Detection of Trace Amounts of Lysergic Acid Diethylamide in Sugar Cubes

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A method for the detection of trace amounts of lysergic acid diethylamide in sugar cubes is described. The free base is extracted from aqueous sodium bicarbonate solution with methylene chloride and hydrogenated with Adam's catalyst. The product is examined by gas chromatography and its identity confirmed by thin-layer chromatography of the eluate which yields two characteristic spots—one blue, the other yellow—on spraying with *p*-dimethylaminobenzaldehyde. The yellow spot exhibits strong blue fluorescence when viewed under ultraviolet light prior to application of the reagent.

THE NEED for sensitive procedures to detect lysergic acid diethylamide (LSD) in narcotic seizures was illustrated in a previous communication from this laboratory (1). The recent discovery of the illegal sale of sugar cubes impregnated with the psychotomimetic drug focused anew the authors' attention on existing analytical methodologies and prompted them to develop an additional microphysicochemical technique for its detection and identification. Exploratory experiments aimed at direct application of gas chromatography to the analysis of LSD were unsuccessful. Due to low volatility, the compound could not be recovered even when using columns of low packing ratio and operating at high column temperatures. Consideration was, therefore, given to hydrogenation of the drug prior to gas chromatography as a means of eliminating its unsaturation (C_9-C_{10} bond) and thereby increasing its stability.

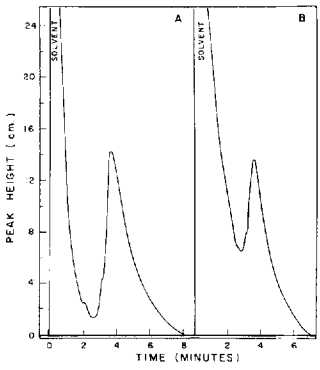

Fig. 1.—Gas chromatograms of hydrogenated LSD. Key: A, reference sample; B, sugar cube extract (exhibit J568). Column temperature: 270°; injector temperature: 290°; nitrogen flow: 22 ml./min.; sample volume: 1 μl.

TABLE I.—THIN-LAYER CHROMATOGRAPHY OF HYDROGENATED LSD

Sample	Spot	Chromatographic Data: Color Observed: Under U.V. Light	After Spraying	*Rf* Value	Relative *Rf* Value[a]
Hydrogenated LSD	1	Blue fluorescence	Faint yellow	0.81	1.04
	2	...	Blue	0.78	1.00
Gas chromatographic eluate, 3–4 min.	1	Blue fluorescence	Faint yellow	0.81	1.04
	2	...	Blue	0.78	1.00
Hydrogenated LSD soln. stored for 2 wk.	1	Blue fluorescence	Faint yellow	0.81	1.04
	2	...	Blue	0.78	1.00
	3	...	Blue	0.54	0.69

[a] Reference: spot 2.

The present communication describes the successful application of this approach to the detection of the psychotomimetic drug in sugar cubes and provides additional identity tests based on thin-layer chromatography of the effluent gas chromatographic peak.

EXPERIMENTAL

Materials

Lysergic Acid Diethylamide Tartrate.—LSD 25 (courtesy Sandoz Ltd., Dorval, Quebec, Canada).

Sugar Cubes.—(*a*) Specimens seized by officers of the Royal Canadian Mounted Police (exhibit J568) and (*b*) specimens prepared by impregnation with aqueous solutions containing 1 mg. of LSD/ml., and drying in a stream of warm air (50°) for about 5 min.

Methods

Extraction of LSD.—The drug was isolated in accordance with the following procedure (2). The sugar cube was dissolved in 10 ml. of distilled water, 0.5 Gm. of sodium bicarbonate was added, and the free base was extracted with four 5-ml. portions of methylene chloride. The lower layer was withdrawn through a piece of cotton wool placed in the stem of the separator, care being taken to minimize exposure of the isolate to light and heat. The extract was evaporated to dryness in a gentle stream of nitrogen.

Hydrogenation of LSD.—The sample (reference compound or material extracted from a sugar cube) was dissolved in 1 ml. of methanol and hydrogenated at atmospheric pressure for 3 hr. using 10 mg. of Adam's catalyst. After filtration, the solution was gently concentrated to 0.1 ml. in a slow stream of nitrogen.

Gas Chromatography.—An Aerograph Hi-Fi,

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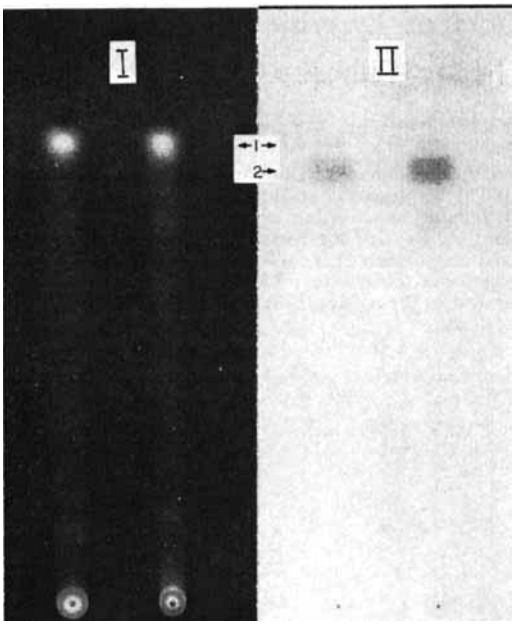

Fig. 2.—Thin-layer chromatograms of hydrogenated LSD. Key: I, observed under U.V. light; II, observed after spraying with *p*-dimethylaminobenzaldehyde; A, reference sample: product from hydrogenation of 1.8 mg. LSD in 0.1 ml. methanol. Volume applied: 2 μl.; B, sugar cube (exhibit J568). Product from hydrogenation of sugar cube extract in 0.05 ml. of methanol. Volume applied: 4 μl.

model A-600-C, equipped with hydrogen flame ionization detector, was employed. A glass tube was inserted into the injection port to minimize degradation of the sample at the metal surface of the preheater. The column, a stainless steel tube (5 ft. × 1/8 in.) was packed with micro glass beads (60 mesh) coated with 0.2% of silicone rubber SE-30. By means of a stream splitter, eluates were collected in capillaries packed lightly with methanol moistened glass wool.

Thin-Layer Chromatography.—*Thin-Layer Plates.*—Glass plates (20 × 20 cm.) coated with aluminum oxide G (Merck). Layer thickness 250 μ.

Solvent System.—Chloroform–ethanol (96:4) (3).

Detection.—Following migration of the solvent front (15 cm.), plates were observed under ultraviolet light (3660 Å.) and subsequently sprayed with a solution of *p*-dimethylaminobenzaldehyde (2 Gm.) in concentrated HCl (20 ml.) and ethanol (80 ml.) (4).

RESULTS AND DISCUSSION

The product obtained by catalytic hydrogenation of LSD could easily be subjected to gas chromatography. A main peak (retention time: 3.6 min.) and two slight shoulders (retention times: 3.1 and 2.1 min., respectively) were observed (Fig. 1). In order to obtain more reproducible retention time data, ergonovine maleate hydrogenated in accordance with the procedure described was used as internal reference. Relative retention time of hydrogenated LSD: 1.64.

Thin-layer chromatographic analysis of the effluent emerging between 3 and 4 min. served to confirm the gas chromatographic identification. The thin-layer chromatogram of hydrogenated LSD exhibited a blue fluorescent spot when viewed under ultraviolet light. After spraying with the reagent, this spot acquired a yellow coloration, while another intense blue spot appeared at a slightly lower R_f value (Table I and Fig. 2). These same spots were observed when the gas chromatographic eluate was similarly examined. Solutions which had been kept for several days showed a number of additional but faint spots, among which one at R_f 0.54 was most prominent.

The thin-layer chromatographic technique was found to be superior to the gas chromatographic technique in that it allowed the characterization of LSD concentrates which failed to produce gas chromatographic peaks. Thus, when a sugar cube impregnated with 50 mcg. of LSD was processed as described, only a shoulder appeared on the descending portion of the solvent peak in the gas chromatogram at 3.6 min., while the corresponding eluate yielded a convincing thin-layer chromatogram.

REFERENCES

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