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Chromatographic and Spectroscopic Profiles of *Cannabis* of Different Origins: Part I

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ABSTRACT: High-resolution capillary gas chromatography with flame ionization detection and mass spectrometry (GC and GC/MS) and high-performance liquid chromatography (HPLC) were used to establish complex chemical profiles (chemical signatures) of *Cannabis* samples of known origin. Over 100 compounds could be differentiated, including noncannabinoids (terpenes, alkanes) as well as minor and major cannabinoids and their acids. A characteristic peak pattern was found within a limited number of specimens of identical origin. Correlation studies on the basis of peak area ratios [$A(x)/A$(i.s.)] showed the feasibility of tracing *Cannabis* chemically to its country of origin. Several forensic science applications for the chromatographic and spectroscopic profiles of confiscated *Cannabis* samples are discussed, such as detection of additives (phencyclidine), differentiation of chemotypes, and monitoring of tetrahydrocannabinol (THC) potency.

KEYWORDS: toxicology, marijuana, chemical analysis, *Cannabis*

Herbal *Cannabis* (*Cannabis*, marijuana), *Cannabis* resin (hashish), and extracts of *Cannabis* resin (hashish oil) are still the most abused illicit drugs of the world. It is estimated that over 8000 tons (725 mg) of *Cannabis* are being consumed in the United States each year. The majority of this material is smuggled into the country from major *Cannabis*-producing countries such as Colombia, Mexico, Jamaica, and Thailand. More recently an increase of the domestic production has been observed.

In an effort to combat drug abuse, the current U.S. Administration policy has been multifaceted. One of the major efforts to reduce availability of the drug is through enforcement and interdiction. To have a successful interdiction program, it is important to know where the illicit drug is coming from so that resources can be allocated where most needed to stop shipments. There are reasons to believe that *Cannabis* from one country is being shipped to the United States through intermediate countries, for example, Colombian or Thai *Cannabis* through Mexico to the United States. Consequently, a seizure of *Cannabis* at the Mexican border does not necessarily mean that it is produced in Mexico. A procedure to deter-

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mine the country of origin of a *Cannabis* sample is thus of great importance in law enforcement and forensic science applications.

Attempts have been made in the past to classify *Cannabis* based on its country of origin with little success [*1–3*]. This is due to the fact that only major cannabinoids (tetrahydrocannabinol, cannabidol, cannabichromene, and so forth) were examined. In addition, methods having low resolution power and specificity, like conventional gas chromatography (GC) on packed columns and with flame ionization detection, were used. A more recent suggestion is that minor cannabinoids and noncannabinoids be analyzed for tracing *Cannabis* products to their geographical origin [*4,5*].

In 1976, Novotny et al. [*6*] reported preliminary data relative to the use of a high-resolution glass capillary column for GC analysis of marijuana samples of different origin. The authors indicated that the chromatograms appeared to be different in certain details and suggested that a correlation between chromatographic data and geographical origin of marijuana samples might be possible.

In the present study, we report on an analytical procedure which allows acquisition of complex chemical profiles of *Cannabis* samples. The chromatographic and spectroscopic data of a *limited* number of samples confiscated in five different countries are given. Several forensic science and law enforcement applications for the proposed method are discussed.

Method and Materials

Cannabis *Samples*

Illicit marijuana and hashish samples were obtained from the Drug Enforcement Administration (DEA). They were seized at different locations in Mexico, Colombia, Jamaica, Thailand, and the United States. One sample was taken from legal *Cannabis* cultivations at the University of Mississippi.

Standards and Chemicals

Cannabinoids—The following compounds were isolated from cannabis or synthesized at the Research Institute of Pharmaceutical Sciences, University of Mississippi, or supplied by the National Institute on Drug Abuse (NIDA): cannabigerol (CBG), cannabichromenic acid (CBCA), cannabichromene (CBC), cannabidiolic acid (CBDA), cannabidiol (CBD), Δ^9-(trans)-tetrahydrocannabinolic acid A (THCA-A), Δ^9-(trans)-tetrahydrocannabinolic acid B (THCA-B), Δ^9-(trans)-tetrahydrocannabinol (THC), Δ^9-(trans)-tetrahydrocannabivarin (THCV), Δ^9-(trans)-tetrahydrocannabiorcol (THC-Cl), Δ^8-(trans)-tetrahydrocannabinol (8-THC), cannabicyclol (CBL), cannabielsoin (CBE), cannabinolic acid (CBNA), cannabinol (CBN), cannabivarin (CBV), 9,10-dihydroxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol (DHTHC), cannabicitran (CBT), and cannabiripsol (CBR).

Spiro-indans—Cannabispirol (CBS), cannabispirenone (CBSO), cannabispiran (CBSA), and canniprene (CPR) were isolated from cannabis.

Terpenes—Caryophyllene oxide was obtained from Aldrich Chemical Co. Inc. (Milwaukee, Wisconsin), α-terpineol and β-caryophyllene were supplied by Roth Co. Chemische Fabrik (Karlsruhe, Federal Republic of Germany) through Atomergic Chemetals Corp. (Plainview, New York), allo-aromadendrene and longifolene by Fluka Chemical Corp. (New York).

Alkanes—Heptacosane and nonacosane were obtained from Aldrich and heneicosane from Varian Association (Houston, Texas). Phencyclidine hydrochloride (PCP) was obtained from the U.S. Pharmacopea standards, phenanthrene (internal standard [i.s.]) from Aldrich.

Solvents—High-performance liquid chromatography (HPLC) grade or reagent grade

quality, obtained from Fisher Scientific Co. (Fair Lawn, New Jersey) or Baker Chemical Co. (Phillipsburg, New Jersey).

Silylation reagent—N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) was obtained from Pierce Chemical Co., Rockford, Illinois.

Extraction

Dried, pulverized herbal *Cannabis*, 100 mg, or *Cannabis* resin, 50 mg, was extracted with 1.0 mL of methanol-chloroform (9:1), containing 0.2-mg/mL phenanthrene as internal standard, by sonication during 15 min. An aliquot of 2 μL of the filtered extract was used for HPLC analysis. For GC and gas chromatographic/mass spectrometric (GC/MS) analysis, 100 μL of the extract was diluted with 900 μL of methanol and aliquots of 1 μL were injected.

Capillary Gas Chromatography (GC)

The GC profiles of *Cannabis* extracts were all generated in the splitless mode (split vent activation time: 30 s) with a Varian 3300 gas chromatograph (Varian Instruments, Palo Alto, California), fitted with a Durabond fused silica capillary column (30- by 0.25-mm inside diameter [ID]) coated with DB-1 (J & W Scientific, Inc., Rancho Cordova, California) at a film thickness of 0.25 μm. The (FID) signal was recorded on a Fisher Recordall recorder 5000 in series with a Hewlett-Packard 3390 A integrator. The oven temperature was programmed from 70 to 250°C at a rate of 5/min. The injector and detector were maintained at 250 and 300°C, respectively. Helium was used as the carrier gas at a velocity of about 25 cm/s, air at 300 mL/min and hydrogen at 30 mL/min as detector gases, and helium at 30 mL/min as makeup gas. All GC profiles were recorded at an attenuation of 8 and a chart speed of 0.5 cm/min.

Capillary Gas Chromatography-Mass Spectrometry (GC/MS)

For the acquisition of the GC/MS profiles, the same GC and separation system as described above was used. The column was linked via open-split interface with a Finnigan Ion Trap Detector System (Finnigan MAT, San Jose, California) consisting of an ion trap detector (ITD), an IBM XT personal computer, and an Epson FX-80 II printer. The ITD system was operated with software version 3.0. The temperature of the transfer line and the ion trap manifold was set at 250 and 220°C, respectively. The scan range was m/z 70 to 500, and the scan rate was set at 1 scan/s. The peak area ratios [peak (x)/peak (i.s.)] were calculated by peak integration using the quantitation program.

Cannabinoid acids and polar noncannabinoids isolated by semipreparative HPLC were identified by GC/MS as their trimethylsilyl (TMS) derivatives. After evaporation of the HPLC fractions, the residue was dissolved in 50 μL acetonitrile and 50 μL BSTFA (+ 1% TMCS), sonicated and heated during 15 min at 50 to 60°C. The reaction mixture was evaporated under a stream of nitrogen just to dryness, redissolved in 100 μL hexane by sonication, and 1 to 2 μL injected into the GC/MS system.

High-Performance Liquid Chromatography (HPLC)

The HPLC profiles were acquired on a system consisting of a Waters M 6000-A pump, a U6K injector (Waters Assoc., Milford, Massachusetts), an LDC/Milton Roy variable-wavelength ultraviolet (UV) detector (Laboratory Data Control, Riviera Beach, Florida), and a Fisher Recordall recorder 5000 (Bausch & Lomb, Houston Instrument, Austin, Texas) with a HP 3390 A integrator (Hewlett-Packard, Palo Alto, California). Separation of *Cannabis* extracts was performed at ambient temperature on a Beckman Ultrasphere 3-μm ODS

column (75- by 4.6-mm ID; Rainin Instrument Co., Inc., Woburn, Massachusetts) using a mobile phase of methanol:water containing 1% acetic acid 77:23 at a flow rate of 1.8 mL/min. The profiles were recorded at 230 nm and 0.1 AU full scale. For peak identification by GC/MS the main compounds were isolated by analytical-preparative HPLC, using a self-packed Spherisorb 5-μm ODS-1 column (250 by 4.6 mm ID) [7] and methanol:water containing 5% acetic acid 85:15 as mobile phase at a flow rate 1.5 mL/min.

Results and Discussion

For the acquisition and the comparison of a large number of complex chemical profiles, it is important to use a simple, rapid, efficient, and standardized *extraction procedure.* Among the tested solvents (methanol, chloroform, dichloromethane, cyclohexane) a mixture of methanol-chloroform (9:1) was found to extract over a wide polarity range the highest amount of noncannabinoids and cannabinoids. Especially for milligram-scale specimens and thermolabile compounds, for example, cannabinoid acids, we recommend the use of an ultrasonic bath for extraction and not a soxhlet apparatus as proposed by Novotny et al. [6]. The resulting extracts, which contain phenanthrene as internal standard, can be used without further purification or partition for the chromatographic and spectroscopic characterization by capillary GC and by HPLC.

A DB-1 fused silica capillary column showed the necessary separation power to establish GC profiles with more than 100 different compounds (Figs. 1 to 8). A high number of peaks is important to minimize the risk of coincidental agreement of profiles. Mono- and sesquiterpenes, alkanes, spiro-indans, cannabinoids, and nitrogen-containing compounds (for example, phencyclidine [PCP], Fig. 8) can be analyzed within the same run. The same column was also used in our laboratories for the determination of gasoline residues and alkaloids in coca paste specimens [8]. Even after several hundred runs, the column still provided excellent resolution, good peak shape, and high baseline stability during temperature programming. The reproducibility of the GC method (extraction included) was examined by repetitive runs of an identical specimen and measuring the relative retention times (RRT) and the peak area ratios $A(x)/A$(i.s.). The coefficient of variation was found to be less than 1% for RRT and $A(x)/A$(i.s.). The splitless injection technique together with FID and the specific MS detection provide the required high sensitivity and allow "chromatographic fingerprinting" down to the picogram level. The identity of 22 compounds was established by comparing RRT and mass spectra with those of standards. Some peaks (Table 1) were identified tentatively by using published MS data [9-11]. The chromatographic and spectroscopic data of all detected compounds are summarized in Table 1, and the chemical structures, pharmacological activities, and so forth of identified compounds are reviewed in Ref 12. The quantitative evaluation of the profiles was done by calculating $A(x)/A$(i.s.) of identified and unidentified compounds versus the internal standard phenanthrene (i.s.).

For the sample comparison, only area ratios were used of peaks, which (1) could be detected by FID and MS, (2) had a minimal peak area of 200 counts and a minimal signal-to-noise ratio of 5:1, (3) exhibited a reasonable mass spectrum, and (4) were not obviously GC artifacts. As demonstrated by Figs. 1 and 2, showing the GC and GC/MS profiles of a Mexican specimen, a good correlation was usually found between chromatograms obtained by FID and those obtained by MS detection. Figures 3 to 6 show the GC profiles of *Cannabis* originating from Jamaica, the United States, Colombia, and Thailand. Some of the main characteristic differences in the peak pattern are indicated by an arrow (▼). The corresponding peak area ratios in Table 1 are italicized. The chemical signature given here for one *Cannabis* specimen per origin was found to be typical for a limited number of specimens. Only two (Jamaica) to five (Mexico, Colombia, Thailand) *Cannabis* specimens with authenticated origin other than the United States were available to develop the methods for profiling and to study the feasibility of tracing *Cannabis* chemically to its country of origin.

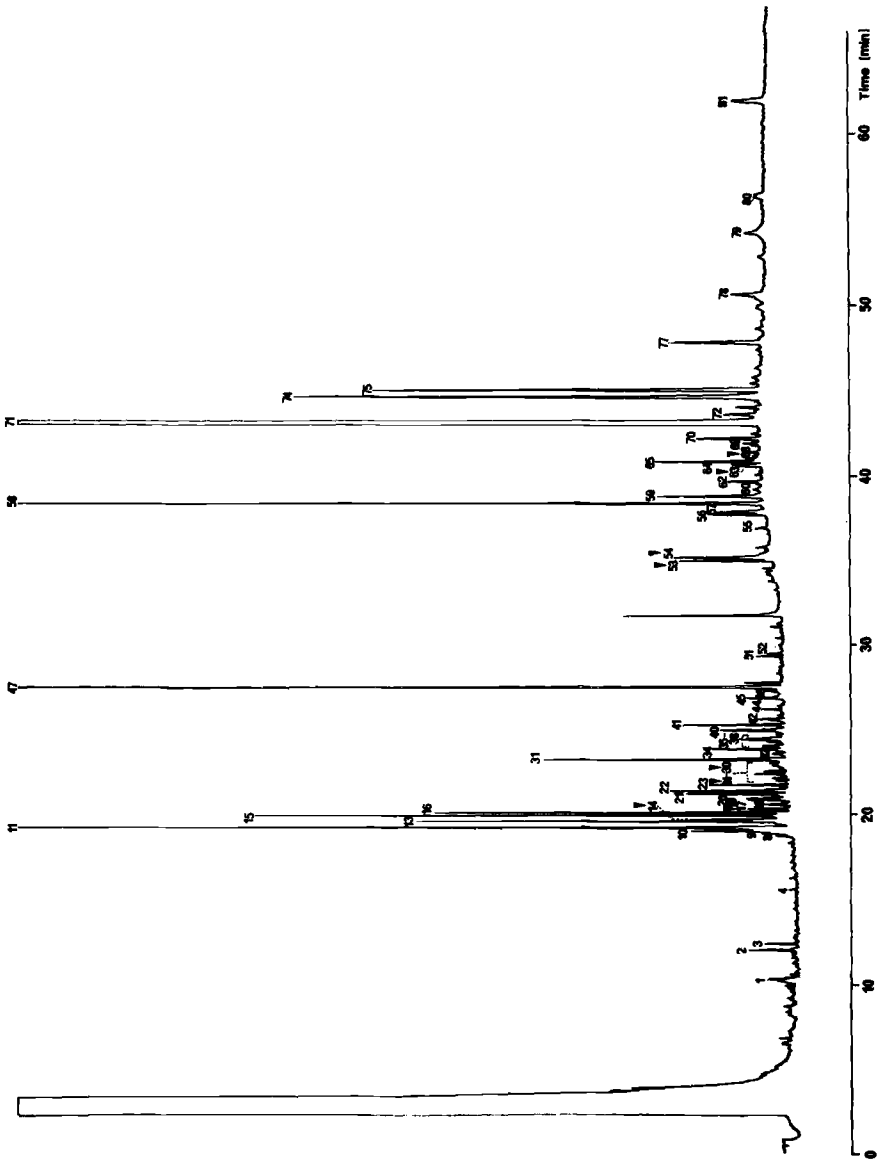

FIG. 1—*GC profile of* Cannabis *"Mexico." For peaks, see Table 1.*

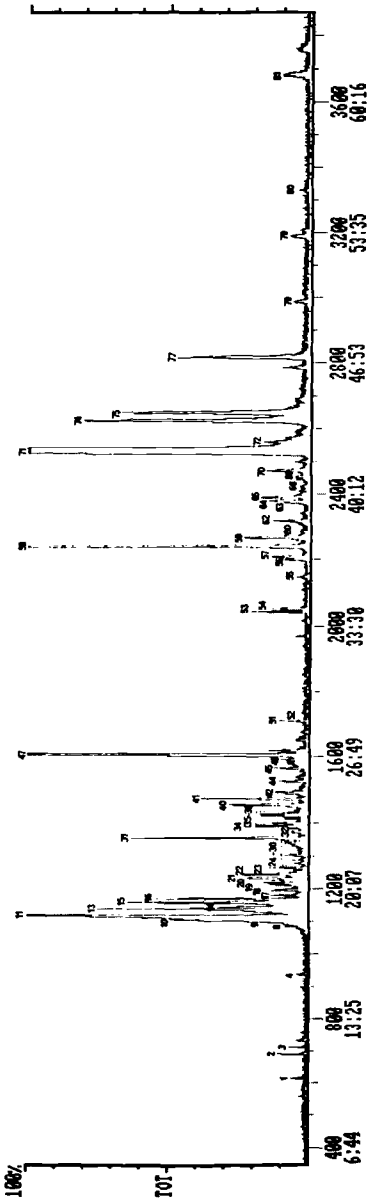

FIG. 2—*GC/MS profile (Reconstructed Ion Chromatogram [RIC]) of* Cannabis *"Mexico." For peaks, see Table 1.*

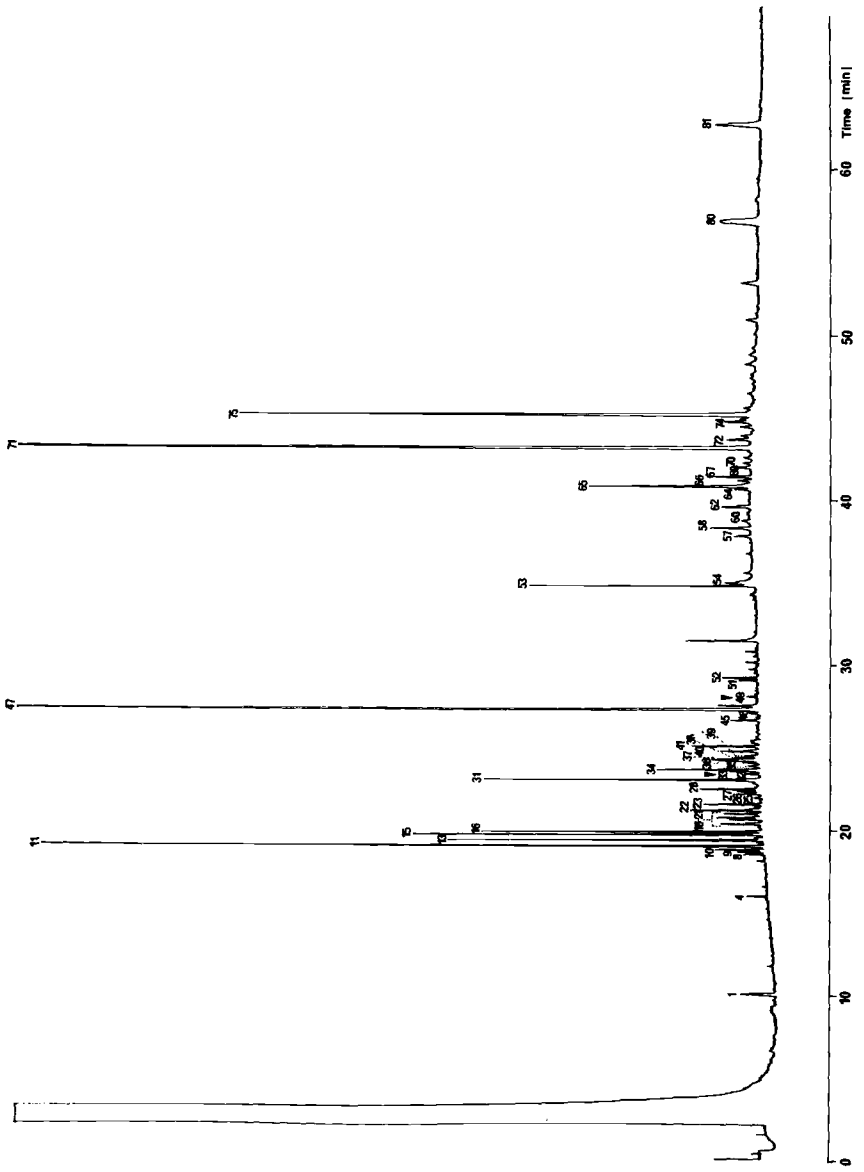

FIG. 3—*GC profile of* Cannabis *"Colombia." For peaks, see Table 1.*

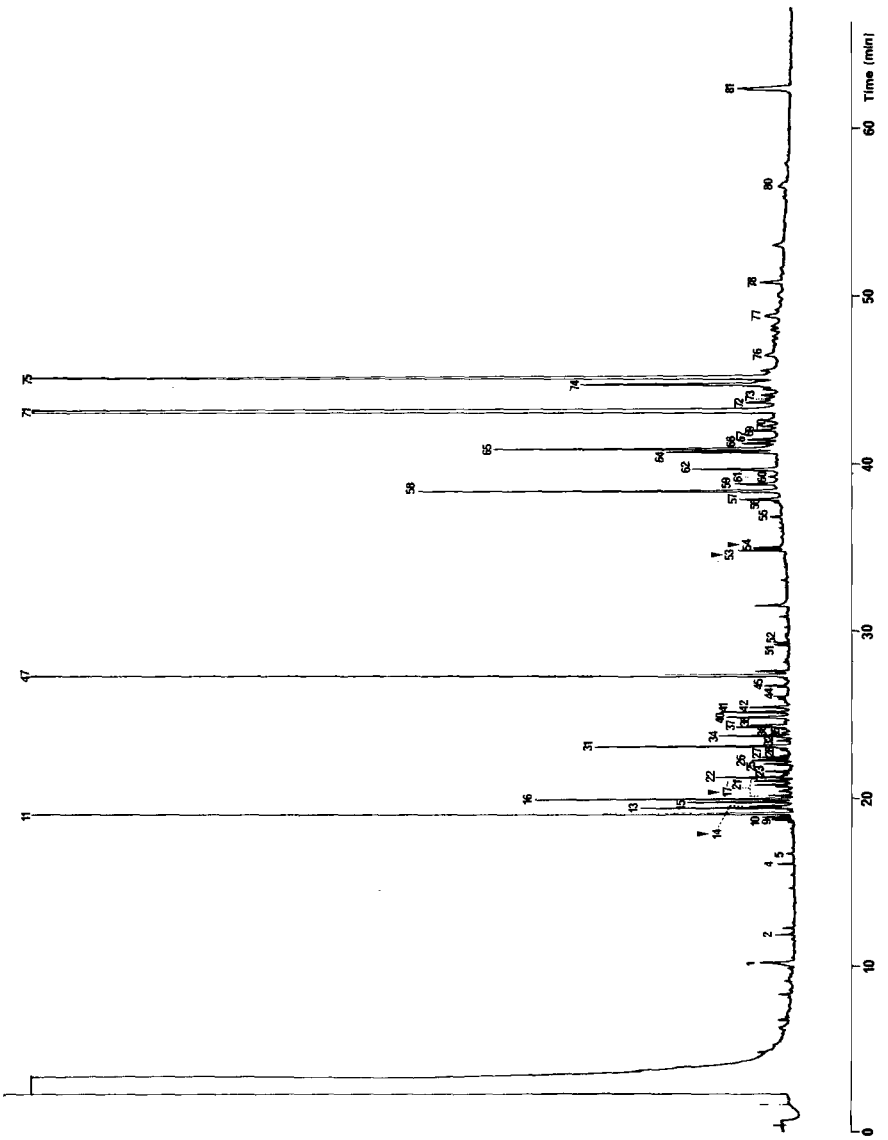

FIG. 4—*GC profile of* Cannabis *"Jamaica." For peaks, see Table 1.*

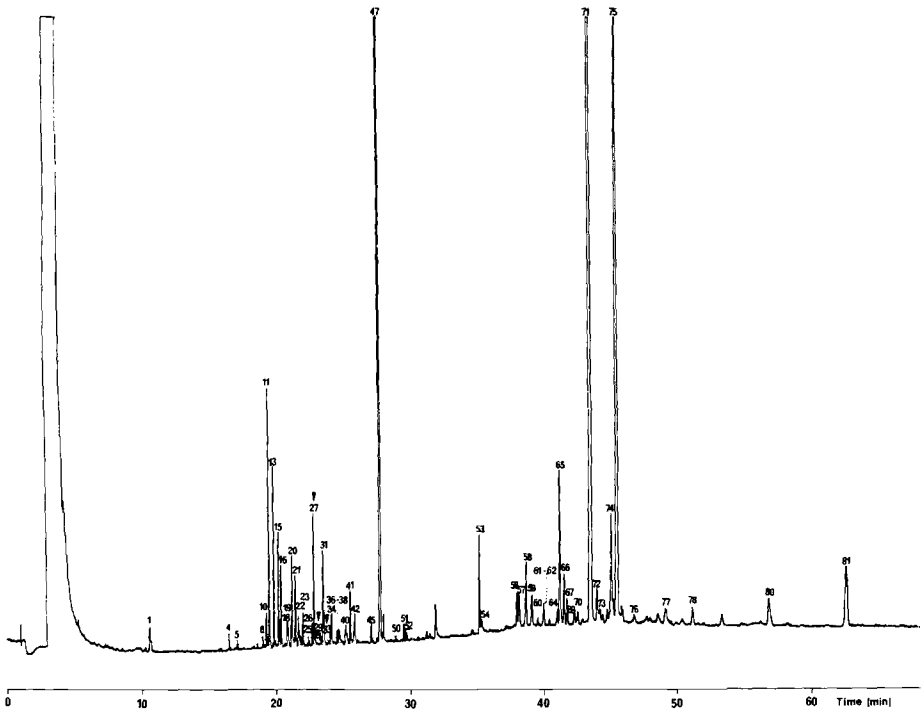

FIG. 5—*GC profile of* Cannabis *"Thailand." For peaks, see Table 1.*

Most of the diagnostically important peaks are present in the terpene region (RRT <1.000). For example, Peak 12 is typical for *Cannabis* "USA," Peaks 14 and 17 (allo-aromadendrene) are only found in *Cannabis* "Mexico" and "Jamaica," Peaks 30 and 68 only in *Cannabis* "Mexico." Peak 27 and 29 are characteristic for *Cannabis* "Thailand," Peak 49 for *Cannabis* "Colombia." Similar ratios of Peak 53 (heneicosane, C-21 alkane) and 54 (tetrahydrocannabiorcol) are characteristic for *Cannabis* "Mexico" and "Jamaica," whereas Peak 53 dominates in all other origins.

Note the missing Peak 31 in *Cannabis* "USA," identified as caryophyllene oxide. This sesquiterpene is formed by oxidation from caryophyllene (11) and is supposed to be the essential volatile compound sniffed by narcotic dogs [*13*]. The influence of maturity, age, storage conditions, and so forth on Compound 31 and other terpenes is subject of ongoing work.

Several studies have shown the daily and monthly fluctuation of major cannabinoids (THC, CBD, CBC, and so forth) in *Cannabis* independent of its geographical origin [*14,15*]. Therefore, their ratios are not significant and cannot be correlated to any geographical origin. Until now it is not known if the minor cannabinoids, for example, cannabicumaronone (66) or C-4 analogs (63), undergo the same cyclic variation as the major cannabinoids. A large number of specimens has to be analyzed to verify if the presence (or absence) of such cannabinoids is typical for a certain origin.

As can be seen in Fig. 7, the GC profile of a hashish specimen is characterized by a larger number of peaks in the terpene region. Hashish and hashish oil are much more frequently encountered in the European illicit market. This is illustrated by the fact that in 1983 there was more than twice as much hashish confiscated in Europe as marijuana (94 714 kg of hashish, 40 826 kg of marijuana, and 455 kg of hashish oil) [*16*]. Profiling and correlation studies of hashish and hashish oil specimens will also be part of extensive future work on chemical signatures and pattern recognition of these products.

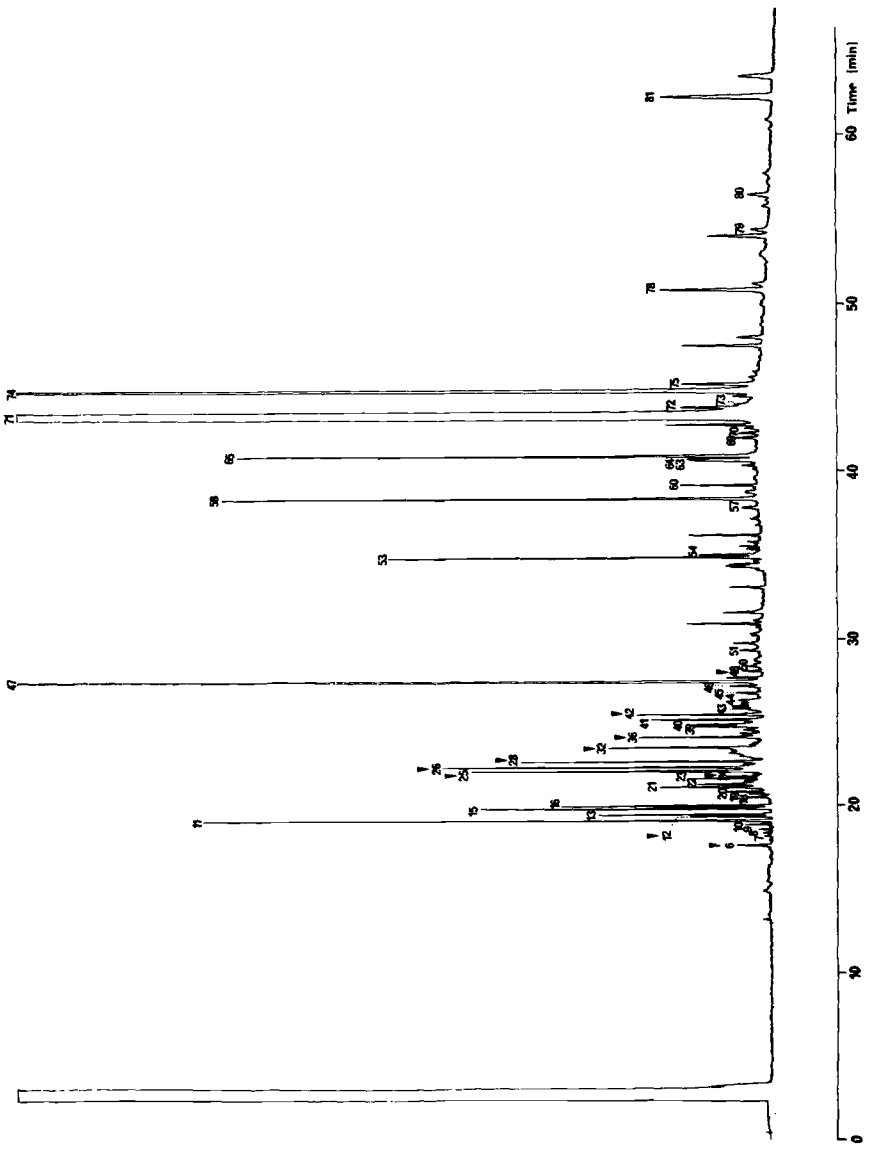

FIG. 6—*GC profile of* Cannabis *"USA." For peaks, see Table 1.*

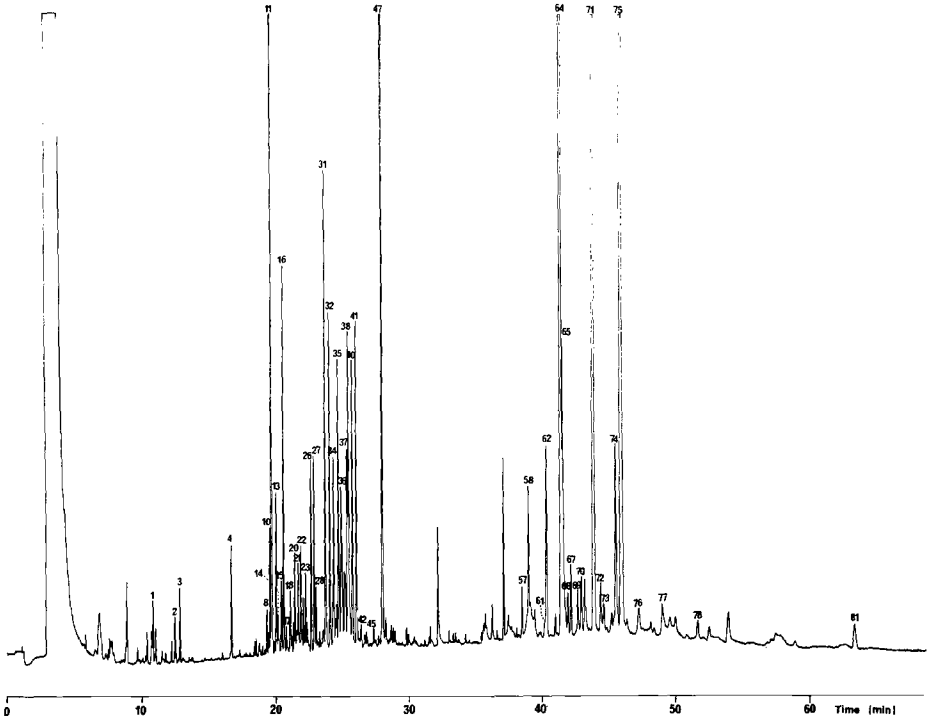

FIG. 7—*GC profile of a hashish sample. For peaks, see Table 1.*

The usefulness of GC and GC/MS profiles to detect adulterants or additives is demonstrated with Fig. 8 showing the GC profile of a *Cannabis* fiber type sprayed with 1% phencyclidine (PCP). The PCP peak appears at RRT 1.114 and shows a mass spectrum with *m/z* 243 (M^+) and 200 (base peak). Phenylhexene, the thermal decomposition product of PCP, gives a peak at RRT 0.651 with *m/z* 158 (M^+) and 129 (base peak). Most of the *Cannabis* street samples containing PCP are confiscated in the Washington area today.

Because the complex chemical profiles are unique for a given specimen, the characteristic peak pattern could be used for comparison of samples confiscated at different locations but presumably originating from a common lot. More data are necessary to support this application, which could be important for drug enforcement and intelligence.

The efficiency of 3-μm reversed-phase columns for the *HPLC profiling* of cannabinoids in *Cannabis* products and quantitative screening of THC metabolites of urine specimens has already been reported previously [*7, 17, 18*]. On a short ODS-column (75 mm), with acidified methanol-water as mobile phase and operating under isocratic conditions, up to 45 different compounds were observed in a Mexican marijuana specimen using UV detection (Fig. 9). Longer columns (150 to 250 mm) require gradient-elution to avoid excessive retention times and peak broadening of compounds with high κ'-values. More than 20 compounds, including minor and major cannabinoids and their acids as well as some highly polar noncannabinoid phenols, could be identified. This was done by comparing the RRT with those of standards and by isolating the peaks with semipreparative HPLC followed by GC/MS analysis. The chromatographic and spectroscopic data of the HPLC profiles are given in Table 2.

HPLC is the preferred method to acquire profiles of thermolabile and highly polar *Cannabis* constituents which need a derivatization procedure (silylation, acetylation, methylation) for GC analysis. Such compounds include cannabinoid acids (THCA, CBDA, CBCA, and so forth) and dihydroxylated noncannabinoid phenols (cannabispirol, canniprene, and so

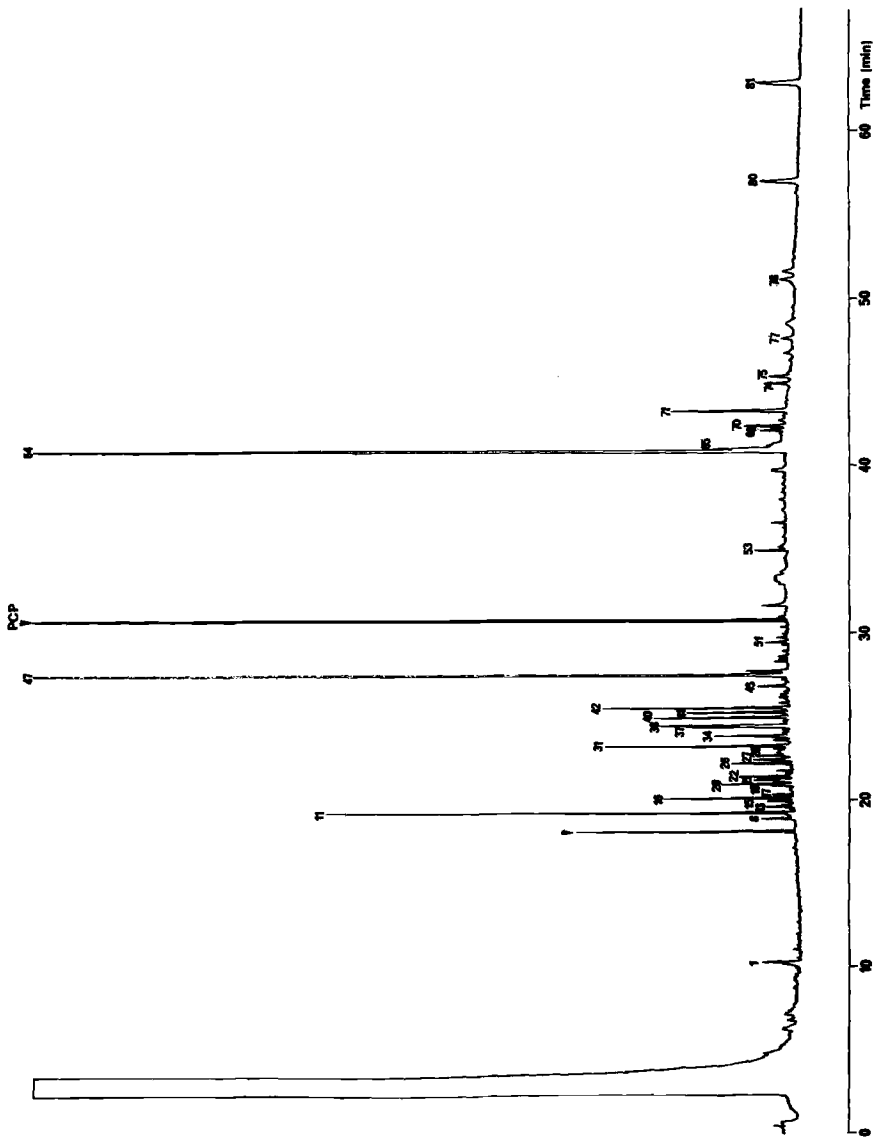

FIG. 8—*GC profile of a fiber-type* Cannabis *sprayed with 1% phencyclidine (PCP). For peaks, see Table 1.*

TABLE 1—*Relative retention times, mass spectra, and peak area ratios of the GC/MS profiles of* Cannabis *"Mexico," "Colombia," "Jamaica," "Thailand," and USA."*

Peak	RRT	*m/z*		Compound	Peak Area Ratios[a]				
		M^+	100%		MEX	COL	JAM	THA	USA
1	0.385	144	101		20	5	5	5	
2	0.428	135	135	monoterpene	30		14		
3	0.436	(154)	93	α-terpineol	15				
4	0.580	150	107	monoterpene	10	20	41	79	
5	0.611	138	138	monoterpene			10	14	
6	0.648	150	117	monoterpene					*20*
7	0.659	204	93	sesquiterpene					5
8	0.684	204	91	sesquiterpene	5	22		42	9
9	0.687	204	91	longifolene	10	55	167		5
10	0.690	204	93	sesquiterpene	320	145	202	124	32
11	0.695	204	91	caryophyllene	981	584	674	507	558
12	0.699	204	93	sesquiterpene					*65*
13	0.702	204	93	sesquiterpene	436	290	175	374	167
14	0.720	204	93	sesquiterpene	*124*		*71*		
15	0.725	204	93	sesquiterpene	250	215	122	200	131
16	0.729	204	93	sesquiterpene	212	188	191	116	201
17	0.734	204	91	allo-aromadendrene	*37*		*18*		
18	0.740	202	119	sesquiterpene	39	64	31	135	21
19	0.761	204	93	sesquiterpene	42	29	27	83	8
20	0.763	204	91	sesquiterpene	64	49	59	235	58
21	0.769	204	91	sesquiterpene	120	51	56	150	139
22	0.773	220	93	sesquiterpene	108	90	48	79	52
23	0.796	204	91	sesquiterpene	47	135	26	72	29
24	0.799	222	91	sesquiterpene	*18*				*27*
25	0.805	204	93	sesquiterpene	18	12	38	23	*237*
26	0.810	204	79	sesquiterpene	29	5	32	47	*133*
27	0.814	222	93	sesquiterpene	16	26	22	*175*	
28	0.816	204	93	sesquiterpene	5	95	27	26	*200*
29	0.832	220	93	sesquiterpene	5			*34*	
30	0.840	222	93	sesquiterpene	*34*				
31	0.844	220	79	caryophyllene oxide	259	278	244	220	
32	0.852	222	161	sesquiterpene	18	30	17		*181*

TABLE 1—*Continued.*

Peak	RRT	m/z		Compound	Peak Area Ratios[a]				
		M^+	100%		MEX	COL	JAM	THA	USA
33	0.871	220	77	sesquiterpene		*36*		*32*	
34	0.873	222	96	sesquiterpene	67	111	102	80	
35	0.877	222	79	sesquiterpene	37	27	9		
36	0.882	222	161	sesquiterpene	24	20	12	46	*231*
37	0.885	220	91	sesquiterpene	42	39	65	36	
38	0.887	222	136	sesquiterpene	47	60	62	75	
39	0.890	222	149	sesquiterpene		45			61
40	0.913	222	79	sesquiterpene	109	76	163	60	44
41	0.920	222	95	sesquiterpene	125	85	107	138	175
42	0.927	222	119	sesquiterpene	42		95	144	*224*
43	0.949	220	81	sesquiterpene					16
44	0.955	222	83	sesquiterpene	31		29		20
45	0.985	184	184		50	40	33	30	33
46	0.995	220	124	sesquiterpene	44	28			5
47	1.000	178	178	internal standard (i.s.)[b]	1000	1000	1000	1000	1000
48	1.028	220	79	sesquiterpene					*31*
49	1.033	?	109			*35*			
50	1.035	220	110	sesquiterpene				22	9
51	1.069	?	71		29	29	24	45	5
52	1.071	220	123	sesquiterpene	10	40	10	20	
53	1.271	(296)	71	heneicosane	*78*	211	59	289	112
54	1.290	258	258	tetrahydrocannabiorcol	*52*	5	*50*	67	12
55	1.346	286	203		13		22		
56	1.380	244	189	dehydrocannabispiran	31		8	45	
57	1.384	314	314	cannabicitran	75	3	111	120	5
58	1.411	286	271	tetrahydrocannabivarin	626	52	633	275	115
59	1.421	246	176	cannabispiran	154		123	42	
60	1.445	300	257		14	9	23	10	10
61	1.453	314	231	cannabicyclol			21	5	
62	1.455	282	267	cannabivarin	55	3	217	120	
63	1.492	300	285	tetrahydrocannabinol-C4[c]	*28*				5
64	1.494	314	231	cannabidiol	74	8	376	151	21
65	1.498	314	231	cannabichromene	72	50	473	246	64

66	1.520	328	285	cannabicumaronone[c]		3	110	220	
67	1.525	328	285			7	23	219	
68	1.534	302	219		*10*				
69	1.553	314	299	Δ^8-tetrahydrocannabinol	7	5	56	62	10
70	1.559	330	330	cannabielsoin	66	5	15	25	10
71	1.596	314	299	tetrahydrocannabinol	1264	826	1315	1767	1164
72	1.607	314	297		66	5	121	308	15
73	1.610	308	252	dehydrocannabifuran[c]			23	134	5
74	1.646	316	193	cannabigerol	551	3	596	430	425
75	1.671	310	295	cannabinol	287	248	1334	2503	19
76	1.714	310	295	cannabifuran[c]			5	10	
77	1.779	330	330		309		115	257	
78	1.873	(380)	71	heptacosane	11		5	5	30
79	2.009	?	71		13				5
80	2.092	?	81		5	36	5	103	5
81	2.316	(408)	71	nonacosane	42	17	27	24	12

[a]Peak area ratios of compound (*x*) versus internal standard (i.s.), multiplied by 1000. Italic ratios are characteristic. MEX = Mexico, COL = Colombia, JAM = Jamaica, THA = Thailand, USA = United States.

[b]Phenanthrene.

[c]Identified on the basis of literature data [*9–11*].

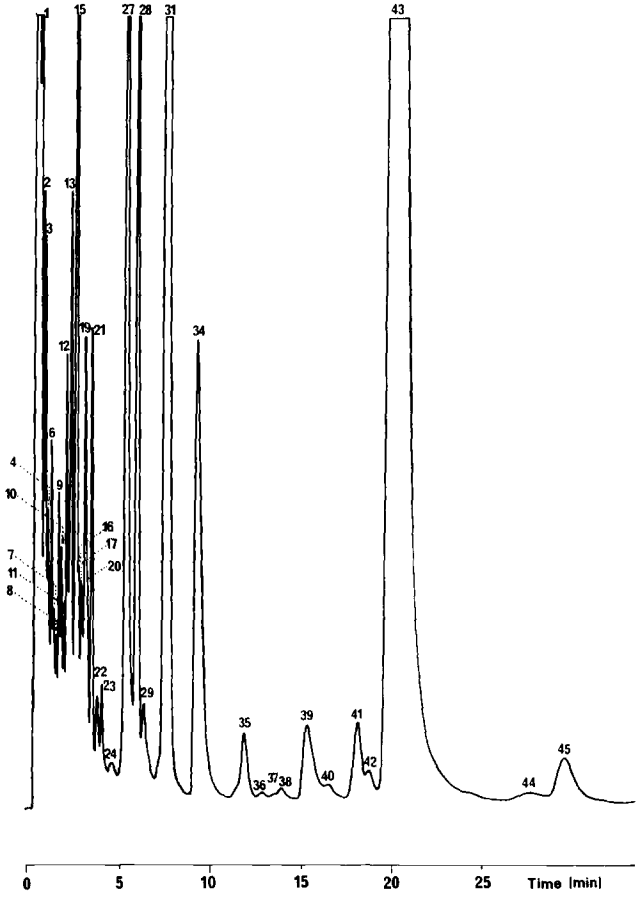

FIG. 9—*HPLC profile of* Cannabis *"Mexico." For peaks, see Table 2.*

forth). Because the ratios of cannabinoid acids and their decarboxylation products (THC, CBD, CBC, and so forth) strongly depend on age and storage conditions of the analyzed material [*7*], HPLC profiles may provide useful information about the history of a *Cannabis* specimen. The ratios of CBD and THC allow a quick differentiation of *Cannabis* chemotypes (drug, fiber, intermediate) or monitoring of the THC potency of confiscated samples. Because HPLC profiles established on reversed-phase columns and with UV detection do not give any information about lipophilic compounds such as mono- and sesquiterpenes, their use for correlating peak patterns and origins is limited.

Conclusions

High-resolution capillary gas chromatography (GC) with FID and MS detection is the method of choice for the chromatographic and spectroscopic profiling of cannabis products. High-performance liquid chromatography (HPLC) on small-particle size columns is recommended for the screening and ratioing of neutral and acidic cannabinoids and the rapid discrimination of different *Cannabis* types (drug, fiber, and so forth). The GC profiles of

TABLE 2—*Relative retention times and peak area ratios of the HPLC profiles of* Cannabis *"Mexico," "Colombia," "Jamaica," "Thailand," and "USA."*

Peak	RRT	Compound	Peak Area Ratios[a]				
			MEX	COL	JAM	THA	USA
1	0.269	canabispiran	310	5	295	393	93
2	0.331	canabispirol	130	20	58	46	
3	0.370		140		66	101	74
4	0.425		120	10	35		
5	0.468			4	36	15	
6	0.495	canniprene	120	186	85	77	31
7	0.535	tetrahydrocannabinolic acid B	70	5	38		
8	0.600		50	5	65	6	13
9	0.647	dihydroxy-Δ^6-tetrahydrocannabinol	90	168	159	177	15
10	0.694		90	9	93	42	55
11	0.757		60	33	94	106	3
12	0.803	tetrahydrocannabiorcol	150	47	237	210	5
13	0.895		280	108	70	50	
14	0.930				54	53	
15	1.000	internal standard (i.s.)[b]	1000	1000	1000	1000	1000
16	1.052	cannabivarin	60	10	152	42	
17	1.113	cannabidiol	90	43	5		89
18	1.150			40	118	123	
19	1.185	cannabigerol	240	34	177	147	52
20	1.230	cannabielsoin	50	34	50	50	5
21	1.322	tetrahydrocannabivarin	170	32	143	42	11
22	1.442	cannabidiolic acid	50	5	267	26	98
23	1.525		40	5	5	27	39
24	1.716		10	5	16	20	1
25	1.730			5			
26	1.910			5			
27	2.010	cannabigerolic acid	770	5	31	273	1735
28	2.220	cannabinol	540	1073	1736	2309	27
29	2.385		80	47	85	63	30
30	2.671						31
31	2.835	tetrahydrocannabinol	2830	1256	2079	1861	667
32	3.010	cannabicyclol		5	50	5	

TABLE 2—*Continued.*

Peak	RRT	Compound	Peak Area Ratios[a]				
			MEX	COL	JAM	THA	USA
33	3.175	Δ^8-tetrahydrocannabinol		22	20	5	5
34	3.500	tetrahydrocannabivarinic acid	630	2	341	45	231
35	4.425	cannabichromene	90	345	485	282	93
36	4.809		10	4	9		27
37	5.025	cannabinolic acid	5	1	18	9	
38	5.231		10				24
39	5.830	cannabicitran	160	5	215	218	11
40	6.286		20	7	1		64
41	6.750		120	73	26	30	90
42	7.000		30		5	3	27
43	7.515	tetrahydrocannabinolic acid A	7340		4591	2803	17759
44	10.200		10		5	24	130
45	11.500	cannabichromenic acid	120		1	23	5

[a]Peak area ratios of compound (x) versus internal standard (i.s.), multiplied by 1000. MEX = Mexico, COL = Colombia, JAM = Jamaica, THA = Thailand, USA = United States.

[b]Phenanthrene.

Cannabis specimens with the same authenticated origin show a similar, characteristic peak pattern. Correlation studies with a limited number of specimens indicate that it could be possible to determine the origin of a *Cannabis* specimen on the basis of its chemical signature. A confirmation of this approach will need to be carried out through the analysis of a large number of specimens of known provenance. Other factors than the geographical origin that could influence the chemical profiles, such as time of harvesting (maturity), age of the samples, storage conditions, and seed shipment from one country to the other, have to be studied. The statistical evaluation of the chromatographic and spectroscopic data would be facilitated by the use of an automated data acquisition system and special software for pattern recognition.

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