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CASE REPORT

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GC-MS Analysis of Hashish Samples: A Case of Adulteration with Colophony

ABSTRACT: This report describes the analytical characterization of 16 hashish samples confiscated in Italy. The samples were solvent extracted and subjected to GC-MS analysis for the separation and quantitation of the main cannabinoids. One of the analyzed samples was shown to contain extraneous compounds, identified as resin acids characteristic of colophony (rosin). Colophony is a natural resinous product obtained from various species of pine, spruce, and larch; it is a skin sensitizer and its fumes produce nonspecific irritation that can cause bronchial asthma. Similar adulterations of hashish have not been reported previously; therefore, at present there is no information about the effects of smoking colophony or a combination of hashish and colophony. It is presumed, however, that such a combination would be highly detrimental to the health of the user.

KEYWORDS: forensic science, hashish, adulteration, colophony, gas chromatography-mass spectrometry

Hashish, also known as kif, consists of the Δ^9-tetrahydrocannabinol (THC)-rich resinous glandular trichomes, as well as other minute plant particles, isolated from the female flowers of the cannabis plant. It is separated from the plant via various sieving methods, including a cold-water separation.

The material is compressed into blocks that are easily stored and transported. Pieces are then broken off, usually mixed with tobacco or marijuana, and smoked in bongs, pipes, joints, or hookahs (1).

In the common production of hashish, adulteration with other substances is not usual.

Colophony (rosin) is a natural resinous product obtained from various species of pine, spruce, and larch; the resins are solid and generally translucent and glassy. They vary in color from faint yellow to dark brown—the more the contaminants, the darker the color (2–4).

The major components of colophony (about 90%) are resin acids; the remaining fraction is composed of esters, aldehydes, and alcohol (5). Resin acids are diterpenes of abietic and pimaric acids. Abietic acid has conjugated double bonds and it oxidizes more readily than pimaric acid (which has no conjugated double bonds). The structures of the principal resin acids are shown in Fig. 1.

The relative content of these acids in rosin varies both with the method of extraction and the type of wood, growth site, handling, and storage.

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Colophony is widely used, in industry, daily life, and medical supplies, because it is a relatively inexpensive substance with adhesive properties.

One of the most important uses of unmodified colophony is in electronic solder fluxes, while the main uses of modified colophony are paper sizing, adhesives, paints, varnishes, printing inks, and plasticizers (6). The resin used for violin bows is pure colophony.

Colophony produces vapors and fumes of resin acids that are easily inhaled. Many studies show that colophony is a skin sensitizer (7,8). It is also the third highest cause of occupational asthma (6), especially for workers exposed to fumes generated from cored solder wire containing colophony as a flux (9,10). Colophony fumes produce nonspecific irritation that can cause bronchial asthma (11). Acid components of colophony, such as levopimaric, abietic, podocarpic, and tetrahydroabietic acids, are known to be weak skin sensitizers. However, even though weak, abietic acid is considered the major allergen in nonmodified colophony. The neutral fraction of colophony is also partially involved in colophony allergies (12).

Colophony is chemically modified in different ways to obtain desirable technical properties, and new allergens are created by these modifications (13).

When temperatures increase above 200°C, colophony decomposes to aliphatic aldehydes (formaldehyde, acetaldehyde, etc.). Respiratory and local effects are attributed to these compounds (14). Studies of pyrolysis at temperatures of soldering (between 250°C and 400°C) confirm the presence of formaldehyde as the major compound that is responsible for the toxicity of colophony fumes (15). At present, no studies on combustion of colophony (temperatures between 600°C and 800°C) have been reported.

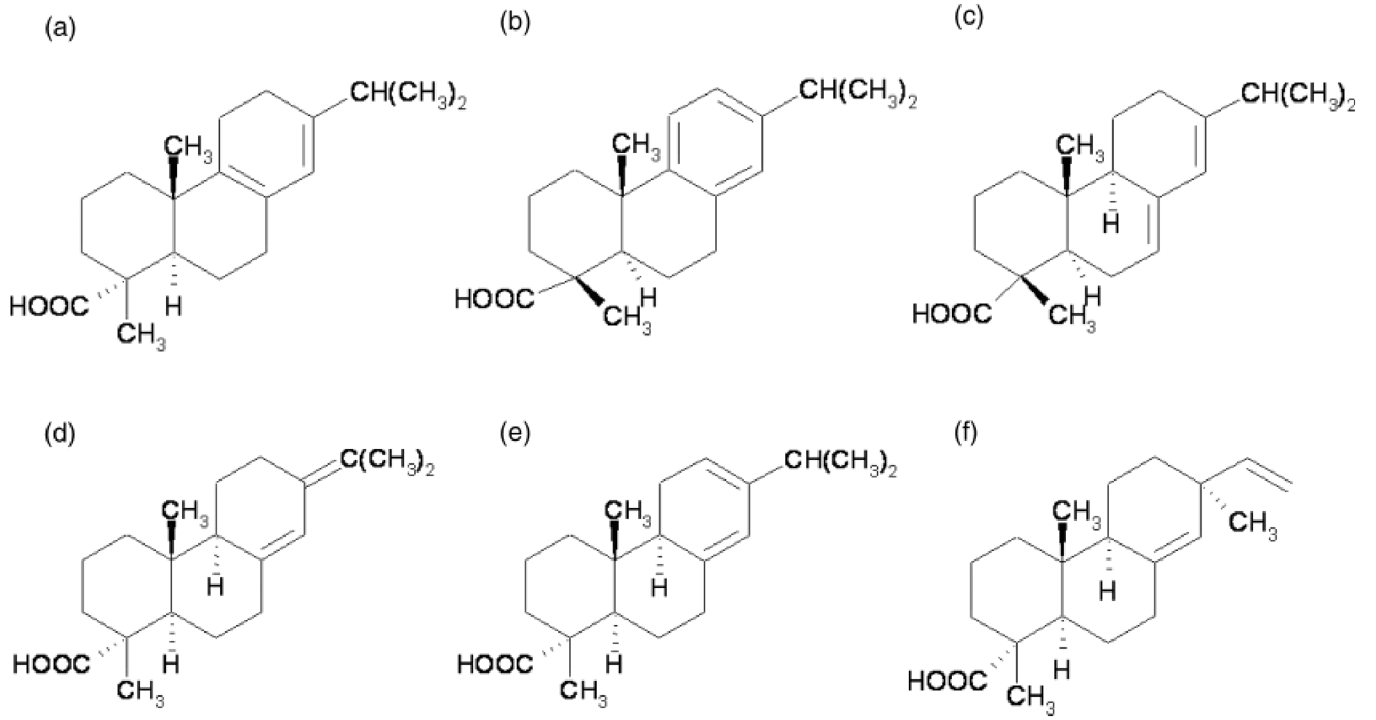

FIG. 1—*Chemical structures of principal resin acids: (a) palustric acid; (b) dehydroabietic acid; (c) abietic acid; (d) neoabietic acid; (e) levopimaric acid; (f) pimaric acid.*

This paper reports the comparison of the composition of typical hashish with a case of hashish adulterated with colophony. The presence of colophony in hashish has not been previously reported, and little information concerning hashish with odors of pine resin was found on a nonofficial website of Italian hashish consumers.

Methods

Investigation was carried out on 16 hashish samples confiscated in Italy. A sample of pine colophony purchased in a specialized shop (Bresciani, Milan, Italy) was also analyzed in order to confirm its presence as an adulterant in hashish.

Docosane internal standard solution (1000 ppm in petroleum ether, 1 mL) was added to 100 mg of ground hashish sample (or colophony), and extracted with 60 mL of petroleum ether by magnetic stirring for 1 h.

The organic phase was then filtered, concentrated to 3 mL, and injected (1 μL, split 20:1) into the GC/MS system. GC-MS analysis was performed on an HP-5890 Series 2 gas chromatograph coupled to an HP-5971 mass selective detector (Hewlett-Packard, Palo Alto, CA).

GC conditions: oven temperature increased from 80°C to 260°C, at 20°C/min, after an initial hold at 80°C for 3 min; injector temperature: 280°C; detector temperature: 285°C; and helium gas flow: 0.8 mL/min at 80°C.

GC column: capillary column SE 52 (30 m, 0.25 mm i.d., 0.25 μm film thickness).

MS conditions: ion source temperature: 180°C; electron impact: 70 eV; and acquisition mode: scan (50–500*m/z*). The response factor for THC was calculated utilizing a standard solution.

Results and Discussion

All samples were analyzed by GC-MS, and the percentages of already defined THC, cannabinol, and cannabidiol were determined; samples ranged from 1.12% to 5.39% THC. All except one sample showed a similar GC-MS qualitative profile, as reported in Fig. 2*a*.

Only one sample showed an anomalous profile. Its GC-MS profile was more complex than other samples (Fig. 2*b*); moreover, it showed the lowest level of THC, as reported in Table 1. The anomalous sample, however, showed the typical characteristics of hashish (resinous aspect, odor, shape, etc.); the presence of cannabinoids in this sample, although low, indicates the presence of

TABLE 1—*Percentage of cannabinoids in hashish samples.*

	No	%THC	%CBD	%CBN
"Normal" hashish samples	1	0.65	1.06	0.46
	2	1.42	1.08	0.14
	3	1.73	1.38	0.21
	4	3.02	2.32	0.48
	5	1.72	1.46	0.29
	6	5.39	3.07	0.43
	7	1.12	1.30	0.17
	8	1.56	1.70	0.23
	9	1.79	1.25	0.34
	10	3.30	2.09	0.40
	11	2.37	1.72	0.50
	12	3.81	2.38	0.43
	13	2.79	3.14	0.40
	14	3.23	3.59	0.55
	15	3.89	2.23	0.26
"Anomalous" hashish sample	16	0.65	1.06	0.46

THC, tetrahydrocannabinol; CBD, cannabidiol; CBN, cannabinol.

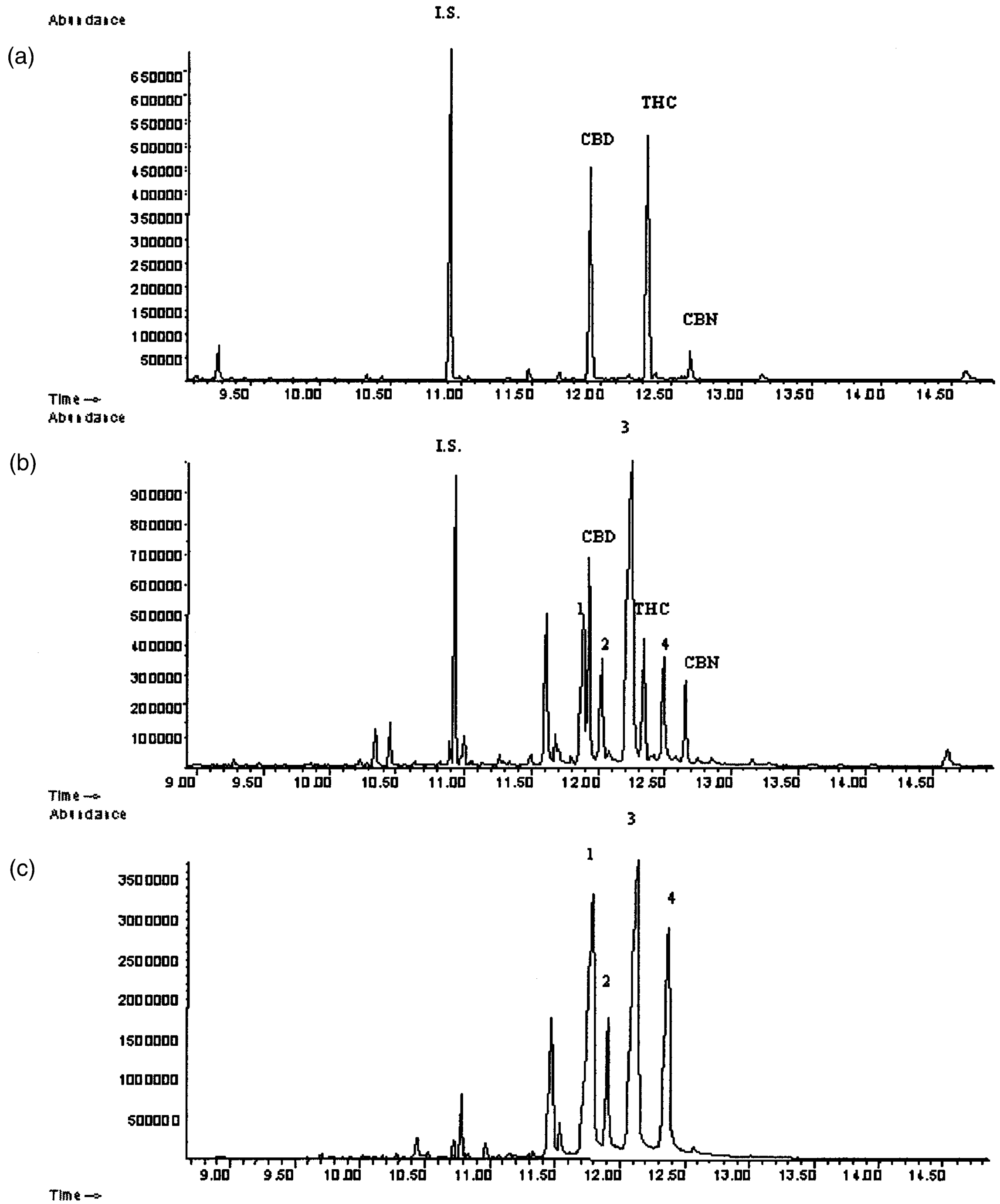

FIG. 2—*GC-MS spectra of (a) normal hashish sample; (b) anomalous hashish sample; (c) sample of colophony: 1, palustric acid; 2, dehydroabietic acid; 3, abietic acid; 4, neoabietic acid.*

hashish. The lower amount is the consequence of the dilution caused by the adulteration with colophony.

Mass spectra of the extraneous peaks in the anomalous hashish sample were identified by comparison with library mass spectra, and with mass spectra stored from previous work concerning the characterization of colophony (1).

Identification of colophony was then confirmed analyzing under the same instrumental conditions a real sample of pine colophony; the obtained chromatogram is shown in Fig. 2*c*, and the mass spectra of the characteristic acid components of colophony are shown in Fig. 3.

These results verify the adulteration of hashish with colophony.

The health effect of hashish smoking are well documented, but the possible effects of smoking colophony or the possible synergistic effects of colophony and hashish inhalation are unknown. However, the documented adverse effects of colophony fumes would suggest that smoking such a combination would be highly detrimental to the health of the user. Additional studies on the pyrolysis and combustion of colophony are needed to better understand its possible effects on human health.

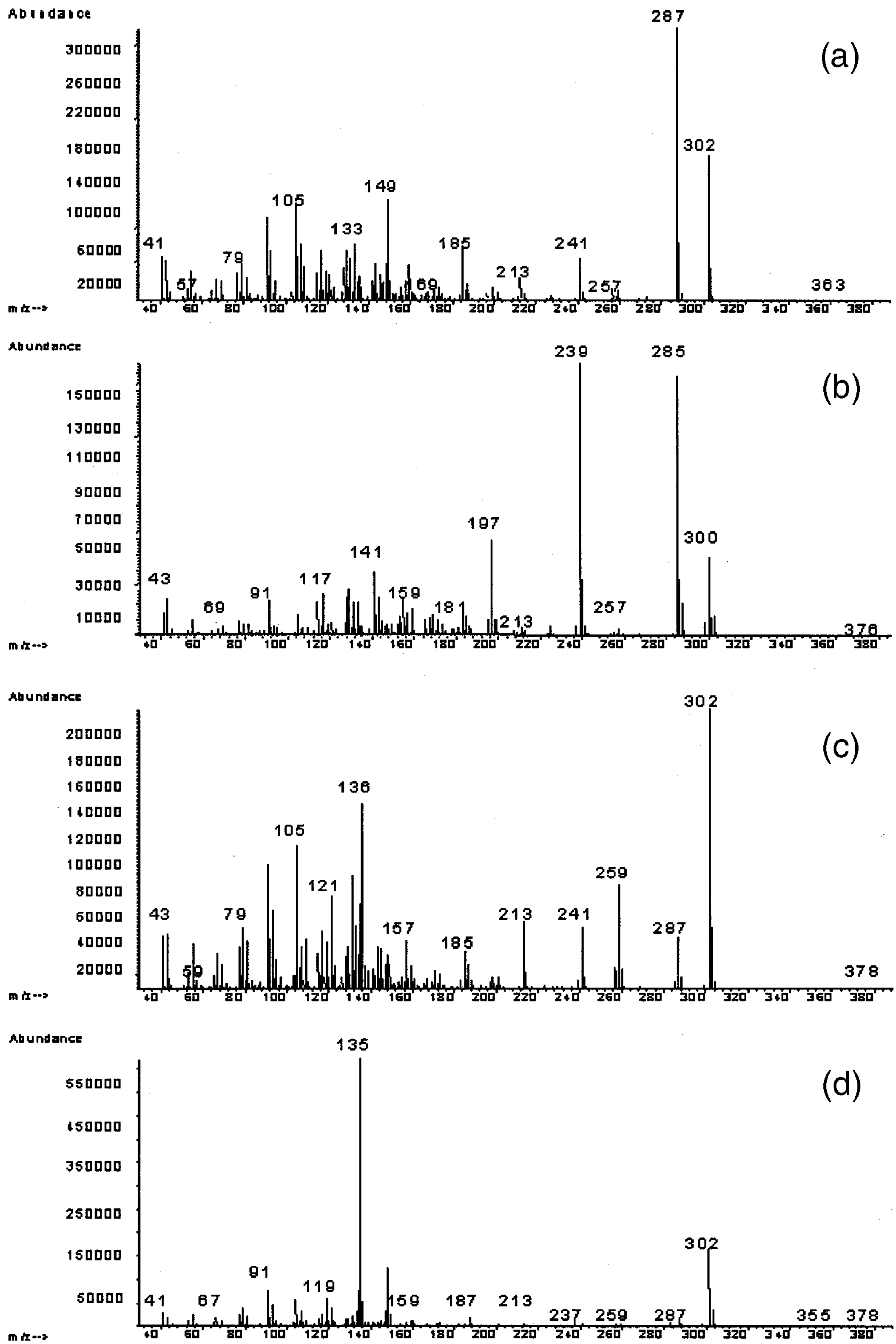

FIG. 3—*Mass spectra of principal resin acids identified in colophony: (a) abietic acid, (b) palustric acid, (c) dehydroabietic acid, (d) neoabietic acid.*

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