- INTELLIGENCE ALERT -

“SPICE” - PLANT MATERIAL(S) LACED WITH SYNTHETIC CANNABINOIDS OR CANNABINOID MIMICKING COMPOUNDS

The Customs and Border Protection (CBP) - Chicago Laboratory (Illinois) recently received five small, resealable, bright foil packets containing dull olive-colored plant material(s), labelled as “Spice Gold,” “Spice Silver,” “Spice Diamond,” “Genie,” and “Yucatan Fire” incense (see Photo 1, right, and Photos 2 - 3, next page), all reputedly laced with various synthetic cannabinoids or synthetic cannabinoid mimicking compounds, notably “HU-210” [(6αR,10αR)-9-(hydroxymethyl)-6,6-dimethyl-3-(2-methyloctan-2-yl)-6α,7,10,10α-tetrahydrobenzo[c]chromen-1-ol]; see Figure 1, next page]. The exhibits were selected from a shipment containing approximately 1,500 such packets that were detained by a CBP agricultural specialist at an express parcel service hub in Wilmington, Ohio. The items were not smuggled but were rather part of a formal entry. Standard marijuana analyses (microscopy) of the materials were negative. Analysis of extracts by
GC/MS in the scan mode with split injection indicated only the presence of a large amount of vitamin E and other, smaller amounts of various natural products. However, when the extracts were derivatized with N,O-bis(trimethylsilyl)acetamide and injected splitless with selected ion monitoring, HU-210 was found in very small but verifiable amounts in every packet (not quantitated). The results were confirmed against a standard. These were the first such submissions to the laboratory.

[Additional Laboratory and Editor’s Notes: In addition to the above-named products, there are at least two other such herbal products: “Skunk,” and “Sence.” These products are currently being encountered nationwide. They, and the synthetic cannabinoids and cannabinoid mimic compounds they contain, are also the subjects of widespread discussion and speculation on the Internet. Based on anecdotal reports, HU-210 is hundreds of times more potent than THC; thus, the trace amounts detected in the above case are physiologically active, and these materials may be viewed as “stealth marijuana.” The reference standard of HU-210 used in this case was purchased from Cayman Chemical of Ann Arbor, Michigan. The ions selected for the analysis were m/z 446 (100%), 530 (molecular ion), 447, 474, and 356. Note that HU-210 is named in several different ways; for example: (6aR,10aR)-3-(1,1’-dimethylheptyl)-6a,7,10,10a-tetrahydro-1-hydroxy-6,6-dimethyl-6H-dibenzo[b,d]pyran-9-methanol. HU-210 is controlled (Schedule I) in the U.S. (See: http://www.deadiversion.usdoj.gov/drugs_concern/spice/spice_hu210.htm), and products containing it and similar cannabinoids are controlled within the U.S. and in a number of other countries, including Austria, Canada, Germany, the Netherlands, and Switzerland. In addition to HU-210, there are at least half a dozen other compounds with similar structures, plus several unrelated compounds that have cannabinoid mimicking effects (notably JWH-018 (1-pentyl-3-(1-naphthoyl)indole), that are being used to adulterate the plant materials in “Spice” and similar products. An article presenting mass spectral data and background information on these compounds was recently published on line (not yet published in hard copy); see: Auwarter V, Dresen S, Weinmann W, Muller M, Putz M, Ferreiros N. “Spice” and other herbal blends: Harmless incense or cannabinoid designer drugs? Journal of Mass Spectrometry 2009.]
BLOTTER ACID MIMIC (ACTUALLY CONTAINING A MIXTURE OF 4-CHLORO-2,5-DIMETHOXYAMPHETAMINE AND 4-BROMO-2,5-DIMETHOXYAMPHETAMINE) IN WARNER ROBINS, GEORGIA

The Georgia Bureau of Investigation - Central Regional Crime Laboratory (Macon) recently received one square of tie-dyed blotter paper, suspected LSD (see Photo 4). The exhibit was seized in Warner Robins (approximately 25 miles south of Macon) by personnel from the Houston County Sheriff’s Office, pursuant to a domestic dispute call. Analysis of extracts by GC/MS and HPLC, however, indicated not LSD but rather a 2 : 1 mixture of 4-chloro-2,5-dimethoxyamphetamine (DOC) and 4-bromo-2,5-dimethoxyamphetamine (DOB) (not quantitated but a moderate loading based on the TIC). The Georgia Bureau of Investigation has previously seen blotter acid mimics that contained either DOC or DOB, but this is the first submission that contained a mixture of both compounds.

* * * * *

“LEMMON 714” QUAAALUDE MIMIC TABLETS (ACTUALLY CONTAINING DIAZEPAM) IN DUPAGE COUNTY, ILLINOIS

The DuPage County Crime Laboratory (Wheaton, Illinois) recently received one partial and five whole white, round tablets, 14 millimeters in diameter, with a “LEMMON 714” logo on one face and single-scored on the opposite face, apparent Quaaludes (see Photo 5). The exhibits were seized by a local agency investigating a drug overdose (details sensitive). Analysis of methanol and chloroform extracts of one tablet (mass 0.88 gram) by GC/MS, however, indicated not methaqualone but rather diazepam (not quantitated, but a high loading based on the TIC). This was the first ever submission of Quaalude mimic tablets to the laboratory.

[Editor’s Note: An overview of similar diazepam-containing “LEMMON 714” Quaalude mimic tablets was presented in a recent issue; see: Microgram Bulletin 2007:40(1):5-6.]
ECSTASY MIMIC TABLETS (ACTUALLY CONTAINING DIPHENHYDRAMINE OR DIPHENHYDRAMINE AND CAFFEINE) IN LAKE COUNTY, OHIO

The Lake County Crime Laboratory (Painesville, Ohio) recently received a submission of eight round, blue tablets imprinted with a logo of two females back-to-back and four round, purple-speckled tablets imprinted with a logo of an automobile (see Photos 6 and 7), and a separate submission of another one of the blue tablets, all suspected Ecstasy. The first set of tablets were acquired in Lake County (approximate 40 miles east of Cleveland) by an unnamed police department (no further details). The single tablet was also seized in Lake County, by a different police department (also unnamed), incidental to a traffic stop. Both sets of tablets were approximately 8 millimeters in diameter and 4 millimeters thick. Analysis of the blue tablets (approximately 300 milligrams each) by color testing, GC/MS, and FTIR, however, indicated not MDMA but rather diphenhydramine. Analysis of the purple-speckled tablets (approximately 365 milligrams each) by the same techniques indicated a 3:1 mixture of diphenhydramine and caffeine. In both cases, the loading of the diphenhydramine was fairly high (not formally quantitated). These are the first submissions of Ecstasy mimic tablets containing only diphenhydramine or a diphenhydramine/caffeine mixture to the laboratory.

* * * * *

ECSTASY MIMIC TABLETS (ACTUALLY CONTAINING A MIXTURE OF 1-(3-CHLOROPHENYL)PIPERAZINE AND CAFFEINE) IN ALLIANCE, OHIO

The Canton-Stark County Crime Laboratory (Canton, Ohio) recently received two round tablets, one small and green and the other typically sized and blue, alleged “Triple Ecstasy” (purportedly an unusually potent form of Ecstasy; no photos). The exhibits were acquired in Alliance, Ohio (east of Canton) by an Alliance Police Department Special Investigative Unit (no further details). The green tablet was approximately 5 millimeters in diameter and 5 millimeters thick, weighed 170 milligrams, and had a 5-point star logo. The blue tablet was approximately 8 millimeters in diameter and 5 millimeters thick, weighed 270 milligrams, and had a deeply cut triangle logo. Analysis of both tablets by color testing (Marquis - negative), FTIR, and GC/MS, however, indicated not MDMA but rather a 3:2 mixture of 1-(3-chlorophenyl)piperazine (mCPP) and caffeine (not quantitated but a high loading based on the TIC). This is the first submission of Ecstasy mimic tablets containing mCPP, and also the first submission of a small Ecstasy mimic tablet, to the laboratory.
INTELLIGENCE ALERT

OXYCONTIN MIMIC TABLETS (ACTUALLY CONTAINING A MIXTURE OF HEROIN, CAFFEINE, AND LACTOSE) IN SEATTLE, WASHINGTON

The DEA Western Laboratory (San Francisco, California) recently received two round biconvex tablets, 9 millimeters in diameter, with “OC” imprinted on one face and “80” on the opposite face, apparent OxyContin (see Photos 8 and 9). The exhibit was acquired in Seattle, Washington by personnel from the DEA Seattle Field Division (no further details). The tablets had a green coating over a compressed, light brown powder (actual OxyContin tablets have a lighter green coating over a compressed white powder). Analysis of the tablets (total net mass 0.56 grams) by GC/MS, GC/FID, FTIR/ATR, and 1H-NMR, however, indicated not oxycodone but rather a mixture of heroin (11.6 milligrams/tablet), caffeine (not quantitated), and lactose. This is the first known submission of OxyContin mimic tablets containing heroin to the Western Laboratory.

* * * *

INTELLIGENCE ALERT

ECSTASY COMBINATION TABLETS (CONTAINING MDMA, METHAMPHETAMINE, AND CAFFEINE) IN STAFFORD, VIRGINIA

The DEA Mid-Atlantic Laboratory (Largo, Maryland) recently received one plastic bag containing a total of 236 round blue tablets imprinted with a fly logo on one face and an indiscernible logo on the opposite face (possibly a bear or a buffalo), and 262 round blue tablets imprinted on one face only with the indiscernible (bear/buffalo) logo, both approximately 8.5 millimeters in diameter, suspected Ecstasy (see Photo 10). The exhibits were acquired in Stafford, Virginia by personnel from the Bureau of Alcohol, Tobacco, Firearms, and Explosives. Analysis of the double imprint tablets (total net mass 77.8 grams) by GC/FID, GC/MS, and LC indicated 49.7 milligrams/tablet MDMA, 14.1 milligrams/tablet methamphetamine, and caffeine (not quantitated). Analysis of the single imprint tablets (total net mass 84.7 grams) by the same techniques indicated 46.9 milligrams/tablet MDMA, 12.6
milligrams/tablet methamphetamine, and caffeine (again not quantitated). These were the first submissions of Ecstasy combination tablets with these logos, and also the first submission of Ecstasy combination tablets with logos on both faces, to the Mid-Atlantic Laboratory.

* * * * *

- INTELLIGENCE ALERT -

**L-METHAMPHETAMINE IN HAMMOND, INDIANA AND CHICAGO, ILLINOIS**

The DEA North Central Laboratory (Chicago, Illinois) recently received two submissions, each containing five oblong packages of yellow, crystalline materials, suspected methamphetamine (no photos). The first set was seized by DEA Chicago Field Division personnel from an impounded vehicle in Hammond, Indiana, while the second set was seized by DEA Chicago Field Division personnel pursuant to a warrant search in Chicago (no further details). All ten packages were successively wrapped in layers of clear plastic, baby wipes, and black electrical tape. Analysis of the crystalline material (total net mass 4.3 kilograms) by GC/FID, GC/MS, and IR indicated 95 - 99 % methamphetamine hydrochloride. Additional analysis following derivatization with N-trifluoroacetyl-L-prolyl chloride by GC/FID and GC/MS, however, indicated not d-methamphetamine but rather l-methamphetamine (isomer purity not determined, but high). The North Central Laboratory has received several submissions of l-methamphetamine; however, these are the first large submissions of l-methamphetamine in recent years.

* * * * *

- INTELLIGENCE ALERT -

**CAPTAGON MIMIC TABLETS (CONTAINING d,l-AMPHETAMINE, CAFFEINE, THEOPHYLLINE, AND OTHER COMPONENTS) IN AL ANBAR PROVINCE, IRAQ**

The DEA Special Testing and Research Laboratory (Dulles, Virginia) recently received two separate submissions containing a combined total of 9,382 round tablets of four different colors, all biconvex and imprinted with a Captagon-like logo on one face and a single score on the reverse side, apparent Captagon (fenethylline; no photos). The exhibits were seized in Al Anbar Province, Iraq by U.S. Department of Defense personnel (no further details). The first exhibit contained 4,860 white tablets (8.1 x 3.4 millimeters, total net mass 871 grams), all contained in a package illustrated with an ad for a Toyota SUV and containing a small packet of silica beads (as a desiccant). Analysis by color testing (Marquis, silver nitrate, and barium chloride), GC/FID, GC/MS, FTIR, NMR, and CE, however, indicated not fenethylline but rather d,l-amphetamine (20 milligrams/tablet), caffeine (39 milligrams/tablet), theophylline (14 milligrams/tablet), acetaminophen (11 milligrams/tablet), and lactose. The second exhibit contained 3 different color tablets, all contained in a package illustrated with an ad for a Mercedes-Benz SUV and again containing a small packet of silica beads. The first sub-exhibit contained 980 off-white tablets (8.2 x 3.1 millimeters, total net mass 160 grams). Analysis (same techniques) indicated d,l-amphetamine (7 milligrams/tablet), caffeine (65
milligrams/tablet), theophylline (8 milligrams/tablet), acetaminophen (9 milligrams/tablet), and lactose. The second sub-exhibit contained 2,655 tan tablets (8.3 x 3.7 millimeters, total net mass 469 grams). Analysis (same techniques) indicated d,l-amphetamine (10 milligrams/tablet), caffeine (30 milligrams/tablet), theophylline (39 milligrams/tablet), acetaminophen (21 milligrams/tablet), diphenhydramine (2.1 milligrams/tablet), quinine (2.1 milligrams/tablet), and lactose. The third sub-exhibit contained 887 dark brown tablets (8.3 x 3.4 millimeters, total net mass 156 grams). Analysis (same techniques) indicated d,l-amphetamine (10 milligrams/tablet), caffeine (30 milligrams/tablet), theophylline (38 milligrams/tablet), acetaminophen (21 milligrams/tablet), diphenhydramine (2.1 milligrams/tablet), quinine (2.1 milligrams/tablet), and lactose. In each case, the amphetamine was calculated as the sulfate, while the diphenhydramine and quinine were calculated as the hydrochlorides. All exhibits also contained varying amounts of N-formylamphetamine (not quantitated), probably present as a contaminant from a poorly executed Leuckart synthesis of amphetamine. The Special Testing and Research Laboratory has previously received Captagon mimic and counterfeit tablets, but none with these compositions.

[Editor’s Notes: Fenethylline is a controlled substance in the U.S. (Schedule I). It is a CNS stimulant.]

* * * * *          * * * * *          * * * * *          * * * * *          * * * * *

SELECTED REFERENCES

[The Selected References section is a compilation of recent publications of presumed interest to forensic chemists. Unless otherwise stated, all listed citations are published in English. Abbreviated mailing address information duplicates that provided by the abstracting service. Patents and Proceedings are reported only by their Chemical Abstracts citation number.]

1. Boudreau DK, Casale JF. An in-depth study of the Peruvian Base Llavada (“Washed Base”) technique for purification of crude cocaine base. Microgram Journal 2008;6(3-4):72-81. [Editor’s Notes: Presents an in-depth study of the title technique, which is being used as a substitute method for the traditional potassium permanganate process. The fate of several alkaloid impurities is tracked. Contact: U.S. Department of Justice, Drug Enforcement Administration, Special Testing and Research Laboratory, 22624 Dulles Summit Court, Dulles, VA 20166.]

2. Casale JF, Corbeil EM, Hays PA. Identification of levamisole impurities found in illicit cocaine exhibits. Microgram Journal 2008;6(3-4):82-89. [Editor’s Notes: 6-Phenyl-2,3-dihydroimidazo[2,1b]thiazole and 3-(2-mercaptoethyl)-5-phenylimidazolidine-2-one, known levamisole degradation products, were identified in a “crack” cocaine exhibit. Spectroscopic and chromatographic data are provided. Contact: U.S. Department of Justice, Drug Enforcement Administration, Special Testing and Research Laboratory, 22624 Dulles Summit Court, Dulles, VA 20166.]

3. Casale JF, Orlando PM, Colley VL, Hays PA. Identification of diltiazem impurities / artifacts during the analyses of illicit cocaine exhibits containing diltiazem. Microgram Journal 2008;6(3-4):90-103. [Editor’s Notes: Desacetyldiltiazem and an uncharacterized artifactual compound with an apparent mass of 354 Daltons have been observed in the GC profiles of cocaine exhibits containing diltiazem. The use of methanol as an injection solvent for samples containing sodium bicarbonate causes the formation of these compounds in the injection port. Spectroscopic and chromatographic data are provided for diltiazem, desacetyldiltiazem, and}
4. Corbeil EM, Casale JF. **Determination of cocaine in various South American commercial coca products.** Microgram Journal 2008;6(3-4):109-113. [Editor’s Notes: Cocaine content is provided for several coca products, including coca tea, medicinal tonics and rubs, and alcoholic liquors. The cocaine was separated from the complex matrices utilizing trap column chromatography. GC/MS/SIM was used for identification and quantitation. The cocaine in these products ranged from 0.00 - 0.65 µg/mg. Contact: U.S. Department of Justice, Drug Enforcement Administration, Special Testing and Research Laboratory, 22624 Dulles Summit Court, Dulles, VA 20166.]

5. Daundkar BB, Malve MK, Krishnamurthy R. **A specific chromogenic reagent for detection of diazepam among other benzodiazepines from biological and nonbiological samples after HPTLC.** Journal of Planar Chromatography - Modern TLC 2008;21(4):249-250. [Editor's Notes: Focus is on biological matrices, but also included diazepam standard and diazepam-containing tablets. Developed plates were sprayed with 5% NaOH followed by 1% meta-dinitrobenzene in DMSO. Violet bands were obtained for diazepam; other benzodiazepines (e.g., oxazepam, nitrazepam, lorazepam, chlordiazepoxide, and flurazepam) did not react. The LOD is approximately 5 m g. Contact: Home Dept., State of Maharashtra, Forensic Science Laboratories, Mumbai 400098, India.]

6. Gerlits J. **An Excel based molecular weight calculator.** Journal of the Clandestine Laboratory Investigating Chemists Association 2009;19(1):2-3. [Editor's Notes: Presents the title program. JCLICA is a law enforcement restricted journal. Contact: Utah Bureau of Forensic Services, Southern Utah Crime Laboratory, SUU Technology Bldg 109, 351 W Center St, Cedar City, Utah 84720.]

7. Jones LM, Boudreau DK, Casale JF. **“Crack” cocaine: A study of stability over time and temperature.** Microgram Journal 2008;6(3-4):114-127. [Editor’s Notes: Changes in the appearance, weights, purity levels, and alkaloidal profiles of 146 laboratory-prepared “crack” cocaine exhibits stored under different temperatures and packaging types, were studied over a one year period. An accelerated aging study (elevated temperature, one month) was also performed with 2 “crack” cocaine exhibits, to simulate very long-term or higher temperature storage. The results are presented and discussed. Contact: U.S. Department of Justice, Drug Enforcement Administration, Special Testing and Research Laboratory, 22624 Dulles Summit Court, Dulles, VA 20166.]

8. McGehee MC. **Etodolac: An analytical profile.** Microgram Journal 2008;6(3-4):104-108. [Editor’s Notes: Etodolac (Lodine) has been identified in various submissions of illicit heroin. Analytical data, including GC, IR, Raman, MS, and 'H-NMR, are presented. Contact: U.S. Department of Justice, Drug Enforcement Administration, Northeast Laboratory, 99 10th Avenue, Suite 721, New York, NY 10011.]

9. Moore JM, Casale JF. **The discoloration of illicit drug samples.** Microgram Journal 2008;6(3-4):128-145. [Editor’s Notes: Presents an in-depth study of the browning of cocaine samples over time. The discolored samples were all found to contain a primary aromatic amine (either procaine or benzocaine), a sugar (either lactose or dextrose), and an acid (such as cocaine hydrochloride, boric acid, benzoic acid, etc.) The rate of discoloration of the drug mixtures was both pH and temperature dependant, i.e., the rate of sample browning increased with lower pH and/or higher temperature. All discolored samples that contained procaine or benzocaine also
contained N-formylprocaine or N-formylbenzocaine, respectively, and these are therefore *bona fide* “marker” compounds for the browning of illicit cocaine. Contact: U.S. Department of Justice, Drug Enforcement Administration, Special Testing and Research Laboratory, 22624 Dulles Summit Court, Dulles, VA 20166.]

10. Ogata J, Kikura-Hanajiri R, Yoshimatsu K, Kiuchi F, Goda Y. **Detection method for the ability of hemp (Cannabis sativa L.) seed germination by the use of 2,3,5-triphenyl-2H-tetrazolium chloride (TTC).** Yakugaku Zasshi 2008;128(11):1707-1711. [Editor’s Notes: A rapid detection method to assess the ability of Cannabis seeds to germinate is presented. The respiratory enzymes in viable seeds convert colorless 2,3,5-triphenyl-2H-tetrazolium chloride into red 1,3,5-triphenylformazan (dead seeds remain colorless). Under optimum conditions, the viability of seeds could be determined within 20 minutes. Contact: National Institute of Health Sciences, 1-18-1 Kamiyoga, Setagaya-ku, Tokyo, Japan 158-8501.]


12. Person EC, Sunderson NS. **Liquid - liquid extraction of phenylephrine.** Journal of the Clandestine Laboratory Investigating Chemists Association 2009;19(1):4-7. [Editor's Notes: Presents techniques for more efficient extraction of phenylephrine (the compound substituted for pseudoephedrine in many cold and allergy medications). *JCLICA* is a law enforcement restricted journal. Contact: California State University - Fresno, 2555 E. San Ramon Ave. SB70, Fresno, CA 93740.]

13. Sarwar M, Taylor S, Majeed I. **A specific screening color test for diazepam.** *Microgram* Journal 2008;6(3-4):63-71. [Editor’s Notes: Presents a new, highly specific color test for the screening/presumptive identification of diazepam. Treatment of diazepam with alkaline DMSO produces a reddish color which gradually changes to yellow with passage of time. The LODs were 20 μg for diazepam extracted from tablets, and 2 μg for diazepam standard. Contact: Cuyahoga County Coroner’s Office, 11001 Cedar Avenue, Cleveland, OH 44106.]


15. da Silva MJ, dos Anjos EV, Honorato RS, Pimentel MF, Paim APS. **Spectrophotometric cocaine determination in a biphasic medium employing flow-batch sequential injection analysis.** Analytica Chimica Acta 2008;629(1-2):98-103. [Editor’s Notes: The method uses cobalt thiocyanate as a complexing reagent. In the reaction, two phases are formed; the superior (pink) contains an excess of cobalt thiocyanate solution, while the lower layer (blue) contains the cocaine - cobalt thiocyanate complex. An optic fiber sensor records the absorbance at 630 nm. The detection and quantification limits were 29.4 mg L-1 and 98 mg L-1, respectively. Throughput was 12 samples per hour. The method offers a low-tech alternative to GC/FID and GC/MS for routine quantitation of cocaine. Contact: Departamento de Quimica Fundamental, Universidade Federal de Pernambuco, 50740-550 Recife, PE, Brazil.]
16. Talaty N, Mulligan CC, Justes DR, Jackson AU, Noll RJ, Cooks RG. Fabric analysis by ambient mass spectrometry for explosives and drugs. Analyst 2008;133(11):1532-1540. [Editor's Notes: DESI-MS was applied to a variety of fabrics. Drugs listed in the abstract were heroin, cocaine, and methamphetamine. LODs are in the picogram range. Analyses were performed without sample prep, and were carried out in the presence of common interfering chemicals and contaminants. Throughput is high. Contact: Department of Chemistry, Purdue University, West Lafayette, IN 47907.]

Additional References of Possible Interest:


4. Macias MS, Harper RJ, Furton KG. A comparison of real versus simulated contraband VOCs for reliable detector dog training utilizing SPME-GC-MS. American Laboratory 2008;40(1):16-19. [Editor's Notes: A dissipation study of the five major components of marijuana revealed that alpha- and beta-pinene dissipated at an exponential rate, limonene and myrcene at an almost linear rate, and beta-caryophyllene at very little over the course of 30 minutes. There was poor alert response when testing mixtures of these five components. Contact: International Forensic Research Institute, Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199.]