct!

Product advertised at the web page

Bags found in the premisses of companies (A+B)in Ljubljana

Many thanks to my small but excellent team!



Thank you for your attention!